VAPOUR SORPTION EQUILIBRIA AND OTHER WATER-STARCH INTERACTIONS; A PHYSICO-CHEMICAL APPROACH

"The source of all knowledge is the knowledge of God"

Bahá'u'lláh (1817-1892)

Promotor: dr. J. Lyklema, hoogleraar in de fysische en kolloidchemie

7a. Dichtheidsmetingen aan zetmeel o[illegible]e en apolaire fluïda leveren verschillende waarden op. Wegens de po[illegible]eving waarin zetmeel zich gewoonlijk bevindt is de huidige gewoonte om waarden voor de zetmeeldichtheid te gebruiken, verkregen door meting onder apolaire vloeistoffen of lucht, vaak onjuist.

Dit proefschrift, Sectie 3.3.
T.J. Schoch, H.W. Leach, 1964. page 101 in R.L. Whistler (ed) Methods in carbohydrate chemistry. Vol. 1. Ac. Press, New York/London.

7b. Voor het opstellen van tabellen voor dichtheden van waterige zetmeelsuspensies voor praktisch gebruik, is het voldoende om per zetmeelsoort van één water-zetmeel verhouding nauwkeurig dichtheid en watergehalte te bepalen. Voor berekening van de andere waarden kan een simpel additief verband worden gebruikt, doch niet de functie welke werd voorgesteld door Nara en medewerkers.

Dit proefschrift, Sectie 3.3 en Appendix 1.
S. Nara, K. Yamaguchi, K. Okada, 1968. J. Jap. Soc. Starch Sci. 16(5): 5.

8. De hoeveelheid niet-oplossend water in een polymeer-water systeem, waarvan de dampdrukisotherm bekend is, verschaft aanzienlijk meer informatie over de mate van ideaal gedrag van de gebruikte oplosbare stof binnen het ontstane mengsel, dan over de waterbinding aan het polymeer. Het is dan ook niet juist dat Duckworth op grond van dergelijke metingen concludeert dat het zgn. monomoleculaire water geen effectief oplossend vermogen bezit.

R.B. Duckworth, 1981. page 314 in L.B. Rockland, G.F. Stewart (eds) Water activity: influences on food quality. Ac. Press, New York/London.

9. Vooral door de ontwikkeling van technologieën voor de winning van plantaardige eiwitten is de mens, voor het eerst sinds zijn ontstaan, in staat om zelf eiwitrijke voedingsmiddelen samen te stellen. De unieke voordelen van dierlijke produkten zijn hierdoor achterhaald.

10. Vanwege het vermogen mengwarmten nauwkeurig en snel te kunnen meten, verdient immersiecalorimetrie als karakteriseringstechniek voor oppervlakken van levensmiddelen-polymeren aanbeveling.

11. In het algemeen wordt vrouwenemancipatie gezien als een westerse beweging welke omstreeks de jongste eeuwwisseling is ontstaan. Minder bekend is dat belangrijke sporen ervan reeds te vinden zijn in Iran omstreeks 1844. Aanleiding hiertoe gaven de leringen van Siyyid Alí Muhammad (de Bab) over de fundamentele gelijkwaardigheid van man en vrouw.

Shogi Effendi, 1932. The dawn-breakers. Bahá'í publishing trust, Wilmette Ill.

12. Op religieus gebied zal geen werkelijke οἰκουμένη tot stand komen, tenzij de wereldreligies elkanders stichters gaan erkennen als boodschappers van dezelfde God, echter gezonden op verschillende tijden in verschillende culturen.

13. Een verstandig vader bakert zelf.

Proefschrift van C. van den Berg
Vapour sorption equilibria and other water-starch interactions; a physicochemical approach
Wageningen, 14 oktober 1981

STELLINGEN

NN08201, 864

1. Voor de beschrijving en analyse van experimentele isothermen van gelocaliseerde sorptiesystemen verdient de isothermvergelijking welke resulteert uit de theorieën van Guggenheim, Anderson en de Boer de voorkeur boven die van Brunauer, Emmett & Teller.

Dit proefschrift, Sectie 4.3.
E.A. Guggenheim, 1966. Application of statistical mechanics. Clarendon Press, Oxford.
R.B. Anderson, 1946. J. Am. Chem. Soc. 68: 686.
J. H. de Boer, 1953. The dynamical character of adsorption. Clarendon Press, Oxford.
S. Brunauer, P.H. Emmett, E. Teller, 1938. J. Am. Chem. Soc. 60: 309.

2a. Hydroplastisch zijn polymeren waarvan de glasovergangstemperatuur daalt tot beneden kamertemperatuur bij toename van het watergehalte. Om deze reden zijn de amorfe polymeren in biologische materialen naast thermoplastisch ook hydroplastisch.

2b. Het belang van het eventueel overschrijden van de glas-rubber overgang van levensmiddelenpolymeren tijdens bijv. fabricageprocessen waarbij het watergehalte verandert, wordt onvoldoende onderkend.

3. Capillair-condensatie speelt als mechanisme van dampdrukverlaging in levensmiddelen geen rol van betekenis.

4. Gasadsorptie in homogene gelocaliseerde multilagen volgens Brunauer, Emmett & Teller en dampspanningsverlaging van ideale oplossingen volgens Raoult worden door mathematisch identieke vergelijkingen beschreven. Dit illustreert op treffende wijze de ontoelaatbaarheid van uitspraken over achterliggende sorptiemechanismen louter op basis van de toepasbaarheid van een bepaalde isothermvergelijking.

Dit proefschrift, Hoofdstuk 4.

5a. Kristallen van zetmeel bevatten steeds water als essentieel deel van hun kristalrooster.

Dit proefschrift, Secties 2.4 en 3.2.

5b. Om deze reden gaat de algemeen veronderstelde overeenkomst tussen kristallen van cellulose en zetmeel niet op voor wat betreft hun relatie tot water.

S. Nara, A. Mori, T. Komiya, 1978. Starch/Stärke 30: 111.
H.T.K. Rück, 1977. page 114 in 4th Intern. dissolving pulps conference. Tappi, Atlanta.

5c. Tijdens de opname van dit "kristalwater" zwellen B-type zetmeelkristallen enigermate, en blijven de kristalafmetingen niet constant zoals Wu & Sarko stellen.

Dit proefschrift, Sectie 3.2.
H.C.H. Wu, A. Sarko, 1978. Carbohydrate Research 61: 7.

6. De dubbele helix welke Sarko en medewerkers recentelijk voorstelden als conformatie voor kristallijn B-amylose is aanzienlijk minder waarschijnlijk dan hun oudere voorstel dat de helix enkel is.

H.C.H. Wu, A. Sarko, 1978. Carbohydrate Research 61: 7.

C. van den Berg

Vapour sorption equilibria and other water-starch interactions; a physico-chemical approach.

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. C. C. Oosterlee,
hoogleraar in de veeteeltwetenschap,
in het openbaar te verdedigen
op woensdag 14 oktober 1981 des namiddags te vier uur
in de aula van de Landbouwhogeschool te Wageningen.

ABSTRACT

van den Berg, C. (Section Process Engineering, Department of Food Science, Agricultural University, Wageningen, the Netherlands), 1981. Vapour sorption equilibria and other water-starch interactions; a physico-chemical approach. Doctoral thesis, Agricultural University, Wageningen. 186 + 12 pp., 40 figs, 17 tables, 361 refs, 2 app., English and Dutch summaries.

A model was developed on the basis of the literature for binding of water on solid starch by means of a combined sorption mechanism. Equations based on the theory of localized sorption on homogeneous surfaces (Langmuir and Brunauer, Emmett & Teller) were derived. An equation with three parameters from the theories of Guggenheim, Anderson and de Boer described experimental isotherms adequately up to a water activity of 0.9 and one based on polymer-solvent interaction (Flory and Huggins) above that value. The experimental isotherms of water vapour on native starch were affected by temperature, gelatinization, partial hydrolysis and separation in components (amylose and amylopectin).

Free descriptors: water activity, starch structure, binding of water by starch, vapour sorption, isotherms, crystallinity of starch, glass-rubber transition, thermo-dynamic functions, physical properties, theory of localized sorption on homogeneous surfaces, polymer-solvent interactions, isotherm equations, literature review.

VOORWOORD

De wording van dit proefschrift is in enkele opzichten te vergelijken met de nauwkeurige meting van een sorptie-evenwicht tussen zetmeel en waterdamp. Niet alleen is de gemeten waarde het resultaat van de inzet van meerdere mensen, ook de instellingsduur van het eigenlijke evenwicht was voor fysische adsorptieprocessen relatief lang en de uitkomst niet zelden verrassend. Dit werkstuk reflecteert onvermijdelijk een deel van mijn vorming, ervaringen en specifieke interessen. Mijn erkentelijkheid gaat uit naar allen die hiertoe hebben bijgedragen. Veel dank ben ik verschuldigd aan mijn ouders voor hun vele goede zorgen en de mogelijkheden die zij mij boden een studie te volgen.

Mijn belangstelling voor het hier behandelde onderwerp werd gestimuleerd door een viertal ontwikkelingen. Tijdens mijn studie aan de Landbouwhogeschool wekte prof.dr.ir. H.A. Leniger mijn interesse voor de fysische technologie van de verwerking van landbouwprodukten, en wat later meer specifiek voor het belang van de wateractiviteit van levensmiddelen. Onder Leniger's leiding startte binnen de afdeling reeds vroeg onderzoek hiernaar door ing. J.A.G. Weldring. Prof.dr. W. Pilnik bracht als brede achtergrond de leer van levensmiddelen in, waarbinnen polymeren zo'n belangrijke rol spelen. De systematisch kwantificerende aanpak van fysische en kolloïdchemische verschijnselen door prof.dr. J. Lyklema, mijn promotor, sprak me steeds sterk aan. Later werd deze kwantificerende tendens verder versterkt door de fundamentele proceskunde die werd ingevoerd door prof.dr.ir. S. Bruin, als krachtig hulpmiddel voor een geïntegreerde aanpak van velerlei problemen. Jou, Solke, ben ik tevens bijzonder erkentelijk voor je belangrijke stimulans en ruimte om deze studie binnen de sectie Proceskunde te verrichten.

Hooggeleerde promotor, beste Hans, jouw creatieve en bemoedigende begeleiding zijn steeds een onmisbare drijvende kracht geweest achter de voorbereiding van dit proefschrift. Op onze gesprekken zie ik met grote voldoening en dankbaarheid terug. Een deel van de in dit proefschrift vermelde resultaten werd verkregen tijdens een uitgebreid onderzoeksproject naar meting en interpretatie van dampdrukisothermen van voedingsmiddelen en hun componenten. Niet bevroedde ik dat de aanvankelijke keuze van zetmeel als ogenschijnlijk "stabiele" component uiteindelijk zo verstrekkend zou zijn. Grote bijdragen aan dit voornoemde project leverden vooral ing. Johan Weldring en ing. Ido Wolters. Zij bouwden de McBain-balansopstelling en verzamelden daarmee veel nauwkeurige isothermgegevens. Ook immersiewarmten en dichtheden werden gemeten door ing. Weldring. In het kader van hun afstudeerwerk startte ir. Fred Kaper de eerste isotherm-gegevensverwerking per computer, en verschafte ir. Daan Theunissen meer inzicht in de kinetiek van waterdampsorptie aan zetme-

len. Ir. Rob Cleven leverde een eminente bijdrage tot de kennis van B-zetmeelkristallen door Röntgen-onderzoek met medewerking van prof.dr. L. van der Plas (vakgroep Bodemkunde en Geologie).
De prettige collegiale sfeer binnen onze sectie, nu onder leiding van ir. W.A. Beverloo, wil ik gaarne vermelden. Collega ir. Henk Akse maakte het FITABS computerprogramma en ir. Karel Luyben het KOMPLOT programma; beiden gaven waardevolle rekenkundige adviezen. Mw. Ineke van Kreuningen typte een deel van dit document in voorlopige vorm en droeg als administratieve spil van de sectie algemeen belangrijk bij.
Drs. A. Otten (vakgroep Wiskunde) hielp de sorptiemodellen statistisch meester te worden. Dr.ir. W. Bol (Technische Hogeschool, Eindhoven) corrigeerde Sectie 2.1.
Bijdragen aan de gedachtevorming over de boeiende stof zetmeel werden geleverd door dr. J. Muetgeert (Kunststoffen en Rubberinstituut TNO, Delft), drs. P.A.M. Steeneken (Proefstation voor de Aardappelverwerking, Groningen), dr. A.H.A. de Willigen (v.h. verbonden aan genoemd Proefstation) dr. C.G. Vonk (D.S.M., Geleen) en dr. D.R. Kreger (Rijksuniversiteit, Groningen). Drs. Steeneken las en gaf waardevol commentaar op de hoofdstukken 2 en 3 in status nascendi. Dr. P.J. Hoftyzer (AKZO, Arnhem) hielp bij het afschatten van de zo belangrijke fase-overgangstemperatuur van zetmeel. Dr. B. Belderok (Instituut voor Graan, Meel en Brood, Wageningen) bepaalde de gehalten beschadigd zetmeel.
Zetmeelmonsters werden beschikbaar gesteld door AVEBE (Veendam), Proefstation voor de Aardappelverwerking (Groningen) en Compagnie du Benin (Chalons sur Saône, Frankrijk).
De heren C. Rijpma en M. Schimmel (tekenkamer Biotechnion) tekenden met zorg de meeste figuren, waarna de heer A. van Baaren ze fotografeerde.
De correctie van de Engelse tekst in delen werd hulpvaardig verzorgd door mw. Clara van Dijk (vakgroep Fysische en Kolloïdchemie), mr. I. Cressie en mr. C. Rigg (Pudoc, Wageningen).
De lengte van deze dissertatie met nogal wat formules en correcties in het aangeboden manuscript maakte het typen ervan niet alleen tot een kunde doch evenzeer tot een kunst. De dames van de afdeling Tekstverwerking van de Landbouwhogeschool, met name mw. I. Diraoui, ben ik dan ook zeer erkentelijk voor hun vlijt en accuratesse.
Tenslotte, wat zou deze studie zijn geweest zonder de niet aflatende trouw en steun van jou, Wieke. Meer dan enig ander heb jij de ups en downs ervan mee beleefd, je hebt de kinderen opgevangen op momenten dat ze hun vader hadden moeten zien en bleef optimistisch over de afloop.

CONTENTS

SYMBOLS

List of symbols most frequently used

a	surface occupied by one sorbed molecule
a	relative activity
a_w	relative water activity
C_B	B.E.T. adsorption constant
C_G	G.A.B. sorption constant
C_L	Langmuir adsorption constant
C_T	sorption constant related to the second molecule sorbed on a site
E	constant related to sorption entropy
f	fugacity
G	Gibbs free energy of sorption
g	adsorption constant in the G.A.B. theory (eqns 4.22, 4.26)
H	enthalpy of sorption
j	accommodation factor or reduced partition function of sorbed molecule
K	G.A.B. sorption constant related to multilayer properties
K'	G.A.B. sorption constant K corrected for sorption entropy
k	Boltzmann constant
K,k	(and other symbols where indicated) empirical constants
M	molecular weight
m	moles of gas striking the adsorption sites per second
N	number of sorbed molecules
N_s	number of sorption sites
N(w)	number of water molecules
N(s)	number of solute molecules
n	number of sorbed molecules per site
p	pressure
Q	partition function of canonical ensemble
q	partition function of one molecule
R	ideal gas constant
S	entropy of sorption
S'	swelling parameter
T	absolute temperature
V	volume
v	partial molal volume
W	mass fraction of water on dry substance
W_1	value of W at completed monolayer
Z	average chain length between junctions in polymer network
β	volume ratio of polymer segment and sorbate molecule
Δ	difference
γ	activity coefficient

γ'	composed parameter in Hill & Rowen extension of the Flory-Huggins theory
θ	degree of sorption site occupancy (N/N_s)
ι	sorption site creation function
λ	absolute activity
μ	chemical or thermodynamic potential
Ξ	grand partition function of grand canonical ensemble
ξ	grand partition function per sorption site
δ	relative adsorption time
τ	adsorption time
ϕ	volume fraction of polymer
χ	polymer-solvent interaction parameter (Flory-Huggins theory)
Ω	number of realization possibilities
ω	weight fraction

Subscripts

1,2,...,i	number in series
exc	excess part of function
g	glass-rubber transition
h	half occupied
is	isosteric
ℓ	bulk liquid
m	multilayer or melting (eqn 3.2)
p	polymer
s	solute, or surface (eqn 4.55)
u	polymer unit (monomer)
v	variable number
w	water

Superscripts

id	ideal
o	standard

The best of humanity is like water and starch; both substances serve all.

adapted from Lao-Tse (Sixth Century B.C.)

1 INTRODUCTION

1.1 GENERAL BACKGROUND OF THIS WORK

Knowledge of the interactions between water and biological products is of great importance. Not only does water play a paramount role during the biological growth of these products, but it also profoundly influences almost all properties of biological materials after their harvest or death. So water influences directly or indirectly all kinds of technological processes that are carried out with biological products.

Probably the most fundamental relation which describes the interaction between water and a solid is that between the *water activity* and the *water content* of the obtained mixture of water and solid (sorption complex) at a certain temperature. This relation, the water sorption isotherm, gives an impression of how strongly water is bound by the solid. Applying this to solids of biological origin we see that for the practice of preservation technologies these isotherms supply essential information . All forms of deterioration are related to the available water. For example, microbes which are usually the cause of most rapid decay processes of biological products, very seldomly grow below a water activity of 0.7. Therefore in a food preservation technology, besides determination of the amount of water, the water activity (or equilibrium relative humidity) has become a major control variable. Until recently, the water activity could be determined only by direct measurement. The last two decades, however, some progress was made in the theoretical estimation of water activity in foods and other systems, since it was realised that the water sorption isotherm of a system directly relates the thermodynamic potential to the mass fraction of water in the system.
Nowadays, for relatively simple mixture of water and some sugars, or some other substances over limited water concentration ranges, the water activity can be theoretically predicted with reasonable accuracy. But as soon as the solids become complex, as is the case with biopolymers, these methods fail. Here further experimental information on the specific interactions between water and the solids is required to develop more realistic models.

This thesis deals with the interactions between solid starch and water. Both substances are very common. Starch is the main component in the food of man and his domesticated animals, and water is ubiquitous. However, both substances are by no means simple, and this applies even more to their interactions. Water molecules like to sorb on a clean starch surface, especially at ambient and lower temperatures. This is demonstrated dramatically by the fact that for example at room temperature about 1½ weight % of water in the atmosphere is in equilibrium with as much as 20 weight % of water in potato

starch. Dry starch is a good desiccant.

The present study does not pay much attention to the typical gelling behaviour nor to solutions of starch which occur near a water activity of unity. These aspects dealing with starch in its dissolved state have received ample attention (e.g. Banks & Greenwood, 1975). However, since the classic work of Katz ended in 1938, relatively little work was carried out on the physics of the solid (or in this case rather: semi-solid) state of starches. In the development of starch science chemical aspects have always been emphasized.

The background of the treated subject is broad and nowadays of great importance. Besides their role in foods, native starches in isolated form have become very important raw materials for a great number of products. Thomas J. Schoch (1969), after devoting a lifetime to starch problems, pointed out that there are generally two different kinds of starch science. The first is practical technology involved in (usually minor) improvement in applications of starch in industrial processes and products. Most of this research still proceeds empirically by trial-and-error in order to find the optimum product for a specific use, with relatively little effort to understand the basic mechanisms involved. The second approach is theoretical. Mostly concepts are developed about ideal starch molecules under idealized conditions. This basic research has significantly contributed to our knowledge of the nature and structure of starch and its components, but it has not been of great help in solving problems arising in the application of starch and its products. (A notable exception here is the commercial separation of amylose and amylopectin mentioned in Subsection 2.5.3). In order to bridge the gap between both areas, Schoch proposed mid-area studies in "mechano-chemistry" of starch. Perhaps "applied physical chemistry" would be a more common and appropriate name. Anyway, Schoch's analysis is still correct in the view of the present author. In the author's opinion basic and applied research into water relations and solid state physics of starch should dominate this mid-area approach.

In the last few years carbohydrate (including starch) science has been formally designated as innovation area number one at the target lists of several major westers countries. This is mainly because starch and cellulose (and their many derivatives), contrary to mineral oil, are derived from renewable resources and by their very nature are less harmful to the environment. However, major developments are hampered by the lack of fundamental knowledge. Important progress in the development of native starch-based products may be anticipated when the problems concerning the structure of the native starch granule and the role of water have been elucidated. In particular physical modifications of native starches and new derivatives prepared in the solid state would become possible, and existing processes would be better understood.

This study aims at contributing to this area in particular by review and analysis of (i) the physical structure of native starch, (ii) the role of water in its different parts, (iii) the glass-rubber and melting transitions and other physical properties like density and heat of mixing as a function of water content, and (iv) the prevailing sorption mechanisms. Since several of these aspects have a general character, the study also contributes to the knowledge of water binding by biopolymers in general. The author hopes that his results and views may be an incentive for further thinking on this fascinating subject by applied starch technologists, fundamental starch reseach workers, food scientists and engineers who are interested in water relations of biological products.

1.2 OUTLINE OF THIS STUDY

Native potato starch which is representative of the family of starches and industrially important was chosen as the main object of this study. Of this substance much is already known. At many instances our results obtained with this substance are compared with those of native wheat starch which exhibits a somewhat different granule structure and another crystalline pattern. With regard to their water vapour sorption behaviour the influence of several treatments will also be investigated.

By way of introduction this report starts in Chapter 2 with the introduction of the substances water and starch. Special attention is paid to the physical structure of the starch granule and its crystallinity because water plays a specific role in it.
This outline may serve as a general background for Chapter 3 where the main water relations of starch are discussed. The properties of the solid state of starch are profoundly influenced by the action of water. Based on an analysis of these, a general model of water vapour sorption on dry starch is given. This chapter is a synthesis of data from literature and results from own investigations with mainly thermodynamic techniques. In this chapter also the proposed crystal structure prevailing in native potato starch is shortly described.

In order to quantitatively interpret the obtained sorption isotherms on the basis of the proposed sorption model, it is necessary to first review, analyse and extend available sorption theories (Chapter 4). It will be shown that broadly speaking two sorption mechanisms together govern the interaction between water and dry starch. Chapter 5 describes the experimental methods used. In Chapter 6 the isotherm equations belonging to the various sorption theories are compared with experimental sorption isotherms of water vapour on several starches. Differences between the natures of these star-

ches, resulting from different origins and treatments are reflected in the isotherm properties. In conclusion a combined sorption isotherm model is proposed.

2 WATER AND STARCH

2.1 WATER AND ITS ACTIVITY

2.1.1 General

Water is the mobile low molecular component of the water-starch system and therefore deserves special attention with regard to its nature and properties determining sorbability. As outlined in the introduction, the knowledge of water has grown considerably during the last few decades, and so has the literature (e.g. Eisenberg & Kauzmann, 1969; Franks, 1972-1979; Erdey-Grúz, 1974; Berendsen, 1967). For introductory reading, the reviews of Lück (1976) and Berendsen (1979) are interesting. Some aspects and properties of water relevant to our purpose will be discussed in the remainder of this section.

2.1.2 Water molecules

It is generally agreed that in many respects water is a unique substance, with rather unusual properties. When for instance compared with other ten-electron systems (ammonia or hydrogen fluoride) or with the dihydrides of other elements from the sixth group of the periodic system (H_2S, H_2Se and H_2Te), the freezing point and the boiling point of water are surprisingly high, see Table 1.

Table 1. Comparison of freezing and boiling points (K) at 101.3 kPa of hydrides of elements neighbouring oxygen in the periodic system of elements.

	freezing point	boiling point
NH_3	195	240
HF	181	292
H_2Te	222	269
H_2Se	209	231
H_2S	190	211
H_2O	273	373

Pure water consists of molecules made up of two hydrogen atoms and one oxygen atom. Figure 2.1a shows a schematic model of a water molecule with its basic dimensions in vapour and in ice. The O-H bond energy is 459.3 kJ/mol at 0 K. Because of the high electro-negativity of the oxygen atom, compared

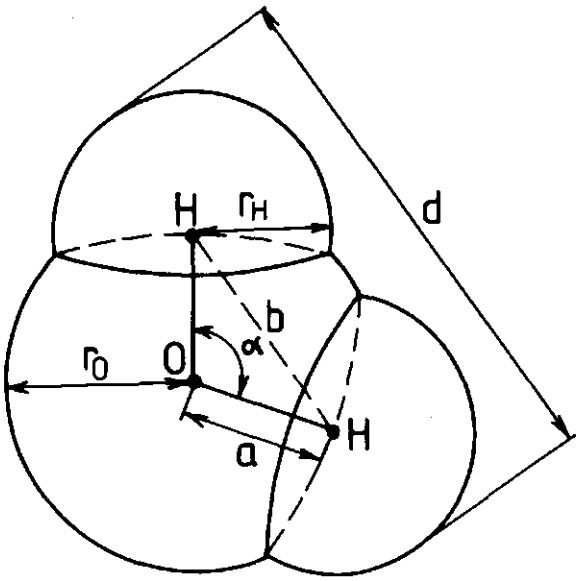


Fig. 2.1a. Schematic model of a single water molecule with van der Waals radii. In the *vapour* state: a = 0.096 nm; b = 0.141 nm; α = 104.5°. In the *ice* state: a = 0.099 nm; b = 0.162 nm; α = 109°.

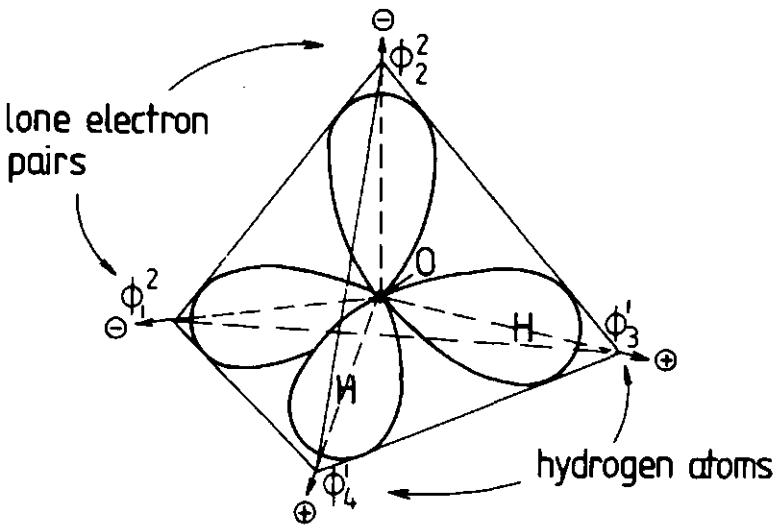


Fig. 2.1b. Schematic tetrahedron indicating the charge distribution in a water molecule. Each point charge is about one fourth of an electron charge. Distances with respect to the oxygen nucleus are 0.1 nm for the positive charges and 0.08 nm for the negative charges.

to the hydrogen, the electronic charge density is enriched around the oxygen. The resulting charge centers are located tetrahedrally around the oxygen (Figure 2.1b). Due to the asymmetry of the charge, the water molecule has a high dipole moment, viz. $6.17 \cdot 10^{-30}$ C.m. (1.85 Debye units). From the directed nature of the orbitals, a 3-dimensional structure follows for a collection of water molecules that are packed as in water or ice. Water molecules are linked by hydrogen bonds with average distances of about 0.177 nm between hydrogen and oxygen (or approx. 0.277 nm between the oxygen nuclei), allowing some deviation (about 20°) from linearity. The hydrogen bond, with average binding energy of about 20.5 kJ/mol, is strong enough to survive several vibration periods (at room temperature one period lasts approx. 10^{-12} s), thus creating some structure in liquid water.

2.1.3 Ice

In pure ice the maximum number of hydrogen bonds are realized. Each molecule has at most 4 bonds, giving a total number of 2 N bonds for a population of N molecules. Some dislocations exist, their number is a function of temperature and the crystallization process. From the heat of sublimation of ice at 273 K (51.1 kJ/mol) it follows that Van der Waal's attraction forces account for only about 20% of total interaction.

At 101 kPa there are two modifications of ice, ordinary hexagonal ice (Ih) that appears upon freezing of water at 273 K and cubic ice (Ic), which is a stable low temperature modification. In these ice forms the hydrogen bonds are directed in tetrahedral symmetry. In Ic ice the oxygen atoms take a position identical to the arrangement of carbon atoms in diamond, whereas Ih ice differs from this only with respect to the position of the next-nearest neighbour molecules (Figure 2.2).

The protons have no fixed place in the crystal, they can take very many configurations, in which they shift approximately each $2 \cdot 10^{-5}$ s (at 273 K). The arrangements of molecules in the ices lead to a rather open structure. Densities are 917 kg/m³ (0°C, 101 kPa) for Ih and 930 kg/m³ (143 K, 101 kPa) for Ic. The openness of structure is well illustrated by the fact that there exists an ice VII modification, the molecules of which take the position of two diamond structures, one occupying the holes left by the other (Eisenberg & Kauzmann, 1969). For pressures above $2 \cdot 10^9$ Pa the ice VII modification is stable at temperatures up to 353 K (80°C) with a density of approx. 1650 kg/m³ (298 K, $2.5 \cdot 10^9$ Pa).

As the arrangement of water molecules as in cubic ice is believed to play a role in B-type starch crystals (Subsection 3.2.4) some additional information follows. Ice Ic can be formed by sublimation of water vapour on sur-

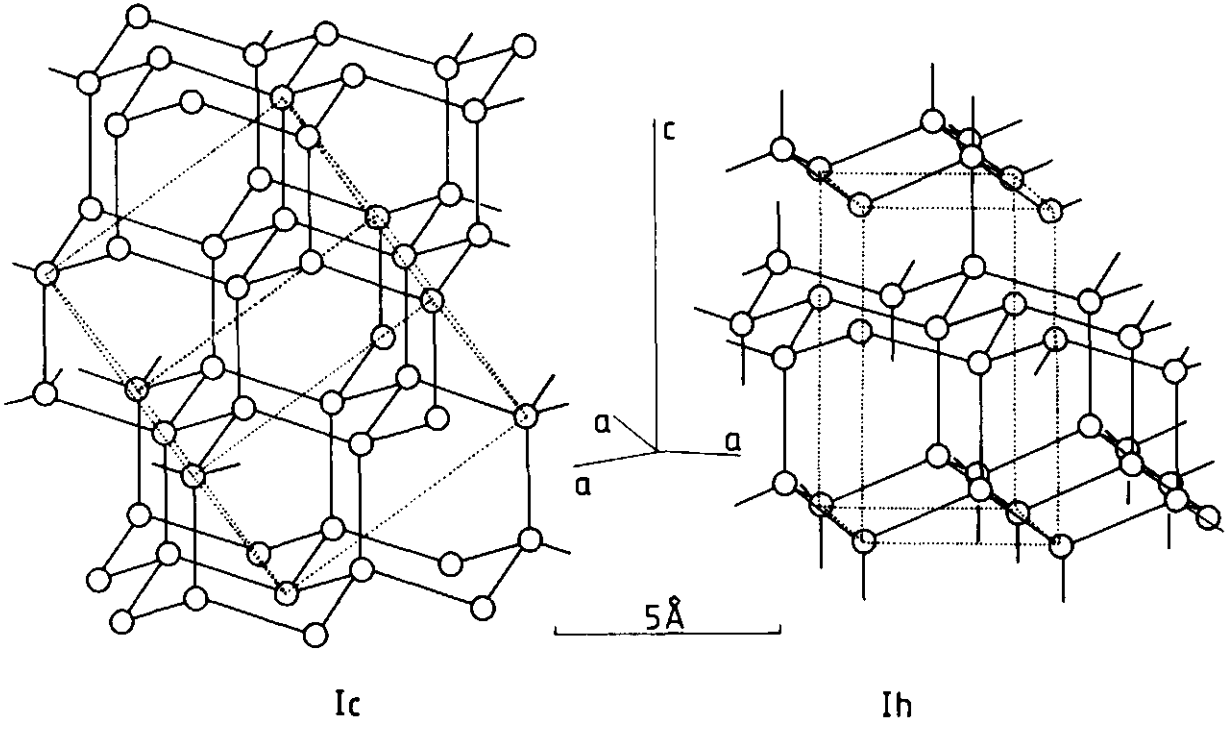


Figure 2.2. The arrangement of oxygen atoms in ices I_c and I_h. The I_c arrangement is isomorphous with that of diamond. The crystalline unit cells are indicated by dotted lines. Redrawn from Eisenberg & Kauzmann (1969).

faces at temperatures between 133 K and 153 K, by warming of vitreous ice (formed at a surface maintained below 113 K), or by treating quenched high pressure ice modifications. Upon further warming, Ic transforms irreversibly into Ih with a small enthalpy change, at temperatures between 143 K and 210 K depending on the history of the sample. The glass transition temperature of pure water is estimated to be 139 K (-134°C) (Kell, 1972; Hobbs, 1974).

Besides the different ice modifications, water molecules are able to form a great number of crystalline structures around small molecules of a less polar nature, e.g. the pentagonal dodecaëder structure around methane (Berendsen, 1968). These clathrate host-structures are not seldom stable at temperatures up to 283 K (10°C) and a few bar pressure. Somewhat comparable water shells with intact H-bonds stabilize apolar groups of biopolymers in water, thus playing an important role in the stabilization of, for example, proteins. NMR spectroscopy showed that water molecules in such a configuration are 2-3 times slower than in the bulk liquid (Zeidler, 1973).

2.1.4 Liquid water

When ice melts, the fraction of open space decreases. The coordination of molecules becomes disordered. The average number of nearest neighbour molecules shifts from 4 to nearly 5. The heat of fusion (6 kJ/mol) indicates that only about 20% of the hydrogen bonds in ice break up, leaving a still relatively open structured assembly of moving molecules forming the liquid. With increasing temperature from 273 K onwards, the open structure is gradually broken down and the density increases until at 277 K this effect is balanced by thermal expansion.

Many aspects of the 'structure' of water are not understood yet. The liquid structure remains continuous until (at high temperatures and pressures) the number of hydrogen bonds has decreased to below ca. 50% of its maximum. Some theories predicting macroscopic properties of water, postulated short living (approx. 10^{-11} s) aggregates of molecules or 'clusters'. Especially the 'flickering cluster' theory (Frank & Wen, 1957) presented a useful work hypothesis for some time. Statistical analysis of hydrogen-bonded assemblies of molecules, however, showed that for water at ordinary temperatures the opposite is rather the case. Breaking of some hydrogen bonds in the structure induces further breaking and creates short living groups of loose molecules in a further continuous structure (Perram & Levine, 1971). Berendsen (1979) found that altogether more than 30 theories on the 'structure' of liquid water have been developed, varying from unordered aggregates via several mixtures of two types of structures to structures with extended clusters of H-bonded networks. Most of the older theories have been outdated by

developments of computer simulation techniques using Monte Carlo methods (Bol, 1979) or molecular dynamics principles. It is expected that improved insight into the structure of the liquid water will be beneficial for the knowledge of water sorbed onto surfaces and all liquid systems containing water.

2.1.5 Water activity

A water vapour sorption isotherm of a substance is the constant temperature relation between the amount of water in the substance and its *thermodynamic relative water activity* (usually abbreviated to *water activity*). This water activity is usually derived from the properties of the atmosphere surrounding and in equilibrium with the substance under study. In the gas phase, water molecules are separated by relatively great distances, at 373 K and 101.3 kPa roughly 10 times their distance in water, which is sufficient to ignore almost completely any non-perfect behaviour among them.

The (relative) activity of any pure substance or component, thus also for water, was originally (1907) defined by Lewis as a ratio of fugacities (see Lewis et al., 1961):

$$a_w = \frac{f_w}{f_w^o} \qquad (2.1)$$

where f_w is the fugacity of water in the mixture at equilibrium, and f_w^o is the fugacity of pure water at standard temperature and pressure. The thermodynamic function of fugacity, or 'escaping tendency', became expedient in order to apply the thermodynamic Gibbs free energy to real substances. For a pure substance fugacity is defined as (Sandler, 1977):

$$f = p \cdot \exp\left(\frac{\mu(T,p) - \mu^{id}(T,p)}{RT} \right) = p \cdot \exp\left(\frac{1}{RT} \int_0^p (v - v^{id}) dp \right) \qquad (2.2)$$

where p is the total pressure; R is the ideal gas constant; T is the absolute temperature; μ is the molar Gibbs free energy or thermodynamic potential of the substance under consideration; the super-script id denotes the ideal gas state and v is the molar volume of the substance. The fugacity becomes equal to pressure at pressures low enough that the system approaches ideal gas behaviour, i.e. $f \to p$ as $p \to 0$.
Gàl (1972; pers. commun.) investigated the difference between water activity (a_w) and the practically generally used *equilibrium relative humidity* or *relative vapour pressure* of the same system and showed that at ambient conditions the difference between the two quantities can be neglected: e.g. at 323 K (50°C) and total pressure of 100 kPa the difference has a maximum of 0.2% (relative), and at 373 K (100°C) and 500 kPa it is 1% (relative) at

maximum. For nearly all water vapour sorption studies this justifies with sufficient accuracy the common equalization of water activity and relative water vapour pressure of the system under consideration:

$$a_w = \frac{p_w}{p_w^o} \qquad (2.3)$$

where p_w is the partial vapour pressure of water in the system and p_w^o is the vapour pressure of pure water at the same temperature and 101.3 kPa total pressure. Equation (2.3) will be used for relating experimental results in this study.

Further in this study use will be made of the quantity *absolute activity* of a component (in our case mostly water), which is defined as:

$$\lambda = \exp(\frac{\mu}{RT}) \quad \text{or} \quad \exp(\frac{\mu}{kT}) \qquad (2.4)$$

depending on whether μ is expressed per mole (mostly in this study) or per molecule; k denotes Boltzmann's constant. This function can be seen as a conveniently expressed thermodynamic potential. Further aspects of this important quantity are treated by Guggenheim (1967).

A discussion of the main aspects of the concept of water activity in relation to its application to food systems has been given by van den Berg & Bruin (1978).

2.2 STARCH, GENERAL ASPECTS AND IMPORTANCE

Starch, or amylum, is the form of carbohydrate reserve in nearly all green plants; it is the major carbohydrate component in food for man and, moreover, in isolated form it has numerous practical applications. About 85 per cent by weight of the world's agricultural crops are cereals - mainly composed of starch - and starchy roots, tubers and stems.
It is produced through photosynthesis via glucose in living plant cells by organelles, called plastids, and deposited in the shape of granules that are insoluble in cold water. For the plant it is a suitable energy reserve; it is macromolecular and almost uncharged so that it does not create significant osmotic pressure. The plastids mentioned before can be either *chloroplasts* or *amyloplasts* (Badenhuizen, 1969). Inside the chloroplasts, starch granules remain very small: they are formed in the stroma, the proteinaceous lamellae in between the chlorophyll-containing layers. Here starch granules act only as a short-term storage of energy accumulated through photosynthesis by the chlorophyll. This type of starch is of no practical interest to man. His prime interest is in starch produced by amyloplasts in plant parts

where it is stored at high concentrations as a carbohydrate reserve to survive periods of unfavourable conditions. These starch granules have diameters ranging from about 2 μm to 100 μm or more. Starch can be isolated readily in relatively pure form from the seeds, tubers, roots and stems by wet milling and separation techniques. Starch owes its unique properties to the presence of mainly two high-polymeric fractions loaded with hydroxyl groups, and the organization of these substances into a semi-crystalline granule which behaves peculiarly when heated in water beyond its gelatinization temperature.

On an industrial scale, starch is isolated from maize (corn), potato, sweet potato, wheat, manioc, rice and, in smaller quantities, from sago and arrowroot (maranta). Estimated world production and sources are shown in Table 2.

Table 2. Sources for world native isolated starch production.
Estimated 1979 world production = 13 million tonnes.

Sources	Proportion of total production (%)
Maize (corn) (Zea mays L.)	76
Potato (Solanum tuberosum L.) and sweet potato (Ipomoea batatas (L.) Lam)	15.5
Manioc* (Manihot esculenta Crantz)	4
Wheat (Triticum aestivum L.)	3
Rice (Oryza sativa L.)	0.7
Sago (Metroxylon sagus Rottb.)	+
Arrowroot (Maranta arundinacea L.)	+

Adapted from data by AVEBE, Veendam.
* other names common in various countries are: cassava or cassada, tapioca, yuoca, ketella, mandioca, aipim.
+ minor quantities of mainly local interest.

Starch is the second largest carbohydrate after cellulose, both with respect to production by nature and utilization by man. The application of starch is very old indeed. Strips of Egyptian papyrus, cemented together with a starchy adhesive, have been dated to the predynastic period of 3500 - 4000 B.C. Other interesting historical notes on starch utilization were compiled by Whistler (1965).

Starting with Nägeli's early work (1858), a vast amount of research on

starch, both purely scientific and technologically oriented, has been going on for more than a century. Although many findings of practical importance were made, it was not before it was realized that the starch granule is not homogeneous, and that reliable methods for separation into the simpler components amylose and amylopectine were found, that more rapid advances in knowledge of the practical uses of this substance were made. Before 1940 starch was regarded by many scientists as a single polysaccharide with a complex molecular architecture. Meyer and co-workers (1940) established the structural non-uniformity of the native starch granule after lengthy discussion in the literature. At the same time, Schoch (see Schoch, 1945) developed reliable methods for fractionating starch into amylose and amylopectin. Since then practical knowledge of starch has grown considerably and so have the applications. Notwithstanding this development, today - still - many aspects of the starch granule and its components are not well understood. The complicated nature of native starch does not yet allow a full understanding of its composition and architecture. For native starch, an illustration of this complication is the observed individuality in properties of each starch grain. Variation is the rule. No two granules are identical. In this respect Banks & Greenwood (1975) suggested that it is probably no exaggeration to say that each granule in a population is unique, differing from its neighbours in fine structure and properties. French (1972) stated that on a molecular scale 'possibly no two branched starch molecules within a single granule are identical'. This heterogeneity has an influence on most starch properties, which makes it somewhat difficult to assign average properties to this material.

Since the Second World War, isolated starches and their derivatives have become very important both as a bulk raw material and a processing aid. The economical importance of starch is illustrated by the fact that starch utilization of a society is directly related to its income. Generally, native and modified starches are applied to improve physical and physico-chemical properties of food products, such as viscosity, gelation, surface, freeze-thaw stability and strength. Further applications are as glue, carriers, binder, filler, emulsifier, moisture buffer and shaping powder etc. Table 3 lists important applications of starch in products and processes, including products derived from starch. This list is not complete. For many applications as a polymer, native starches are not yet sufficiently suitable. Modification of relevant starch properties is obtained by physical (mechanical, pressure or moderate thermal treatment) and chemical (acid treatment, oxidation, esterification, etherification and cross-linking) treatment. In order to retain its easy flow and handling properties, often it is tried to modify starch with retention of its granular structure. Many other carbohydrates can be produced directly from starch, e.g. (malto-)dextrins, oligosaccharides, maltose, glucose, fructose and related sugars. Since starch is a rel-

Table 3. Industrial and household applications of isolated starches.

Foods

Baking products, pie fillings
Custards, puddings, jellies, soups, thickeners and as a general stabilizer
Minced-meat products
Instant and ready-to-eat foods
Sweeteners, glucose and isomerose syrups, maltose
Dietetic food, maltodextrin
Modified starches with numerous specific food applications
Cast powder for shaping liquorice sweets
Indicator for margarine

Paper and wood

Coatings and sizing to improve papers, strength, appearance and resistance
Paper board, board roll sizing, corrugated board sizing, surface sizing and coating, wet-end starches, paper stack sizing, laminates in general
Plywood sizing

Textiles

Warp-yarn sizing to reduce warp-breaks and shredding on looms
Textile finishing, laundry starch to improve stiffness, weight and appearance
Printing starch to thicken dyes and act as a carrier for colour

Chemicals and building materials

Adhesives
Cosmetics
Sugars derived from glucose and maltose
Immobilized enzyme carrier
Pharmaceutical products, e.g. capsules
Polymer additive, e.g. for degradation of packaging materials
Ingredient in insulation foams, abrasives, mortar, gypsum board and fibreglass
Ion exchange material
Flocculating agent for ores
In sandforms for iron-casting, foundry moulds and cores
In oil-well drilling
Binder for ceramics
Starch derivatives for industrial applications

atively cheap, non-toxic, bulk carbohydrate chemical from a renewable resource, it is believed that starch has a great future potential as a raw material both for applications already mentioned and others. As no toxic effect may be expected from physical modifications, new interest has been awakened recently in this starch treatment, but developments in this area are hampered by lack of detailed knowledge of the physical starch structure. New applications of hydrolysed starch products are to be expected, especially when immobilized enzyme reactor technology is further developed and specific chemical reactions become industrially feasible. The generally interested reader is directed to the handbooks of Whistler & Paschall (1965), the series edited by Radley (1953, 1968, 1976a, 1976b) and the series edited by Ulmann (1970-1974). Unfortunately the last series were not completed. They intended to be the most broad and thorough treatise on starch science that appeared until today. The older starch literature before 1926 has been compiled efficiently by Walton (1928), abstracting by that time already 3 485 references. Ulmann (1967) published a bibliography on starch with approximately 21 500 references that appeared until 1966. A Dutch monograph on starch was published by Badenhuizen (1949).

2.3 COMPOSITION, CHEMICAL STRUCTURE AND CONFORMATION OF STARCH

2.3.1 Composition

Pure starch is a mixture of glucans with αD-glucose as the monomer unit. Two distinct types of starch polymers are distinguished, namely *amylose*, a mixture of essentially linear polymers, and *amylopectin*, a mixture of branched polymers. In most starches amylose and amylopectin occur together with some material of *intermediate* nature.

For common starches the content of amylose, normally defined by its typical iodine binding power (measured via titration), ranges between 17 and 30% of the starch material. Typical values are potato 21%, maize 27%, wheat 23% and cassava 20%. Selective breeding has led to other starch types, salient examples of which are amylomaize starch, containing 50-80% amylose, and waxy maize starch, which is almost 100% amylopectin. Pure amylose binds iodine, approximately 20% of its weight, forming the characteristic blue amylose-iodine complex. This complex has been extensively studied in order to determine its exact structure. Teitelbauan et al. (1978) showed recently that the complex is built up of predominantly I_5^- ions within the amylose helix. The non-amylose part is usually considered to be amylopectin. Hence one finds directly the amylose : amylopectin ratio. This ratio is determined by the plant genotype. Amylopectin does not bind iodine in appreciable quantities. The amylopectin-iodine complex formed has a colour varying from reddish (waxy-maize) to violet (potato). It is fundamentally correct to define both

amylose and amylopectin in their pure form in terms of their branching characteristics. In practice, this is not possible for amylopectin because a small quantity of amylose will not be noticed.

In the usual categorization by iodine titration the intermediate starch material fraction, amounting in common starches to about 5-10% of total weight, behaves partly as amylose and partly as amylopectin. Relatively little is known of this fraction. Banks and Greenwood (1975) consider this intermediate material as a separate entity, quite distinct from both amylose and amylopectin. They found this component in considerably greater amounts in high-amylose cereal starches. This starch component will receive no further attention here. In the starches studied, it forms only a minor fraction and it is unlikely that it will show a water vapour sorption behaviour significantly different from both major starch components, which themselves have already comparable water vapour sorption isotherms (Chapter 6).

Besides water, natural starches contain still some *minor constituents*. Worth mentioning for cereal starches are fats and fatty acids, which contribute up to 1-2% of total weight. Furthermore, there are traces of minerals, the cations of which are adsorbed or bound electrostatically to some charged groups in the starch, causing it to have a weak poly-electrolyte nature. Phosphate groups occur in some tuber starches; in potato starch they contribute 0.07 - 0.22% to total weight (Proefstation v.d. Aardappelverwerking, personal communication) and are esterified with the amylopectin fraction as single phosphate esters. Two hydrogen ions of the phosphate group can be exchanged with cations. The cation content and distribution may considerably influence swelling and rheological behaviour (Hofstee, 1962). Water vapour resorption isotherms for two potato starches with different phosphate contents are reported in Chapter 6.

2.3.2 Amylose

Native amylose is a linear polymer of $\alpha 1 \rightarrow 4$ linked (anhydro-)D-glucopyranose units (glucan), with a degree of polymerization (D.P.) of a few hundred up to 10 000 or more, giving molecular weights ranging from 10^4 to 10^6, usually $> 10^5$. Figure 2.3 shows the structural formulae of amylose in Haworth projection. Each molecule has one reducing end group (due to which it shows mutarotation equilibrium in water) and a non-reducing end group. This picture is somewhat idealized because of the occurrence of some $\alpha 1 \rightarrow 6$ bonds in practical amylose preparations.

In recent literature there is consensus on the conformation of the building

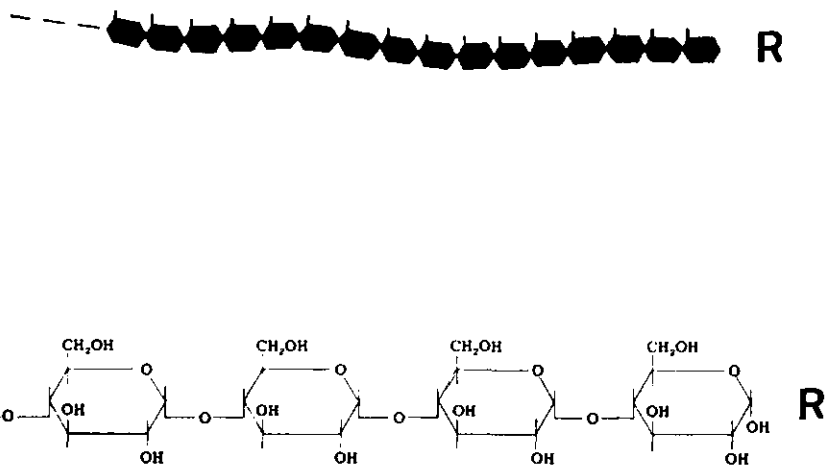


Figure 2.3. Diagrammatic representatation of the structure and structural formulae of amylose. R = reducing end. Adapted from Pazur (1965).

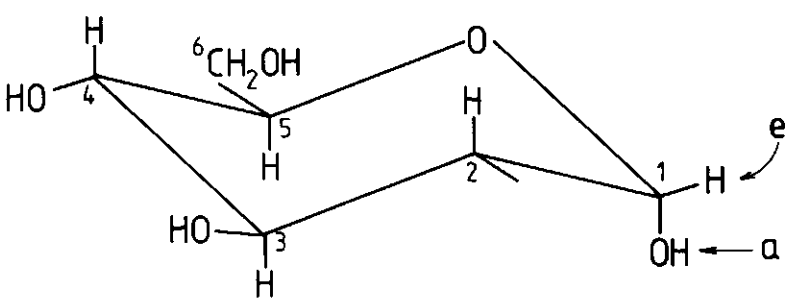


Figure 2.4. $^{4}C_{1}$ chair conformation of αD-glucopyranose. e = equatorially directed; a = axially directed.

unit αD-glucopyranose in $^4C_1$ form*. This conformation, pictured in figure 2.4, has the lowest conformation energy of the existing alternatives because all bonds are staggered and the axial groups do not repel (Rees, 1977).

Due to the α1→4 axial-equatorial linkage, the amylose backbone, immersed in a good solvent, easily forms coils and helices. A variety of helical structures for the amylose conformations have been proposed with 2-8 monomers per turn and one or more H-bonds and sometimes water molecules between the windings. The most persistent proposals in literature are six-membered amylose helices, mainly due to the fact that α-maltamylase decomposes amylose chains into six-membered dextrins (Frey-Wyssling, 1969). Interaction energy calculations showed that only helices with 5, 6 and 7 monomers per turn are intrinsically stable. This argument together with the established hexagonality of the common starch crystals (Subsection 2.4.3) make six-membered helices timely indeed. The actual conformation of amylose in aqueous solutions is still under discussion. Helices, random coils and combinations of both all find support. H-bond breakers such as alkalis are known to unroll the helices into random coils. It is most probable that the nature of the solution plays a predominant role in shifting the conformation in either direction. Amylose helices are much favoured by the availibility of complexing substances (e.g. aliphatic alcohols, thymol and iodine) in the solution. In sufficient concentration some of those substances form with amylose well-crystallized precipitates, a method frequently used for starch fractionation (Subsection 2.5.3). Details on possible amylose conformation in solution are given by for example Jalink (1966), Szejtli & Augustat (1966), Banks & Greenwood (1975) and Brant (1976). The structure of V-amylose, a common starch polymorph obtained from solutions, shows also six monomers per helical turn (Zobel et al., 1967; French & Zaslow, 1972). The helix chirality is most probably left-handed. The size of the unit cell depends on the degree of hydration indicating that water is contained within the crystal. However, next to six-membered amylose helices a variety of inclusion complexes with more than six monomers per helical turn exist (French & Murphy, 1977). With respect to helices and amylose, it is interesting to note that the first helical structure with 6 glucose residues per turn was proposed by Hanes in 1937** for amylose.

More interesting for this study would be to know the configuration, the conformation and the built-up, fine structure of amylose in its solid state in

* The letter C indicates a chair form and the two numerals represent the ring atoms which are above and below the plane respectively, when the ring is viewed from above in such a way that the numbering appears clockwise. In old notation this conformation was designated C 1.

** This was about 15 years before the existence of helical structures was generally accepted after the discovery of the α-helix for proteins.

the starch granule, which is still an unsolved problem. Synthetic (semi-) crystalline amylose preparations show the same crystalline arrangement as native starches where amylopectin is known to be responsible for the crystallinity. An exception to the latter is native amylomaize where amylose is believed to be partially crystalline (Greenwood, 1980). Stretched chains for amylose are very unlikely. With Frey-Wyssling (1969) it is concluded that folded chains (coils) and/or helices must also exist in the solid state.
When aqueous starch solutions are left to stand for some time partial precipitation occurs. This is due to the separation of the amylose component. The amylose molecules align themselves and when the size of aggregates exceeds colloidal dimensions they precipitate.

2.3.3 Amylopectin

Native amylopectin is an α1→4 glucan with about one α1→6 bond per 20-26 monomer units (in potato starch about 25) but otherwise linked α1→4, giving a branched structure (Figure 2.5). With a wide variation, D.P. is larger than 50 000, yielding molecular weights of approx. 10^7 or more, making it one of the largest natural polymers. There are indications that D.P. increases dur-

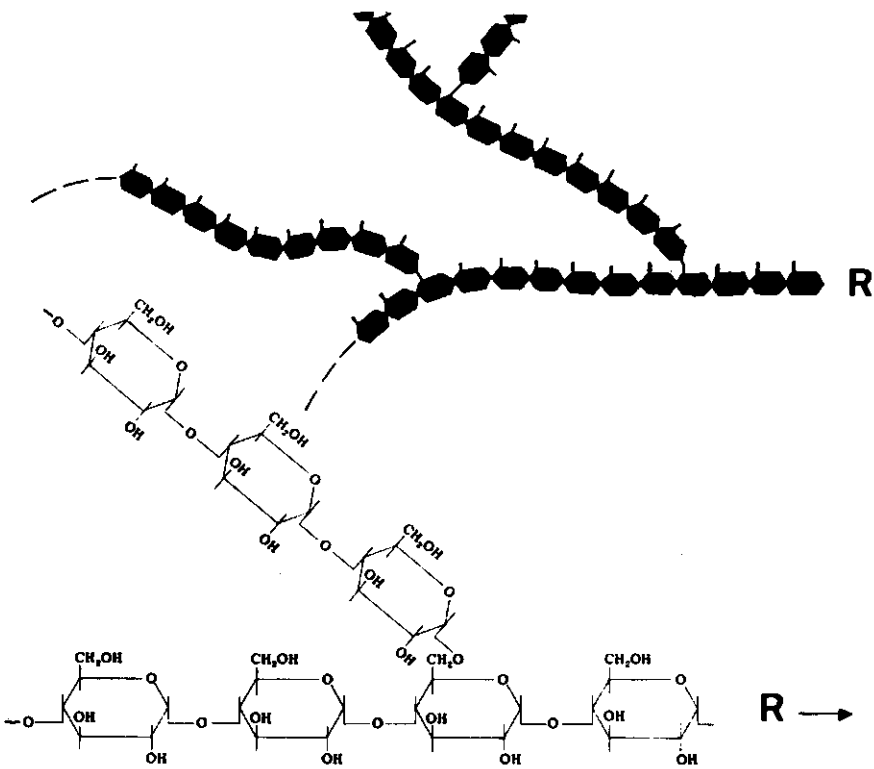


Figure 2.5. Diagrammatic representation of the structure and structural formulae of amylopectin. R = reducing end. Adapted from Pazur (1965).

ing growth of the starch granule: for instance, for a certain sample of potato starch the molecular weight increased from 9.10^6 to 130.10^6; at the same time the average number of branching points increased from 1 per 26 monomer units to 1 per 22 (Greenwood, 1970). The big amylopectin molecule contains one reducing end group and many non-reducing end groups. Enzymatic studies have shown that the branching point distribution is essentially random. The greater part of the molecule is located in end chains. The fine structure of amylopectin has not yet been established. Banks & Greenwood (1975) speculate that it has a two-dimensional structure. Structural studies are complicated by the very large molecular weight and imperfections inherent to the chemical and enzymatic methods.

Proposals for the amylopectin fine structure have been made generally in connection with the native starch fine structure where amylose and amylopectin are intimately mixed. Figure 2.6 shows the most important ones. Three early proposals are: (a) the laminated structure (Haworth et al., 1937), (b) the herringbone structure (Staudinger & Husemann, 1937) and (c) the randomly-branched structure (Meyer & Bernfeld, 1940), usually referred to as the 'tree-like' structure. This model (c) and its successors distinguish three types of branches. The A chain is linked to the rest of the molecule only through its reducing end group; the B chain is linked as an A chain and is also substituted through the C(6)-hydroxyl in one or more of its constituent glucose units to an A or other B chain; the C chain is single and carries the reducing end group. This model was revised after a detailed study by Gunja-Smith et al. (1970), who concluded to an average of 2 branching points per B chain, located close together (d). This revised randomly-branched structure, also named Whelan model, was conluded to be likely by Burchard et al. (1975) from light-scattering experiments.

The following diagrams in Figure 2.6 are fine structure models proposed in more direct relation to the location of amylopectin molecules in the starch grain. Anticipating Subsection 2.4.4 some more information is added than strictly refers to the amylopectin component of starch. Fine structure model (e) with dichotomous branching was proposed by Frey-Wyssling in 1948 (Frey-Wyssling, 1969), taking into account known optical and chemical facts. This model developed finally into a very detailed ultrastructural model for potato starch (Frey-Wyssling, 1974). This model (f) might resemble reality perhaps best as it is in concordance with the main characteristics of potato starch, namely: the microlamellation of the granules (100 nm), the predominance (78%) of amylopectin in the granules, the quantity of terminal segments of the ramified amylopectin which are split off by β-amylase (30%), the proportion between 1→4 and 1→6 bridges in the amylopectin molecule (24:1) and the optical birefringe as interpreted by Speich (1942) (Subsection 2.4). Folded molecules (g) have been proposed by Mühlethaler (1965)

following the structural arrangement of some synthetic polymers. This proposal conflicts with the general belief that amylopectin molecules extend mainly radially instead of tangentially. An early model (h) for the fine structure of amylodextrin (partially hydrolysed native starch), with clearly recognizable descendants for amylopectin configuration in the present, was proposed by Arthur Meyer (1895). From extensive microscopical observations he concluded that fine fibers (trichites) are *radially* located in the starch spherocrystal. The differences between the structures of the concentric starch layers (Subsection 2.4.2) Meyer thought to originate from differences in length and thickness of the indvidual trichites and from more or less dense arrangement and more or less branching points as depicted in the model (h). The fine structure shown in (i) was proposed by Nikuni in 1969 (Nikuni, 1978). Nikuni's model depicts a gigantic starch molecule embracing ultimately the whole starch grain. Although the concept embodied in the model is difficult to argue, it is in direct conflict with the accepted idea that starch is composed of two main components. French (1972), reviewing starch structure, changed the dimensions of Meyer's trichites and proposed a modified trichitic structure (j_1) and also a racemose structure (j_2) in order to cope with the finding that amylopectin is the main crystalline component of the majority of native starches. The model depicted by (k) for waxy maize amylopectin is a result of studies by Guilbot and co-workers (Mercier & Guilbot, 1974), tracing further the results of Gunja-Smith et al. (1970) and proposals of French (1972). The same fine structure (k) has been proposed with slightly modified dimensions for potato amylopectin by the same group of workers (Robin et al., 1974).

Most modern proposals agree that some racemose type structure (Figure 2.6-j_2) characterizes the general arrangement of amylopectin as the major component of common starches. In this connection it should be realized that a few per cent of $\alpha 1 \rightarrow 6$ links between the monomers impart an essential additional flexibility (when compared to amylose) to the molecules, making possible several different packing arrangements. Furthermore, this linkage with its greater flexibility may be envisaged as introducing to the starch granule less crystalline and more accessible regions for hydrolytic attack (Tvaroska et al., 1978). It was surprising to find that the amylopectin component plays a major role in the crystalline arrangement of common native starches (Subsection 2.4.3). Analysis of starch crystals has shown a helical chain conformation in all cases.

The branched structure is in agreement with the inability of amylopectin to form films or threads from solutions. Also the formation of inclusion complexes as well as retrogradation from solutions is much more difficult than it is with amylose. In the commercial starch fractionation process, as described by Muetgeert (1961), precipitates of amylose form within a few minutes, while amylopectin precipitates take a few hours.

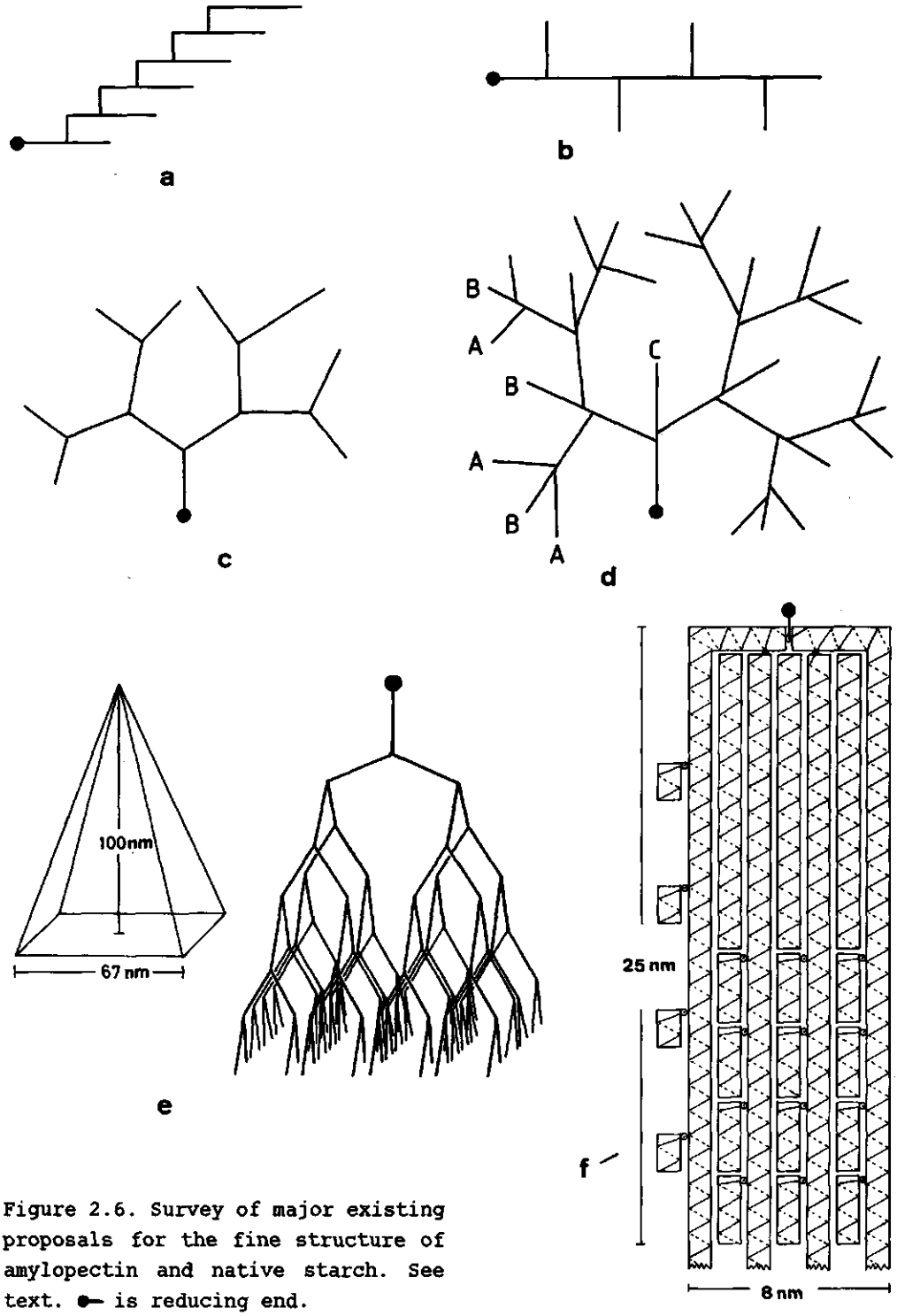
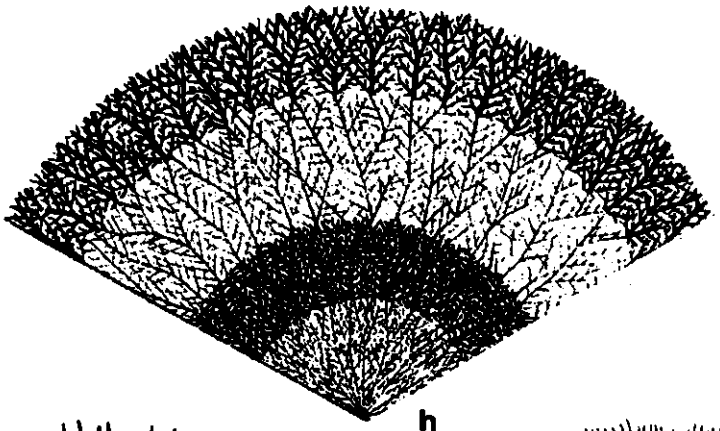
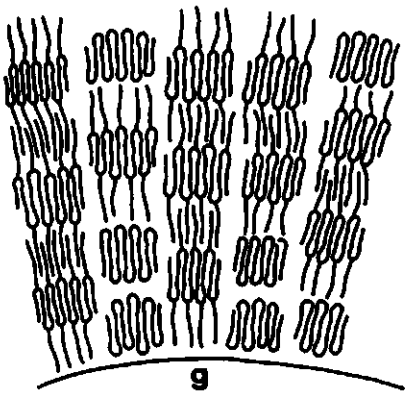
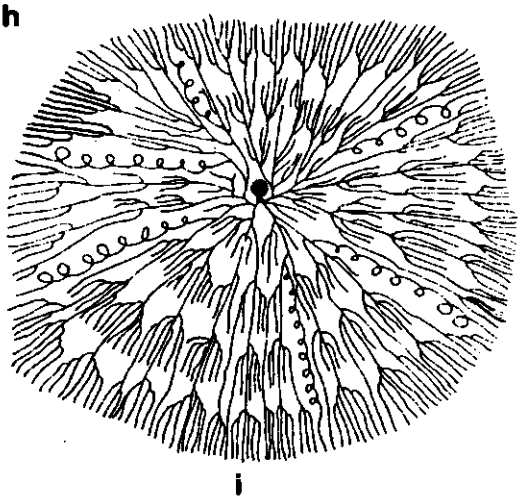
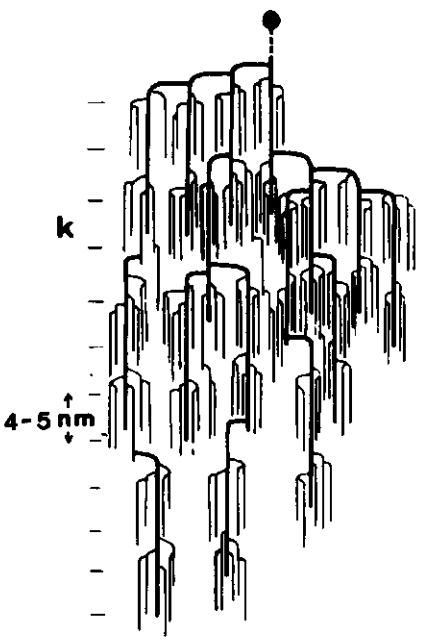


Figure 2.6. Survey of major existing proposals for the fine structure of amylopectin and native starch. See text. ●— is reducing end.









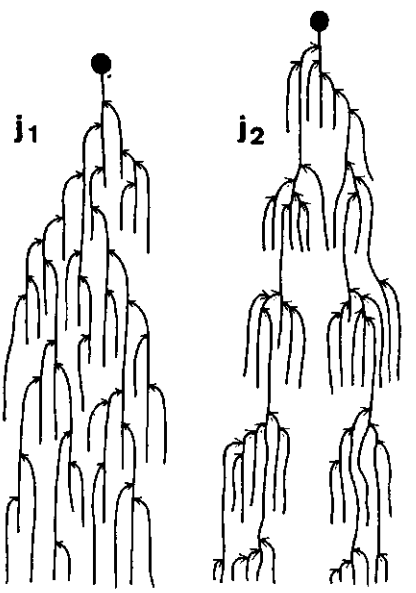


Figure 2.6 (continued)

2.4 PHYSICAL STRUCTURE OF THE STARCH GRANULE

2.4.1 General

As early as 1942 it was said (Kurt H. Meyer, 1942) that the abundant literature on starch is of such perplexing variety and so full of contradiction that a clear comprehension of the starch structure is very difficult to acquire. Although several important matters on the physical structure of starch granules have been elucidated since then, the generally rather confused overall picture still exists. Concerning the interpretation of some phenomena of starch grain behaviour and matters such as (i) the distribution of amylose and amylopectin and their location and organization within the granule, (ii) the porosity of the granule, (iii) the fine architecture of the granule in terms of different units such as blocklets, microgranules or fibres, (iv) the extent of crystallinity and (v) the role of water in the structure, a wealth of conflicting data and interpretations can be found. With starch it is particularly difficult to make the grain fine structure visible. As this structure exhibits very little contrast and is easily destroyed, one is almost never certain that the applied techniques produce no artefacts. Hence it is certainly not surprising that in the same year that Schoch (1941) published some of his pioneering work on starch fractionation into different components, Badenhuizen (1941) still concluded, on the basis of his own extensive research, that starch must be chemically homogeneous. In a way native starch is still a 'polycrystalline product with a hidden structure' (Katz & Rientsma, 1930).
The most salient features of the starch granular structure relevant to this study on water vapour sorption and its background information is summarized in the following subsections.

2.4.2 Appearance

Starch granules vary considerably in size (roughly from 2 μm to 175 μm) and in shape (from spheres to rods assuming nearly all types of regular and irregular shapes). Usually the source of a starch can be identified from its microscopic appearance. The granules are grown as an entity, but can consist of more particles with individual centres of nucleation (compound granule). Some examples of granule appearance under the light-microscope are shown in Figure 2.7. An extensive treatment on starch microscopy is given by Seideman (1966).

Most granules, when containing water, show concentric layers around a place called hilum, which is the centre of nucleation started by the original amyloplast. The single granule grows through apposition and is not formed and then filled with deposits on the inside (Badenhuizen & Dutton, 1956). An

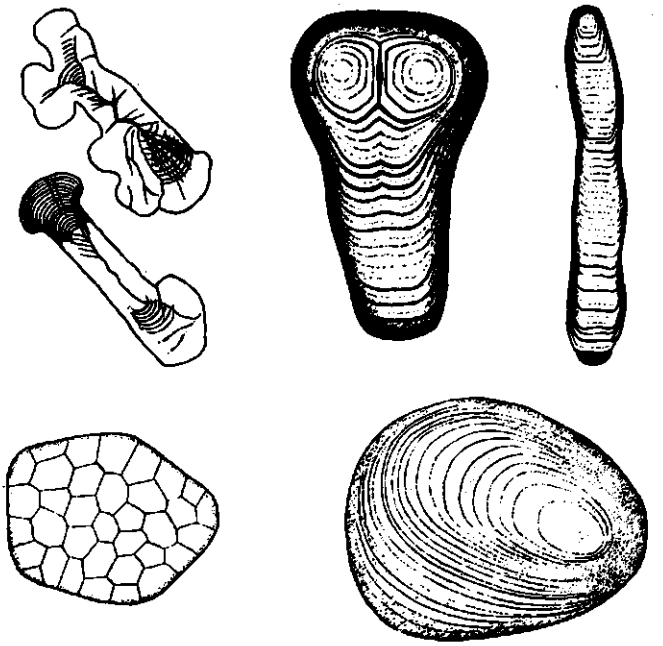


Figure 2.7. Divergent forms of some starch grains from different plants. Upper row from left to right: Two bizarrely formed grains from *Euphorbia myrsinites* (×680). Grain with two hila from *Pellonia daveauana* (×1320). Eccentric grain with part of chloroplast body from *Dieffenbachia seguina* (×500). Lower row from left to right: Complex grain from *Avena brevis* (oat) (×860). Grain from *Solanum tuberosum* (potato) (×1040). From Sterling (1968).

amyloplast membrane surrounds the growing granule (Wetzstein & Sterling, 1978). Most probably this membrane accommodates the enzymatic action at the granule surface through which glycosyl is being deposited at the non-reducing end of the starch molecules during growth. The visible concentric layers in potato starch can be 1-7 μm wide. In cereal starches they are smaller, approximately 0.4 - 1 μm wide. These layers are not visible when dry granules are examined in pentane, which has the same refractive index as water but is incapable of swelling the granule (Hanssen et al., 1953). Nor can the layers of untreated starch grains be detected in the electron microscope with current techniques. Under the electron microscope starch reveals a non-structured homogeneous body. Apparently the layers are regions differing with respect to properties such as swelling behaviour. The concentric layer

formation in potato starch, visible in the light microscope, is caused by the changing carbohydrate concentration due to the day and night rythm of growth (Meyer, 1895) and is emphasized by tangential swelling (Badenhuizen, 1969). Frey-Wyssling & Buttrose (1961) showed that the concentric layers of potato starch, visible in the light-microscope, are already a periodic overlayer. All are built up of a series of finer concentric layers of about 100 nm wide, that, according to Buttrose (1963), are deposited during growth in a periodical 2 hour cycle. When starch has been treated with sulfuric or hydrochloric acid (Nägeli or Lintner treatment), which is generally assumed to hydrolyse the amorphous parts preferentially, the granules show a more pronounced concentric layer structure and are often named 'amylodextrins'. Depending on the starch, it is even possible to dissolve 70% or more of the total starch material without loosing the granule integrity (Buttrose, 1963). Finally after such treatment stable residues remain, soluble in boiling water. Meyer (1895, photograph 8) portrays an amylodextrin skeleton hydrolysed according to Nägeli (1874) as long as 5 years. Because the average D.P. of acid-treated samples has decreased by several orders of magnitude, it is likely that acid degrades starch molecules in both the amorphous and crystalline parts. However, during this degradation the crystalline parts may well pick up amylose molecules of suitable size (D.P. 10^2 - 10^3) that are known to crystallize rapidly (Subsection 2.5.2), leaving the crystalline parts apparently intact and probably of higher crystalline order.

2.4.3 Crystalline nature

The starch granule contains spherulites building a semi-crystalline complex. This complex shows *positive* birefringence in polarized light, giving the typical 'Maltese cross' pattern. Birefringence implies mainly that there exists a high degree of molecular orientation within the granule, without reference to any crystalline form (Banks and Greenwood, 1975, page 247). Starch granules share their typical polarization pattern with several synthetic polymers that form spherulitic structures when they cool from the molten state. It is not unlikely that several starch granule properties can be interpreted in terms of the theory of polymer spherulites. Speich (1942) interpreted the birefringence as a rodlet birefringence superimposed on a positive intrinsic double refraction of the starch itself.

All common native starches except high amylose-starches give well-defined X-ray diffraction patterns, a fact first observed by Scherrer around 1918 (Katz, 1928). Early impressions of the fractional crystallinity were usually higher than 0.5 (Rundle et al., 1944) but actual determination of this crystallinity on the basis of interference intensities of X-ray diagrams revealed values of approx. 30% only. For different potato starch samples Sterling (1960) reports crystallinities of 21% for air-dry native, 27% for air-

dry Lintnerized (acid-treated), 28% for moist native and 34% for moist Lintnerized potato starch. Water contents are not mentioned. Nara et al. (1978) confirmed this in their study on the crystallinity of potato starch at different levels of hydration. Unfortunately they made no correction for the water in the sample so that their crystallinities are not expressed on a dry starch basis. Their overall relative crystallinities range from 0.78 (0.10) to 1.61 (0.41). The sample hydration levels (kg w./kg d.s.) are given in parenthesis. The standard sample with relative crystallinity 1 (0.239) was estimated to have a crystallinity of 25%. Cleven et al. (1978) reported 33% crystallinity for moist (0.4 kg w./kg d.s.) Nägeli-treated potato starch. This value was based on X-ray analysis and the assumption that all water is located in the amorphous part. For tapioca and cereal starches, Zobel & Senti (1960, in Nara, 1978) reported slightly higher values for the crystallinity, around 38%.

Determination of the crystallinity of starch on the basis of water vapour sorption data, such as is useful with cellulose, was applied by Nara (1979) and by Sterling (1960). This method, however, may not be used with starches because its basic assumption, that water remains outside the crystals, is not true for starch crystals, where water on the contrary plays an essential role (Subsection 3.2.4). Meyer et al. (1929) and Katz & Derksen (1930) correctly make mention of 'water of crystallization' in starch contrary to native (I) cellulose crystals that do not contain water. Both references point to the analogy with the dimer units of these polymers, αD-maltose contains water of crystallization, whereas βD-cellobiose does not. A fully dry starch displays an amorphous X-ray diagram. Upon gradual hydration the first interferences appear at 4-5% hydration and increase gradually. As a result the crystallinity value obtained increases upon hydration, which is illustrated by the values of Sterling (1960) and Nara (1979). On a molecular scale this phenomenon can be explained by a distorted crystalline lattice in the dry state that becomes better organized by water molecules which fill the cavities existing within the crystals and at the same time influence the balance of attractive and repulsive forces. Besides this it is possible, as Sterling (1960) suggests, that a (minor) part of the crystallinity increase is due to the rearrangement of less ordened (more amorphous) branches of starch molecules into the crystals when they become more mobile in the increasing amount of diluent. Another argument for the different crystalline nature of starch as compared to for example cellulose was given by Taylor et al. (1961), who showed that all hydroxyl hydrogens of crystalline and retrograded starches are exchangeable with liquid D_2O. Furthermore it is known that native starch is very reactive to some substitution reactions which occur randomly all over the grain.

In contrast to earlier ideas, it is now generally accepted that crystallini-

ty is essentially due to the branched starch component amylopectin. This is derived from the facts that waxy-maize starch (with no amylose) has an X-ray pattern (A type) very similar to that of normal native maize starch (Banks & Greenwood, 1975), and that at elevated temperatures amylose can be leached preferentially from the starch granule while leaving the crystalline structure intact (Montgomery & Senti, 1958). Independently it was known that the crystal type is independent of the amylose content (Badenhuizen, 1971). In this connection it must be remarked also that Meyer (1942) had already attributed the major crystallinity of starch to the gigantic amylopectin molecules that hold the granule together like a network with crystalline fringed micelles at the junctions.

Depending on botanical source and the circumstances of growth and, when applicable, treatment afterwards, starches show a number of different X-ray diffraction patterns, indicating different allotropic modifications (or polymorphs). The early classification of Van Náray-Szabó (1928) was improved by Katz & Van Itallie (1930), and their classification is now generally accepted. Domesticated plants containing native starches can exhibit one out of three basic types of diffraction patterns, classified as A (most cereal starches), B (potato, amylomaize and most retrograded starches) and C (manioc and various bean starches). In nature some other, still unclassified, types can be found. Sterling (1968) states correctly that starch molecules must be both flexible and prone to align with their neighbours in many regular, near or actually crystalline lattices. The crystal structure of these modifications is difficult to fathom. For the crystal type B and recently also for the A crystal models have been proposed that have reasonable probability of being valid. It should be realized that the best current estimates of crystalline space group and unit cell bear only degrees of probability, rather than certainty. The number of X-ray reflections is in fact far too small to indicate the actual atomic arrangements. For polyanhydroglucose $(C_6H_{10}O_5)_n$ (or starch) theoretically about 1000 data would be necessary (Zaslow, 1965). Therefore other methods must assist the analysis. Other problems that obviously complicate the elucidation of the crystal unit cell of starches are the partial crystallinity, the many reflections in the X-ray pattern of small intensity and the slightly changing dimensions of the unit cell with changing hydration. In the present study preference is given to the model for B-type starch as proposed by Cleven et al. (1978).

The C type is interpreted as an intermediate (or a mixture) of A and B. Under suitable circumstances the crystal types change into one another without marked energy effects, indicating that they are closely related. Upon heating of potato starch in a moist atmosphere the B type is converted to the A type via the C type (Sair, 1967). Because this conversion also drastically changes the viscosity pattern (Hofstee, 1962), this heat-moisture treatment

is of great practical significance (roughly: it converts potato-type starch into maize-type starch). Although the method was applied industrially in the thirties, it was first described by Sair & Fetzer (1944). The crystallization of starch into the A, B or C type depends much on temperature and water content (Katz et al., 1930). Hellman et al. (1954) observed for aging starch gels with different water contents that the X-ray patterns of A, C and B do appear at increasing amounts of water. Also starches from soybean seedlings grown at various temperatures exhibit different X-ray patterns. At 30°C an A pattern is preferred, at 13.5°C a B pattern and at 22°C equal amounts of A and B are formed (Hizukuri et al., 1961; Nikuni, 1978). Above approximately 333 K (60°C) *no* starch crystallization takes place and for example bread does not stale for a very long time.

Oriented starch fibres are extremely difficult to prepare, so that for X-ray studies one usually has to be content with powder diagrams. Applying an ingenious microtechnique (Kreger, 1948) to the big eccentric starch grains of the orchid *Phajus grandifolius*, Kreger (1951) could obtain a fibre diagram from a single intact starch grain (B type). From this he established *radial* orientation of the starch molecular branches in the crystallites, being packed together in a *hexagonal* lattice. For the A type crystal modification, Kreger & Nijenhuis (unpublished results, 1952) also obtained a radial fibre orientation and a slightly different hexagonal pattern. Some further details about starch crystals and water are given in Section 3.2.

2.4.4 Ultrastructure

In Subsection 2.3.3 (see Figure 2.6) a brief survey is given of the main proposals of the molecular arrangement and fine structure of starch, in particular its major component amylopectin. Generally both components amylose and amylopectin are intimately mixed in the starch granule. Some starches (e.g. wheat) contain more amylose in the middle of the granule, but generally amylose may be expected to be distributed in a molecularly disperse way within the semi-crystalline amylopectin network. Reviews in the literature on the ultrastructure of starch by inter alia Badenhuizen (1969), French (1972), Hölzl (1973), Banks & Greenwood (1975) and Sarko (1975) present a variety of ideas illustrating the complexity of the matter. Somewhat striking is that few research workers check their results against others and readily generalize their own proposed structural models to cover all starches, making minor modifications when necessary. They do this even though important differences exist among different starch types in patterns of degradation by acid and enzymes.

Based on electronmicroscopic observations with Lintnerized potato starch Sterling (1971; Sterling & Pangborn, 1960) concluded also to a radially

stretched system of long fibres, crossing the layers. The individual microfibrils (Ø approx. 27 nm) in these bundles are thought to be composed of 7 elementary fibrils (Ø approx. 8 nm) in hexagonal array surrounded by amorphous material. Frey-Wyssling (1974) based his model for the potato starch fine structure (Figure 2.6-f) partially on this concept. In this model the amylopectin molecules stretch over the depth of a concentric layer (100 nm). The molecules within the crystallites of the elementary fibrils may well be arranged in the hexagonal lattice as proposed by Cleven et al. (1978). In contrast to this fibrillar concept Sarko (1975) and Mühlethaler (1965) favour a folded arrangement of molecules to fill the concentric layers with radially oriented molecules.

A measure varying between 6 and 10 nm frequently appears in this discussion (Sterling & Pangborn, 1960; Duprat et al., 1974; Robin et al., 1974; Kassenbeck, 1978), usually interpreted as the crystallite length which can be one bundle of molecular branches. Preliminary small angle X-ray diffraction measurements with potato starch Nägeli-amylodextrin (van den Berg, Cleven, Vonk, unpublished results) confirmed the existence of a sharp diffraction maximum of 9.3 nm. A comparable observation was reported by Sterling (1959). A measure of this order commonly occurs with semi-crystalline synthetic polymers. There it is the repeat distance (thickness) of two phase-layers consisting of a crystalline and an amorphous part, as it were a unit cell of the polymer morphology. Assuming this is true also for native potato starch it gives together with the measured value for crystallinity of 33% a crystallite length of at least 3.1 nm. The direction of the crystallite is perpendicular to the layer plane which almost certainly is situated parallel with the concentric layers of the starch granule. For the B starch polymorph with a distance of 1.04 nm per helical turn (fibre period), containing 6 anhydroglucose monomers, exactly 18 monomers are necessary to bridge an entire crystallite of 3.1 nm. This roughly conforms with the average length of the amylopectin side chains (20-26 monomers). The measure of 3.1 nm is close to the value of 2.6 nm for the minimum crystallite size as estimated from the breadth of the strongest X-ray diffraction at 1.58 nm (unpublished results). 3.1 nm is also the size of the enlarged crystal unit cell as proposed by Cleven et al. (1978).

Until now we can only speculate about where water molecules find their location in this structure, when starch is placed in a moist environment. Certain is that water establishes hydrogen bonds with the OH groups of the structure. In the most probable helical structure these groups are located at the outside, making the inside a suitable environment for apolar substances to build inclusion complexes. Although there is some place for water inside the helix, it is unlikely that important amounts of water are located there. Some water is contained in the crystallites, but the main water,

causing the swelling of the starch granule during water uptake, penetrates the amorphous parts (Subsections 3.2.5 and 3.3.3).

The rough basic concept of the swelling starch grain fine structure was formulated by Meyer (1942), combining in fact the *fringe micelle* concept (Hermann et al., 1930) with the early *micelle theory**, which Nägeli (1858) conceived from his investigations of native starch grains and their swelling behaviour. Meyer's concept (Figure 2.8) represents the intermixed linear and branched starch molecules. Wherever linear chain segments parallel each other, hydrogen bonds pull the chains into 'micelles' that are semi-crystalline arrangements or crystallites. The chain flexibility between the crystallites permits swelling of the network in a solvent but prevents ready dispersion and dissolution of the individual molecules. Meyer et al. (1940) estimate the thickness of these crystallites to be 6-10 nm, containing each 50-100 polymer chains, which is the order of Sterling's elementary fibrils.

Since Meyer (1952) the traditional concept of the fringe micelle as a model for the morphology of a semi-crystalline polymer has fallen into the background due to the development of the *paracrystallinity* model by Hoseman (1950, 1962). In this concept the amorphous regions are considered to be defect locations in an overall crystalline matrix. Motions of such dislocations generally do give a better explanation of polymer behaviour than is supplied by the fringe micelle model. Figure 2.9 gives a diagrammatic representation of a proposal of the native starch structure by the author. This proposal is an attempt to combine the paracrystallinity model with some recent concepts of the starch structure, namely the Whelan model of the amylopectin structure, the amylose component occurring in non-crystalline form and the layer concept mentioned above. Essentially it combines the features of several of the proposals given in Figure 2.6 and provides a suitable working hypothesis for the ultrastructure of native starch, at least that of potato.

* It is now almost forgotten but Carl Nägeli's old micelle theory (Nägeli, 1858; Nägeli & Schwendener, 1877) played an important part in the early developments of the theory on the structure of biological macromolecules in general. Nägeli thought biological materials, which not seldom are found to imbibe a mass of water several times their own dry mass without losing their chemical reactivity, to be composed of elementary anisotropic particles that could move with respect to each other. These smallest natural mass particles, 'micelles', were thought to be impenetrable for water. From this Nägeli expressed the opinion that the water imbibing power of a colloid was not determined by the mass of its micelles but rather by their surface area. Because proper concepts of molecules and their interactions were not developed at that time, this theory is only of historic interest, but when reduced to its proper dimensions the emphasis at the close relation between surface area (number of polar groups) and water sorption behaviour may be seen as a remarkably modern view (Subsection 3.1.7).

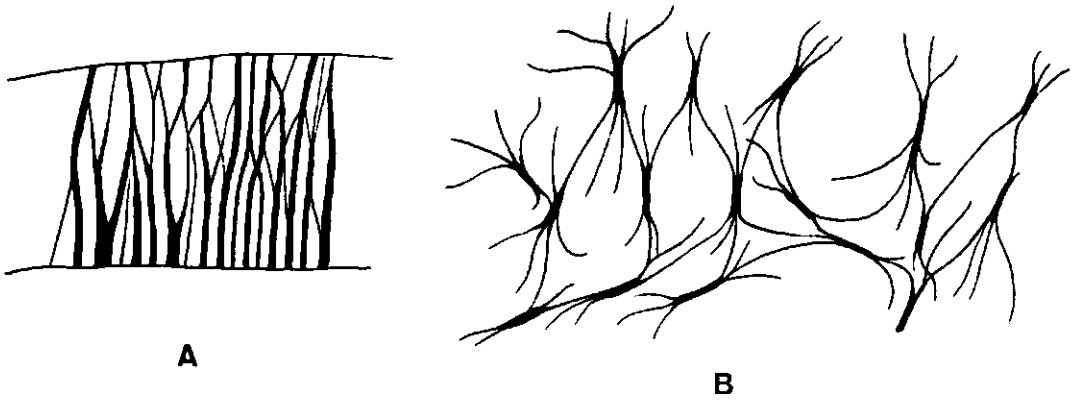


Figure 2.8. Diagrammatic representation of the micellar native starch structure according to Meyer (1942). A. dry; B. swollen.

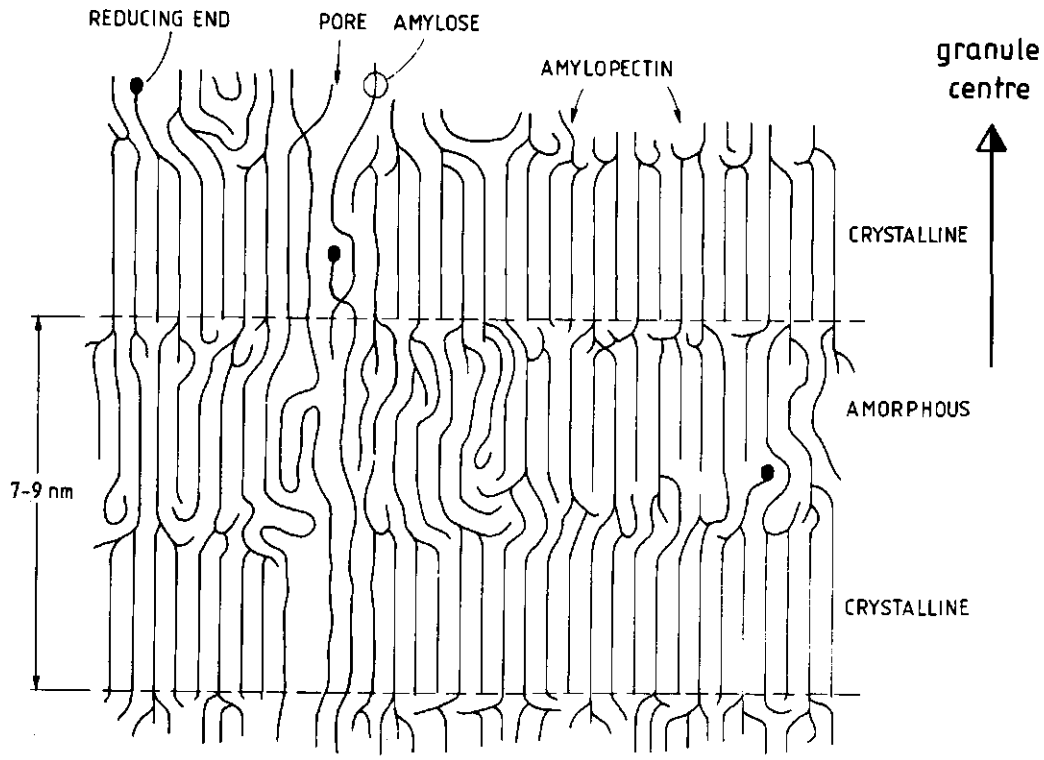


Figure 2.9. Diagrammatically represented proposal of the fine structure (morphology) of native (potato) starch. See text.

2.4.5 Porosity

Airdry and oven-dried native starches are generally not porous. Using potato starch and some other starches, Hellman & Melvin (1950) measured specific surface areas for nitrogen and concluded that only the outer granule surfaces were determined. This could be confirmed by own (unpublished) measurements. However, water vapour and gaseous hydrogen chloride e.g. are known to penetrate the grain rapidly. With sorption from the liquid phase an analogous situation exists. Water, some dyes, reagents, sugars and even molecules as big as cyclodextrins are able to penetrate the water-swollen granule, whereas alkanes and other, even low molecular, dyes remain excluded. But as soon as the granule has lost its birefringence during gelatinization, it is open to many substances that were not able to penetrate before.

Sterling (1973) measured the pore size distribution of wet potato starch by impregnating the granules with diluted $AgNO_3$, subsequent reduction in the sunlight and measurement afterwards of the silver crystal size distribution. He observed many crystals between 0.5 and 25 nm and a small number with sizes up to 75 nm (Figure 2.10). The larger crystals are more abundant in the interlamellar areas of the starch grain between the concentric layers. Although the term 'pore' space quite probably simplifies the real physical relationships within the starch granule (Subsections 3.2.2 and 3.3.1), void

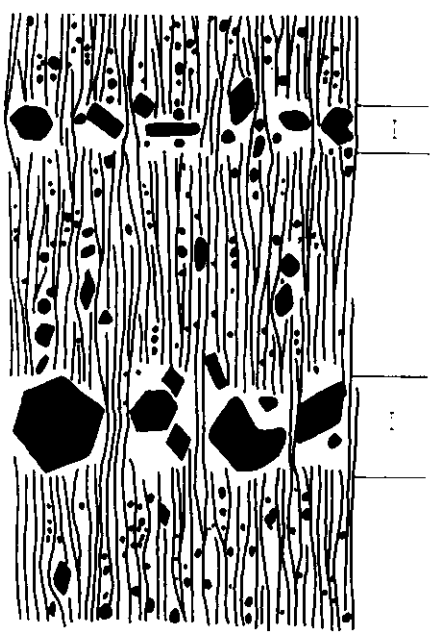


Figure 2.10. Diagrammatic model of silver crystals grown in wet native potato stach. From Sterling (1973).

spaces of this order of magnitude exist in the swollen potato starch granule. It is not possible to say whether artifacts, for instance due to the growth of silver crystals, play a role. For the time being this is one of the best experimental evidences for pore structure we have, at least for potato starch.

It may be concluded with Steeneken (personal communication, 1977) that the effective starch grain porosity for a given substance is depending on the nature of that substance. *Amylophylic* substances are readily absorbed, while *amylophobic* or inert substances cannot penetrate. Amylophylic substances probably *activate* their entry into the starch material by means of some specific interaction with the local starch matrix, such as plasticizing, making penetration possible.

2.4.6 Some conclusions concerning the starch fine structure

- Common native starch granules have a semi-crystalline, radially-oriented spherulitic structure, most probably built up of fibrils, which are likely composed of microfibrillar particles or crystallites interconnected by shared branches of the gigantic amylopectin molecules.

- Crystallites in these fibrils are mainly composed of radially oriented branches of the amylopectin component that are built together in a hexagonal crystalline pattern. The gigantic amylopectin molecules themselves may well pass through several of those crystallites.

- The crystallites contain water as an indispensible component of the crystal architecture. Without water, the crystalline X-ray pattern fades due to distortion of the crystal lattice.

- Due to the periodically changing carbohydrate (or water) concentration during growth, emphasized by tangential swelling, concentric layers develop around the hilum, the original amyloplast and centre of nucleation of the granule. This results in differences in molecular packing density and differences in porosity in the successive layers of the granule.

- Amylose and amylopectin are intimately mixed in the native starch material. The amylose component finds itself mainly in amorphous form dispersed within the semi-crystalline amylopectin network.

- As a result of the rather versatile nature of the starch polymer morphology, it should be seriously considered that some of these conclu-

sions are not valid for all types of starch granular deposits found in nature.

- Although some water is taken up by the crystalline parts of the granule, the major water uptake during granule swelling takes place in the amorphous parts.

2.5 SOME PROPERTIES OF STARCH

2.5.1 Gelatinization

Certainly the most important property of native starches is their power to gelate in aqueous environment at appropriate temperatures. Analysis of this phenomenon shows that native starches possess a very characteristic behaviour, when compared with other gelling agents. Therefore the term *gelatinization* is preferred. In this and later sections this starch property is related to general polymer properties of interest, therefore the main features of starch gelatinization are described.

When suspended in water, airdry starch granules take up water and swell rapidly. To give an impression, a diameter increase for wheat starch granules of 30% and for potato starch granules of 47% and 29% for the major and minor axis respectively, have been reported (Hanssen et al., 1955). On heating a dilute starch suspension (e.g. 5 wt % starch) of common starches the granule shape persists and the grains retain their optical properties until at a certain temperature sudden changes start to take place irreversibly. The granules start to lose their birefringence and swell considerably. Over a temperature range of about 10 degrees centigrade all the granules in the population show this behaviour and *gelatinize*. Katz (1917) named the end of this stage: 'gelatinization of the first degree'. Figure 2.11 shows this loss of birefringence as a function of temperature for three starches. On further heating the grains continue to swell and lose gradually their irregular appearance. They gradually start to resemble huge bellows consisting of swollen grain walls filled with solution. There is a parallel increase in optical transparency, solubility and viscosity. Figure 2.12 shows this general behaviour schematically. Crude amylose starts diffusing out of the grain. Then some grains burst and lose their shape. The rotating viscosity of the mixture increases rapidly to reach a maximum when the entire space is filled with the swollen particles. With sufficient excess water, starch grains are reported to take up even 20-40 kg w./kg d.s. during swelling before they burst. Beyond this point the swollen particles rupture each other, leaving a fluid, characterized by smaller suspended grain wall particles and a strongly reduced viscosity. The second degree of gelatinization is reached eventually at temperatures above 373 K (100°C), when a homogeneous starch

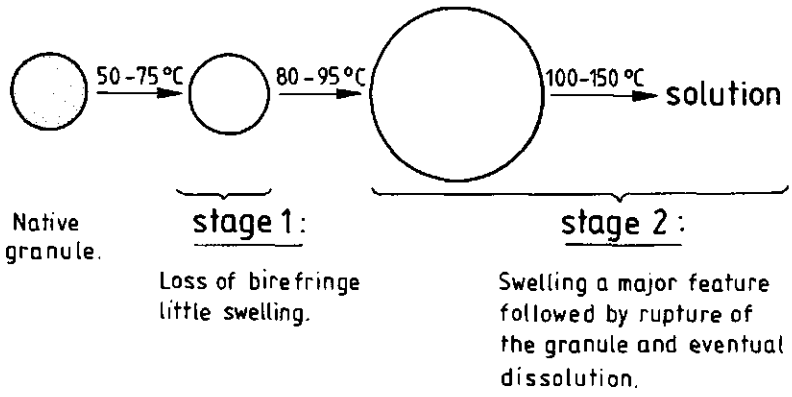


Figure 2.12. Schematic visual behaviour of native starch granule during gelatinization.

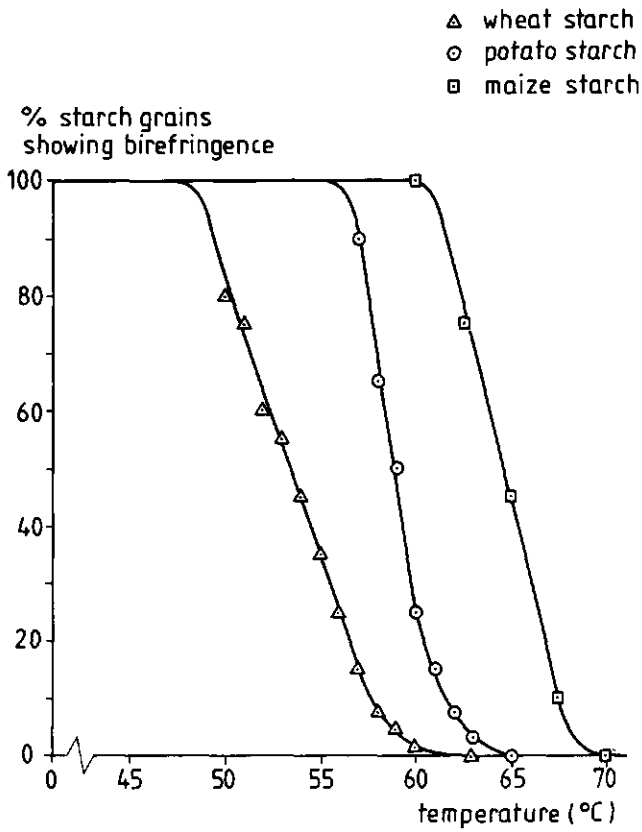


Figure 2.11. Proportion of starch grains showing birefringence as a function of temperature during the gelatinization of some native starches. Based on measurements by van Itallie (1930).

solution is obtained after complete destruction of the granule structure. For example for potato this temperature is approximately 393 K (120°C) and for amylomaize approximately 423 K (150°C).

During gelatinization different starch species show their own characteristic patterns in loss of birefringence, swelling, solubilization and viscosity. In some cases the loss of birefringence proceeds only slowly while the granule already swells considerably. In practice a kind of rotating viscometers with standardized time-temperature programmes, such as the Brabender viscoamylograph, are widely used to measure the viscosity pattern of starches. Figure 2.13 shows this characteristic behaviour for native potato, manioc, wheat and maize starches. Potato starch exhibits exceptionally high viscosity and swelling. This is generally assumed to be the result of relatively weak internal association of the macromolecular chains. This association is counteracted by the presence of ionizable esterified phosphate groups that assist the swelling in water by mutual electrical repulsion. The viscosity patterns suggest a much stronger molecular association for the cereal starches.

Table 4. Temperature range and heat effect of gelatinization (loss of birefringence) of various native starches. Heat effects were obtained by differential scanning calorimetry measurements by Stevens & Elton (1971), adapted.

Starches	Gelatinization temperature range °C	Heat of gelatinization (endothermal) J/g
Potato	56 - 66	22.2
Waxy maize	63 - 72	20.5
Manioc	58.5 - 70	16.7
Maize	61 - 71	15.1
Rice	61 - 76	14.2
Wheat	50 - 61	11.3

During gelatinization a small endothermal heat effect can be detected. Table 4 lists gelatinization temperature ranges and heat effects characteristic for some common native starches. Expressed per glucose monomer of the starch the magnitude of the overall heat effect is only in the order of 1 kT per anhydroglucose monomer or smaller. During this process also the semi-crystalline molecular arrangement of the native starches, as visualized by X-ray diffraction (Subsection 2.4.3), breaks down and in the gel a new X-ray dif-

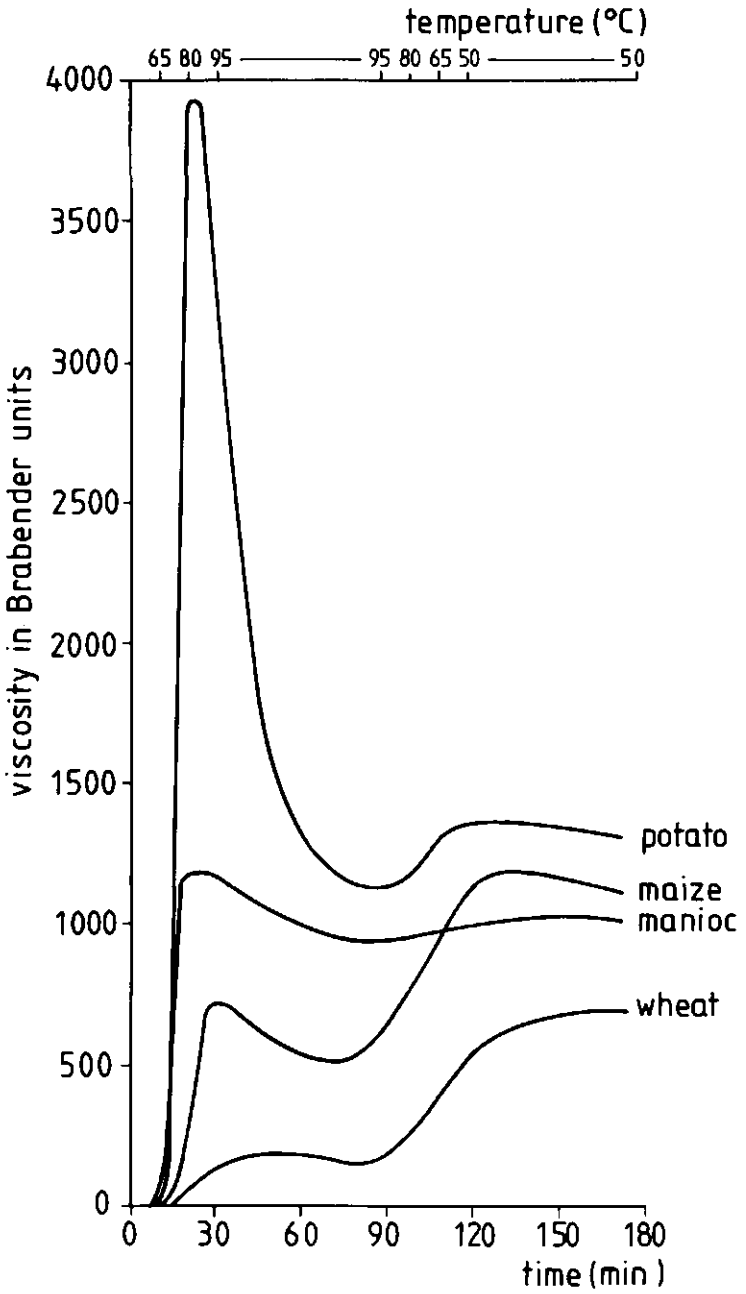


Figure 2.13. Brabender visco-amylograph curves during the gelatinization of some native starches (5 wt % concentration).

fraction pattern can be observed after proper treatment. This new pattern was classified by Katz & van Itallie (1930) as the V type (V = Verkleisterung). They believed that the V polymorph was directly made out of native starch through the gelatinization process. Now it is known (Banks & Greenwood, 1975) that the V type structure is readily formed from dissolved starch molecules (in particular amylose) in the presence of complexing substances, thus an artifact. Van Itallie (1930), studying this crystal transition, admits to have had some difficulties to visualize the new pattern and finally used ethanol to 'stabilize' the structure. He noted that during the transition (of wheat starch) from the A type to the V type both polymorphs are visible simultaneously in a combined pattern, while in the case of B type starches (e.g. potato starch) the pattern disappears completely and a diffuse halo exists over a few degrees centigrade before the V pattern arises. Van Itallie (1930) observed also that disappearance of the native X-ray pattern lagged a few degrees centigrade behind the disappearance of birefringence.

Addition of electrolytes and non-electrolytes, chemical modification and partial hydrolysis, as well as mechanical starch *damage* may profoundly modify these gelatinization characteristics. Mechanical disruption of the starch grain usually leads to a complete loss of gelatinization characteristics. Mechanically damaged starch swells and dissolves in cold water to a large extent. Acid treated starches (Section 2.4), which are known to have a somewhat higher crystallinity, show much less swelling during gelatinization and do dissolve layerwise. This supports the view that the major swelling takes place in the amorphous parts of the granule.

An interesting observation is that after annealing (i.e. heating in water just below gelatinization temperature for a considerable time, for example during 120 h at 323 K (50°C)), the range of temperatures over which a population of native starch granules gelatinize is narrowed considerably and has shifted towards a higher value, near the upper end of the orginial temperature range. For *individual* wheat starch granules Gough & Pybus (1971) observed that the range of gelatinization temperatures reduced from 0.5 - 1.5 degrees centrigrade to less than 0.2 and shifted 4 - 12 degrees centigrade upward. This phenomenon is suitably explained by a recrystallization of defect crystallites.

Since in the process of gelatinization the original crystalline order of the native granule is fully destroyed, the transition is effectively a melting process, onto which the theory of melting of a crystalline polymer in a polymer-solvent system can be successfully applied (Lelievre, 1973). From the shift in gelatinization temperatures after annealing it can be concluded that the real melting point of pure starch crystals in water is somewhat

higher than the ordinary gelatinization range indicates. However, it should be emphasized that gelatinization as such is irreversible. In some cases after just standing or after certain treatments the original crystalline X-ray pattern partially returns, but the native starch grain as *unique* natural deposition does not recover. It can be concluded that during the *first* stage of gelatinization, starch crystallites melt down forming a rearranged polymer network. During the *second* stage this network is broken down further and eventually a molecular solution is formed.

2.5.2 Retrogradation

Retrogradation is the common name in starch science for all changes that occur during storage of a freshly gelatinized starch. This may be flocculation of a starch solution, syneresis of a paste or gel, as well as changes in the starch component of cooked foods such as occur during bread staling. Retrogradation arises from the inherent tendency of starch molecules to align with one another through increased hydrogen bonding and loss of water molecules originally included in the starch matrix. This often leads to a slight increase in crystallinity. Compared with other detectable changes of gelatinized starch, an early indication of retrogradation is the increased resistance of the starch against attack by diastatic enzymes, which is directly related to digestion of starch as a food substance.

Generally important for retrogradation processes are the extent of gelatinization, water content and concentrations of other substances, both electrolytes and non-electrolytes. An interesting observation is that retrograded starch loses its ability to form the blue complex with iodine.
In starch solutions it is mainly the amylose component that aligns, forming an insoluble flocculate (Subsection 2.3.2). In this precipitation process there is a major influence of molecular weight of the amylose. Molecules of intermediate chain length (roughly D.P. 60-500) associate most rapidly (Pfannemüller et al., 1971). Pfannemüller & Bauer-Carnap (1977) reported densely packed, crystalline (fibrillar and rodlike) precipitates being formed even within a few minutes from monodisperse amylose solutions (D.P. 100 and 200). Also early observations by Maquenne (1904, in van Itallie, 1930, p. 71) can be explained by this effect.

During bread staling, however, starch retrogradation is mainly the rearrangement of amylopectin molecules because the amylose component can still be leached readily from staled bread. During bread baking gelatinization usually does not exceed the first degree. Generally the recrystallization of starch, which is an important aspect of retrogradation in many cases, can be detected by changes in the X-ray diffraction patterns. When gelatinized to the first degree only, starch granules tend to retain some memory of their

original structure and upon storage after one or more days they partially return to their original (native) pattern. When gelatinized more completely, upon standing, a B pattern is favoured at ambient temperatures and higher moisture contents. However, at decreasing water contents and increasing temperatures, but remaining below the gelatinization temperature, successively the C pattern and the A pattern were observed (van Itallie, 1930; Hellman et al., 1954).

2.5.3 Fractionation

Basically three different methods of fractionation of starch into its main components, amylose and amylopectin, are currently applied, namely:

a. inclusion complex formation of amylose with specific low-molecular organic compounds at a critical concentration e.g. 1-butanol, thymol or 1-nitropropane,
b. aqueous leaching at elevated temperatures,
c. dissolution at high temperatures in $MgSO_4$ solutions and selective precipitation during subsequent cooling.

The first method, employed by Schoch (1941, 1942) who discovered the crystalline inclusion complex formation with organic compounds, is much in use for analytical preparation purposes in the laboratory. The tedious and incomplete yield method of aqueous leaching, followed by complex formation, is preferred for making very pure amylose preparations. Detailed literature reviews on both methods were given by Schoch (1945), Whistler (1965) and Ullmann (1971). The third method, preparations of which were also incorporated in this study (Chapter 5), is basically a fractional precipitation induced by addition of a nonsolvent. Polymers that differ only in molecular weight show minor differences with respect to their solubility in a binary solvent of given composition, but greater differences in solubility exist between polymers differing in molecular structure. As a consequence, the fractional separation of linear amylose molecules from branched amylopectin molecules may be expected to be nearly quantitative under well-controlled conditions. Applying these concepts of polymer science (Flory, 1953), Bus, Muetgeert & Hiemstra (Potze, 1976) investigated phase diagrams of starch and magnesium sulfate at different concentrations in water and different temperatures. Eventually they designed the industrial process for separation of amylose and amylopectin on that basis. A critical literature review on starch fractionation was written by Muetgeert (1961).

3 WATER RELATIONS OF STARCH

3.1 WATER VAPOUR SORPTION EQUILIBRIUM

3.1.1 General

When a gas and a solid are brought together below the critical temperature of the gas, it is generally found that under equilibrium conditions the mass concentration of the gas is considerably greater near the solid surface than in the bulk-gas phase. As long as there is no electron transfer between gas and solid, this accumulation at the surface is called *physical adsorption*. This phenomenon applies directly to starch and water vapour. The size of the heat effect of the interaction (Section 3.4) points clearly to a localized physical adsorption process, which is further complicated by the fact that water molecules not only sorb on both the external and internal surfaces of the starch polymer but also profoundly influence most properties of the starch when sorption proceeds. In the sorption complex thus created separate properties of both components are mostly no longer distinguishable. Starch has this general property in common with other biopolymers. A general review on the phenomenon of water vapour sorption was published by Gál (1968).

The rather complicated nature of the sorption complex of starch and water may be illustrated by observing a simple experiment. When a completely dried-out starch gel is wetted gradually with water vapour, the initially hard and brittle starch weakens and swells, and finally retakes about the form of the original starch gel while passing through intermediate stages of stiffness. If there was no limit to the swelling of the gel, due to its cross-linked molecules, a true starch solution would have been formed. Thus, in passing through the entire range of water activities, the original solid-vapour system during uptake of water changes gradually into a liquid(like)-vapour system.

A variety of methods exist to study the interaction of water and biopolymers. *Static* (equilibrium) aspects of this interaction are best studied by thermodynamic techniques, such as sorption isotherms, calorimetric and volumetric measurements. Thermodynamic data only do not enable us to make conclusions about molecular models or sorption mechanisms, but together with X-ray diffraction and other techniques to study the structure and nature of the system they become a powerful tool. *Dynamic* aspects of the interaction belong to molecular phenomena occurring with a very short lifetime. These dynamic phenomena are studied with methods such as diffusion, resonance techniques, dielectric studies, neutron scattering and spectroscopy. Some of these techniques monitor rotational and translational movement of water mol-

ecules, so discriminating between water in the bulk and water that is influenced by some additional force. For example infra-red and Raman spectroscopy give information about water-biopolymer hydrogen bonds. As these methods study different dynamic aspects, no single technique may be expected to provide complete details of location, dynamics and interaction energies of the water-biopolymer interaction. They rather add to each other's information, contributing to a large a complicated puzzle.

For starches that cannot be brought entirely into crystalline form, important progress in obtaining a realistic molecular model for bound water may be expected only when the physical structure of starch is further elucidated in detail. Thermodynamic techniques still provide the most significant direct information on the starch-water interaction. In general the present study is largely confined to thermodynamic techniques involving water vapour sorption equilibria, phase and volume relations and heat effects. The last section of this chapter attempts to integrate these findings into a model of the starch-water system.

3.1.2 Defining sorption and water binding

General, mainly macroscopic aspects of starch hydration have been reviewed by Ullmann (1958), Urquhart (1959), Schierbaum & Täufel (1962) and briefly by Badenhuizen (1971) and Wootton et al. (1974). Stute (1980) reviewed mainly the German literature. In this specific starch literature as well as in the more general literature on water relations of foods and biopolymers (Duckworth, 1975) various expressions are in use to describe the special character of water in the vicinity of surfaces. Unfortunately, some of these are ill-defined. Even worse, quite a few authors leave the matter of definition solely to the imagination of the reader. For the interaction of water with biological products generally, and more specifically with foods and its macromolecular components, examples of terms are: bound water, sorbed water, solid-like water, water of crystallization, imbibed water, water of hydration, immobilized water, unfreezable water, ice-like water, non-solvent water, monolayer water and water available for certain processes such as microbial growth and chemical reactions. Some of these terms have different definitions determined by different methods of measurement that lead to different numerical values. Examples of this were given by Karel (1975). Other terms relate to more or less recent ideas about the nature of the water near the macromolecules. Especially the term *bound water* is widely used. In their extensive review on protein hydration, Kuntz & Kauzmann (1974) summarize existing definitions for bound water: *bound water is that water in the vicinity of a macromolecule, the properties of which differ detectably from those of the bulk water in the same system*. They associate three problems with this operational definition. First, each technique measures different

properties of the system; the results can be interrelated, but in practice large discrepancies can arise. Second, it is unlikely that a sharp physical boundary exists that separates bound from bulk water, as in many cases only relatively weak interactive forces are present. Third, the characteristic time associated with many measurements is often long compared to the times for molecular motion of the water. Such measurements will give an average value for all or part of the water in the system. In addition to this, it can be stated that the properties when measured as a function of water content show as a rule a continuous course into bulk properties. A fourth problem directly associated with this definition is that detectability is a function of sensitivity and accuracy of the measurement. Kuprianoff (1958) reviewed the concept of bound water in foods and with Leniger (1957) he already doubted the possibility of defining it correctly.

For the purpose of this study, this discussion is clearly more an illustration of the complexity of the relation between water and macromolecules than an explanation with much practical value. According to the definition of Kuntz & Kauzmann (1974) all the water surrounding a dissolved macromolecule that has a water activity of, say, 0.0025 (this is detectable) below the system water activity, should be considered already as 'bound' water. This bound water for amylose at room temperature can amount to between about 0.45 and 0.70 kg w./kg d.s. (the sorption isotherm is very steep at $a_w = 1$). This water is available for almost any action water is able to perform. It shows the very limited use of this definition. For this reason great care must be taken in defining the specific water relation under study.

In the present discussion on starch-water relations, the term *sorbed water* at indicated *water activity* (a_w) is preferred and to indicate the water content more precisely the terms *moisture ratio* or mass fraction of water (kg w./kg d.s.) will be used, together with the more general term hydration. These terms fit well within the context of this study, which later focuses upon the interpretation of water vapour sorption (or moisture sorption) isotherms of starch. In the literature on moisture sorption isotherms of biological products, the terms *adsorption*, *absorption* and *sorption* are all in use - mostly at variance - to describe the equilibrium relation between water and the biological product. In our discussion the general term *sorption*, coined by McBain (1909) to indicate all processes wherein solids *reversibly* combine with water molecules, will be used. These processes embrace physical *ad*sorption on surfaces, capillary condensation and the formation of liquid and solid solutions (real molecular mixtures), i.e. *ab*sorption. Hayward & Trapnell (1964, page 5) suggested correctly that *ab*sorption can be regarded as essentially *internal ad*sorption, where the sorbate diffuses from the surface of the sorbent into its interior via very fine voids or capillaries, crystal grain boundaries, and by penetration between the atoms of a network.

For localized sorption in such a case, it would be correct to speak of a three-dimensional surface of active sites for sorption, because the majority of active sites are not in free collision contact with the sorbing gas. To indicate the direction of the process, the terms *desorption* (*drying*) and *resorption* (humidification) will be used. This distinction is necessary because usually an important discrepancy (hysteresis) is observed between both directions. The term resorption also indicates that the starches under consideration (as well as all other biological materials) originated under wet conditions. From this point of view it must be advocated that equilibria during desorption for the first time (coming from the original state) give the best representation of the equilibrium relation between water and the original biological material generally better than resorption isotherms do. Although this point must be realized in practical application, it is often of no more than academic interest.

3.1.3 Mass of water in starch

Although internationally standardized methods for the determination of water in many agricultural products, including starches, exist and are widely used, the pairing of a proper definition of the water content with a practical method is still a matter of some controversy. A definition for mass of water in a system, satisfying both practice and theory does not yet exist. For example, Stitt (1958) theoretically defined the mass of water in molecular terms, namely the number of units of H_2O present in which the two H nuclei and the O nucleus have, within specified limits, the same internuclear distances as in water. But such a definition has real significance only if it can be verified by an appropriate experimental method. In practice, water contents are defined in terms of experimental techniques. Nearly all these techniques, at least all those used for standardization for starches and cereals (e.g. International Organization for Standardization - I.S.O., 1968), weigh samples before and after evaporation of, presumably, all the water. This evaporation is obtained by bringing the sample in equilibrium with air of approximately zero relative humidity (zero water activity for the sample) at elevated temperatures. Equilibrium with zero water activity practically defines the mass of water in a system. Because the water vapour sorption isotherm is usually very steep towards the moisture axis when approaching zero water activity, for the correctness of the moisture determination it is of major importance how closely zero humidity is approached. Moreover, the last traces of water are difficult to remove from a starch sample, as they are tenaciously bound (Section 3.4). Heating and/or extreme vacuums are necessary to attain equilibrium within a reasonable time. With standard oven methods, important systematic errors can be made. It is instructive to read the experiences of the Commission 'Vochtgehalte Aardappelmeel' (Moisture Content of Potato Starch), who investigated systematically the different

methods in use in the Dutch potato starch industry and connected laboratories (de Willigen, 1949).

For common native starches, with their small particle sizes, reproducible results are generally obtained by heating the sample under atmospheric conditions to 448 K (175°C) according to Meihuizen (1929), by drying with fresh phosphorous pentoxide (P_2O_5) under vacuum to a constant weight and by storing under high vacuum conditions for more than 5 days. A temperature of 448 K for pure starches is just below their decomposition temperature. Table 5 compares some moisture determination methods using data for potato starch of de Willigen (personal communication, 1980) and some obtained in our own study; both data sources generally agree for P_2O_5 and 403 K (I.S.O., 1968).

Table 5. Equilibrium water contents of native potato starch under some moisture determination conditions.

Method	Drying conditions	Water activity a_w	Mass fraction of water (kg water/kg dry starch)
ventilated oven	378 K (105°C) 24 h	0.97*	0.006 - 0.008[x]
	403 K (130°C) 1.5 h	0.43*	0.001 - 0.002
according to Meihuizen (1929)	448 K (175°C) 25 min	0.13*	0[x]
sorption balance	293 K (20°C) > 5 days pressure < 0.13 Pa	< 0.006	0
dessicator P_2O_5	293 K (20°C) > 3 days pressure < 133 Pa	□ 0.000 003[+]	0

* Calculated for ambient laboratory conditions (50% relative humidity and 293 K).

[+] At 298 K (Handbook of Chemistry & Physics 49th Ed., 1968).

[x] de Willigen (personal communication, 1980).

Other forms of starch, less pure and with other particle sizes, might lead to less reliable results with respect to an accurate moisture determination. It is interesting to note that also with cellulose under atmospheric conditions the last traces of water are not driven off before a temperature of 443 K is reached.

For many biopolymers any moisture determination is found to be not exactly reproducible. This is usually attributed to irreversible changes that occur along with possible trapping of water or slight degradation occurring in the biopolymer when the last specifically bound water molecules are removed. Changes in reactivity and other physical properties of starches due to drying at elevated temperatures (> 318 K) have been reported by Whistler et al. (1959), but no effect of these changes on the moisture determination may be expected. As far as we are aware no such changes have been reported for native starches dried at ambient or low temperatures. Also interesting in this respect is a reproducible and accurate moisture determination, found by D'Arcy (personal communication, 1978), after many years of experience with water relations of keratin (wool). His method, which is carried out in a sorption balance, implies first equilibration of the sample to near saturation by wetting or vapour sorption and subsequently fast drying under high vacuum to remove nearly all water in a short time. Theoretically it may be expected that this method 'freezes in' the swollen polymer structure, by not allowing the polymer chains to move to a more fully shrunken position before the solidification point is reached, so that entrapment of water molecules does not take place and the structure remains 'open'.

3.1.4 Review of water vapour isotherms of starch

Over the years, equilibria for water vapour sorption of starches in some form (either or not native, gelatinized or fractionated) provided an area of intensive research, which is not surprising in view of the wide practical interest. Still, the number and the detailed character of the studies on starch in this respect generally cannot rival the studies published on cellulose. Probably the first, and still one of the most thorough workers was Rakowski (1911), who spent many years measuring full isotherms of carefully washed samples of common native starches in dessicators stored in a thick-walled cabinet, without temperature control or vacuum device. Each measuring point took Rakowski (1911) 1-2 months to equilibrate under these conditions. He investigated influences of another temperature, preliminary sample heating and hysteresis at the vapour equilibrium and performed some scanning experiments. Other references from the literature are Katz (1917), Farrow & Swan (1923), Swan (1926), Sair & Fetzer (1944), Kesler et al. (1946), Anonymus (Proefstation voor Aardappelverwerking, 1947), Hellman et al. (1948, 1950, 1952), Ubertis & Roversi (1953), Bushuk & Winkler (1957), Fish (1957),

Schierbaum (1960), Volman et al. (1960), Guilbot et al. (1961), Taylor et al. (1961), Hofer (1962, in Wolf et al., 1973), Nemitz (1962), Macchia & Bettelheim (1964), Saravacos (1965), Saravacos & Stinchfield (1965), Masusawa & Sterling (1968), Heiss (1968, page 91), Gupta & Bhatia (1969, 1970), Bosin & Easthouse (1970), Hanson et al. (1971), Smith & Tsao (1971), Das et al. (1972), Nirkko (1973), Multon (1972-1974), Chilton & Collison (1974), van den Berg et al. (1975), Duprat (1975, in Tome & Bizot, 1978), van den Berg & Leniger (1976) and Mannheim et al. (1979). Almost certainly, this list is incomplete. Moreover, in the literature many references can be found reporting water vapour isotherms of seeds and tubers that contain at least 80% starch in their dry basis.

Unfortunately only few data in these references can be compared directly, mainly because of the different treatments and methods of measurement (especially with respect to the water content and the attainment of equilibrium) and perhaps also because of differences in sample purity. For instance, drying at high temperatures prior to the isotherm measurement can reduce the hydration capacity of starches significantly (Rakowski, 1911; Sair & Fetzer, 1944; Hofer, 1962, in Wolf et al., 1973; Schierbaum, 1960). Vigorous treatments at 453 K and 473 K, as reported by Katz & Weidinger (1939), even reduced the original sorption capacity at a_w = 0.4 from 0.15 - 0.17 kg w./kg d.s. to 0.12 - 0.14 and 0.08 - 0.11, respectively. Two articles (Anonymus, 1947; Heiss, 1968) do not heed the effect of hysteresis when taking measurements, directly desorbing and directly resorbing an air-dry sample (approx. 0.2 kg w./kg d.s.). Several authors (e.g. Hellman et al., 1953; Guilbot et al., 1961) report resorption isotherms in passing, needing the data only to illustrate other arguments. Still other articles refer to only part of the isotherm or report too few points, or no points at all, which makes it impossible to draw the whole isotherm reliably for interpretation purposes. A general problem here, as well as in the general literature on water vapour sorption equilibria, is that most authors make their isotherm data less useful for others by reporting them only in the form of small graphs from where exact data are difficult to take.

The combined results for native potato starch from some of the mentioned references are given in Figure 3.1, temperatures ranging from 292 to 298 K (19-25°C). Of all starches potato starch is most widely studied. It has a sigmoid isotherm of type II of the B.D.D.T.-isotherm classification described by Brunauer, Deming, Deming & Teller (1940). Compared with other starches potato starch has probably the highest water sorption capacity, but generally the differences in water sorption capacity between the starches are not wide. Even treatments that rupture the physical structure thoroughly do not greatly influence the sorption capacity, which indicates that the chemical structure mainly determines the water vapour sorption capacity of starch.

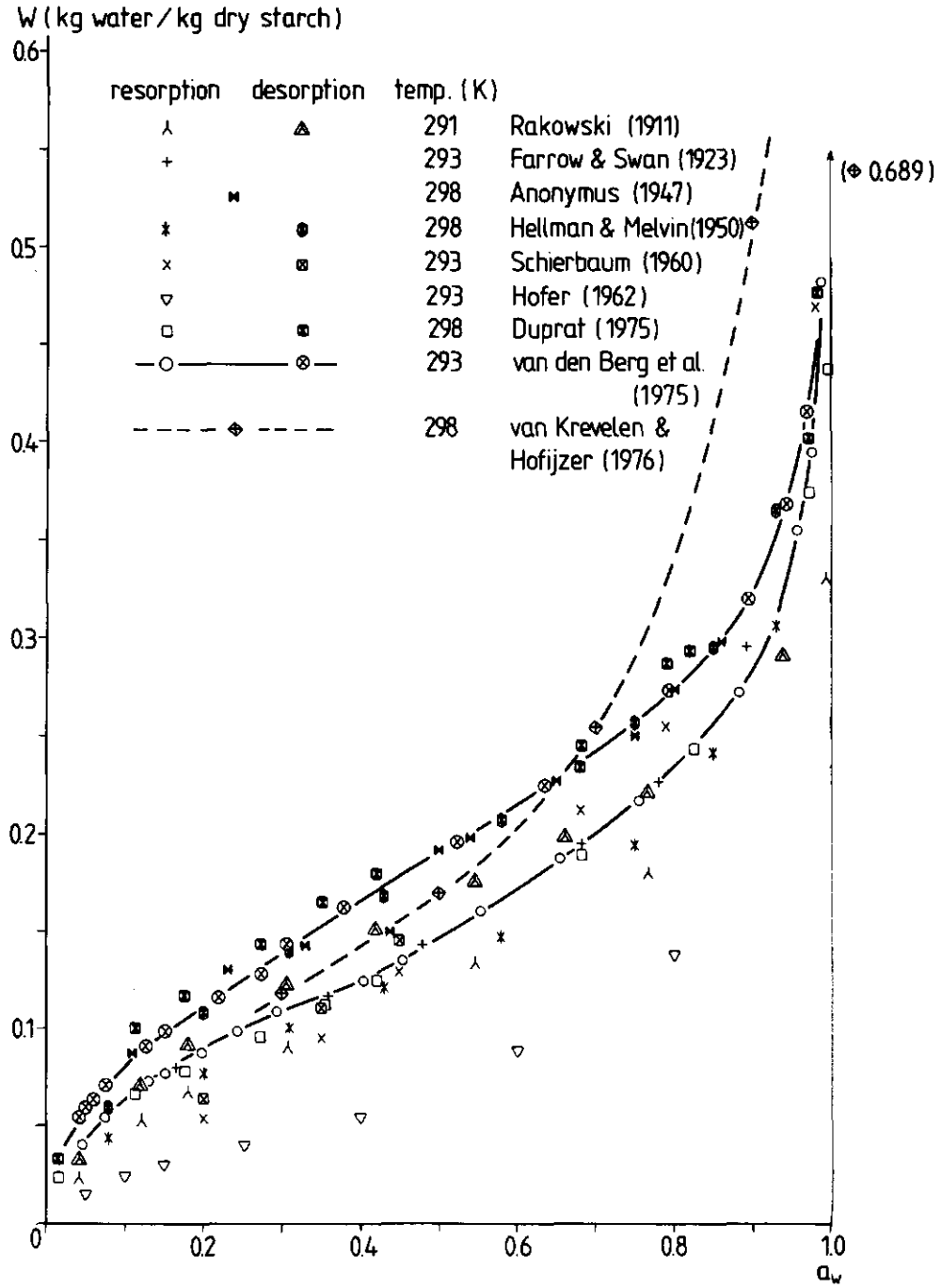


Figure 3.1. Some sorption isotherms of water vapour on native potato starch as reported in the literature. See text.

Figure 3.1 shows that not all references agree. Hofer (1962, in Wolf et al., 1973) reports far too low water contents, while Schierbaum (1960) apparently failed to observe the sigmoid lower part of the isotherm. Except for some of the lower points, the desorption equilibria of Hellman & Melvin (1950), Duprat (1975, in Tome & Bizot, 1978) and van den Berg et al. (1975) correlate fairly well. Apparently also Anonymus (1947) reported equilibrium data for desorption. The resorption equilibria of Farrow & Swan (1923), Duprat (1975, in Tome & Bizot, 1978) and van den Berg et al. (1975) are comparable. Although Rakowski (1911) observed slightly lower water contents than most of the others (probably due to his moisture content method) he reported reproducible isotherms for his conditions. Also plotted in Figure 3.1 are five values, predicted with the method of van Krevelen & Hoftijzer (1976) for polyanhydroglucose (starch), which will be discussed in Subsection 3.1.7. Several of the reported isotherm data that were obtained with the dessicator with the saturated-salt-solution (slush) technique can be corrected by applying revised values for water activity according to the newest insights (Greenspan, 1977; Young, 1967). In order to establish the value of the data given by the mentioned references it might be worthwhile to compare the published material in greater detail, also for other starches. Part of the published material is not sufficiently accessible because several references do not give sample and method descriptions in sufficient detail; this was recently found by Neuber (1978) who collected all available sorption data for maize.

In connection with the fact that the methods of pretreatment and measurement can influence the observed equilibrium, the following finding of Smith & Tsao may be relevant. Of starch sponge, prepared by gelatinization, freezing and thawing, water resorption isotherms were determined in two different ways: (a) through conventional water vapour sorption and (b) by soaking the dry sponge in benzyl alcohol-water mixtures. Benzyl alcohol behaves inertly towards starch. Smith & Tsao (1971) obtained virtually identical isotherms from both methods, which shows that the sorption equilibria are not influenced by the state of aggregation of the other phase used for equilibration.

Some final remarks concern the very low and very high part of the isotherm. Both steep isotherm parts are difficult to measure accurately. The low part because of the difficulties connected with creating and maintaining very low humidities for equilibration. The high part because of the great steepness of the isotherm there: a small change in humidity, for example by a slight temperature change, gives a large response in water content. It is not surprising that the reported maximum sorbed amounts of water at $a_w = 1$ for a material do not seldom show a wide variation.

3.1.5 *Influence of temperature*

Upon increase of the isotherm temperature, water vapour sorption equilibria of starch (and other biopolymers) shift towards a higher water activity at given water content; and lowering of the temperature causes the reverse. This positive temperature coefficient for the water activity is thermodynamically related to the fact that mixing of water and dry starch is an *exothermal* process (Section 3.4). The effect of isotherm temperature for starch was reported by Rakowski (1911), Swan (1926), Bushuk & Winkler (1957), Saravacos & Stinchfield (1965), Morsi et al. (1967), Masuzawa & Sterling (1968) and van den Berg & Leniger (1976).

Rakowski (1911) could not observe a significant difference in equilibrium values between 292.2 K and 303.2 K, which may have been due to his primitive experimental set-up and the small difference between the two temperatures. Swan (1926) made resorption measurements for potato-starch gel films at as much as nine temperature levels, ranging from 293.2 K to 363.2 K (20-90°C). His results show a fairly even trend with an average temperature coefficient for the water activity of approximately 0.0036 K^{-1} at a_w = 0.5. Noteworthy is that at temperatures above gelatinization temperature (approx. 340 K) and water activities higher than 0.9 the isotherms cross the lower temperature isotherms. This effect may be due to liquefaction of the gel, causing it to lose its cross-links and barriers to swelling. Thermodynamically this correlates with *endothermal* mixing. Bushuk & Winkler (1957) reported resorption equilibria for native wheat starch at four temperatures between 293.4 K and 323.4 K. A temperature coefficient at a_w = 0.5 of 0.0030 K^{-1} can be estimated from their results. Saravacos & Stinchfield (1965) measured starch gel resorption equilibria at eight temperatures between 253.2 K and 323.2 K. Their results are more scattered. The estimated average temperature coefficient at a_w = 0.5 above 273 K from these measurements is about three times that of other workers. Clearly their results are in error at subfreezing temperatures. Since ice at 253.2 K (-20°C) has a water activity of approximately 0.81, Saravacos & Stinchfield (1965) even reported some thermodynamically inconsistent results.
Sterling's group determined resorption equilibria for two potato starch samples, for maize amylose and amylomaize at 278.2 K and 298.2 K (Morsi et al., 1967) and for maize starch at 285.2 K and 298.2 K (Masuzawa & Sterling, 1968). Their results show the expected trend. However, the data were reported only in small graphs, plotted against water vapour pressure instead of water activity, which makes exact comparison even more difficult. Moreover, Morsi's measurements (Morsi et al., 1967), at least those for potato starch, were influenced by insufficient drying before resorption. Thus initially scanning equilibria were measured instead of the expected resorption equilibria. Van den Berg & Leniger (1976) reported resorption equilibria for

native potato starch at three temperatures between 275.7 K and 313.2 K, and found an average temperature coefficient at a_w = 0.5 of 0.0034 K^{-1}.

Although for starch no observations of sorption equilibria are available at temperatures of 373 K (100°C) or above, it may be assumed that below the gel-liquefaction point the expected trend continues itself at these temperatures without discontinuity, until decomposition temperatures (approx. 453 K) are reached. Recently, Engelhardt (1979) carefully measured resorption equilibria for beechwood (almost pure cellulose) at four temperatures ranging from 383.2 K to 443.2 K (110°C - 170°C). His results indicate clearly that changes in curvature and position of the isotherms proceed qualitatively in the same direction as observed at lower temperatures. The sigmoid shape of the isotherm is gradually lost at increasing temperatures and the original type II isotherm of the B.D.D.T.-classification changes completely into a type III isotherm not far below the decomposition temperature. Apparently the active sorption sites for localized sorption gradually lose their specific activity at increasing temperatures.

The same trend may be assumed to continue also at low subfreezing temperatures. Some preliminary unpublished measurements performed by the author & van der Loo at 253 K with native potato starch indicate this clearly. Comparable behaviour for some food systems at subfreezing temperatures was observed by Fennema & Berny (1974), and by MacKenzie & Rasmussen (1972) for polyvinylpyrrolidone.

3.1.6 Sorption hysteresis

A significant hysteresis effect is generally observed between desorption and resorption equilibria at ambient temperatures over almost the entire isotherm. The dependence of the sorption equilibrium on its sorption history may be seen as a recurrent characteristic of most biological materials. The hysteresis loop is found to be widest when desorption is started from saturation and resorption from the almost complete dry state. For native potato starch the departure between resorption and desorption value amounts to even approximately 0.05 kg w./kg d.s. at a_w = 0.5 (Figure 3.1). All points inside the hysteresis loop can be attained by appropriate handling and equilibration of the sample via *scanning* curves.

Nearly all research workers agree upon hysteresis as a reproducible phenomenon. The author's results for a native potato starch showed reproducible isotherms for desorption and resorption during four succesive cycli. On the other hand, Rao & Das (1968) found that some typical gel systems narrow their hysteresis loop after eight or more successive desorption-resorption cycli. Sorption equilibria themselves are stable for more than one year. In

practice, however, samples that have been equilibrated during pure resorption or desorption and are stored in closed containers under ambient conditions, have the tendency to shift their water activity towards a value somewhat more inside the hysteresis loop. This apparently points to an inertia in attaining real equilibrium. But most probably this is due to ambient temperature fluctuations causing successive desorptions and resorptions which again may activate changes in the positions of the polymer chains influencing the sorption capacity somewhat. Large differences in step size between the successive resorption equilibrium measurements were also found to have a small influence on the water sorption capacity (van den Berg et al., 1975). Stabilization treatments to eliminate hysteresis were applied to cellulose samples by Wahba et al. (1958) with only very limited success. Hysteresis is confined to a solid state. Taylor et al. (1961) did not find hysteresis for dextran as soon as it entered the dissolved state.

Sorption hysteresis and its cause have received much attention since the early investigations of the water-silica gel system by van Bemmelen (1910). For biopolymers a variety of mainly qualitative explanations can be found. Swelling phenomena; time-dependency of equilibria (e.g. Rakowski, 1911); metastable local domains (Everett, 1967; Kapsalis, 1978); presumed barriers of diffusion (Weldring, personal communication, 1976) and activation energy; different capillary phenomena, such as irregularly shaped pores like ink-bottles (McBain, 1935); and, more specifically for cellulose and starch, a delayed hydrogen bonding or breaking between polymer chains mutually and with water during wetting or drying (Urquhart, 1929, 1959) have all been mentioned. Of general interest is the semi-quantitative theory of Barkas (1949), which assumes the deformations in physical structure and configuration of the material during swelling and shrinking to be partially *inelastic*. Upon desorption, swelling bodies tend to partially retain the open structure they developed during resorption. This leads to smaller tensions and swelling pressures and a larger sorption capacity during desorption. Everett (1967) points out that the only satisfactory theories of hysteresis which persists to very low pressures, assume the penetration of the adsorbate into the molecular structure of the solid. Watt (1980), reviewing water vapour sorption by keratin, mentions kinetic studies which demonstrate that sorption hysteresis can be associated with relaxation processes that take place in the fibres. An abrupt increase in humidity first gives rise to a rapid initial uptake of water by wool to a quasi-equilibrium, and then a slower second-stage uptake during which stress relaxation takes place in the material. Direct desorption from this quasi-equilibrium shows no hysteresis, but desorption after some second-stage uptake has occurred does display hysteresis. This observation indicates that mechanical rearrangement within the fibres is necessary for hysteresis.

As far as the author is aware, none of the existing explanations relates sorption hysteresis directly to the change in state of aggregation occurring during the *glass-rubber* transition caused by the plasticizer action of water as a diluent (Subsection 3.2.2). This change in state of aggregation may well be delayed during desorption and resorption, and as such influence the sorption equilibrium. This transition agrees closely with Barkas' concept of partial inelasticity. Except for capillary phenomena, which presume rigid capillaries that do not exist in plasticized polymeric materials, probably most of the mentioned mechanisms are disparate but complementary aspects of the truth about this complicated phenomenon. This complex behaviour is inherent to the nature of the interaction of water and a solid polymer under ambient conditions.

As apparently no stable sorption equilibria reproducible in all directions exist, the *true thermodynamic equilibrium* character of the observations is in serious doubt (La Mer, 1966; Franks, 1975). Some authors advocate the resorption limb of the hysteresis loop to be the true isotherm (e.g. Bettelheim, 1967; Labuza, personal communication, 1978). In practice, drying processes follow desorption equilibria, while for storage processes knowledge of both limbs of the hysteresis loop at intermediate and high water activities may be important. In the present study it is accepted that the observed equilibria are not only a function of the experimental conditions but also of the history of the sample. Desorption and resorption limbs of the hysteresis loop describe somewhat different systems. Both types of equilibria will be considered as *true* for the sample under the particular conditions and history. Careful experimental determinations by the author and others have shown that a permanent hysteresis effect exists for many biological materials. The boundaries of this effect refer to desorption from the wet condition and resorption from the dry condition; both isotherms are measured with small successive intervals.

A final remark concerns the effect of temperature on hysteresis, which can be illustrated with an observation from the study of cellulosic materials, which in our opinion may apply equally well to starch. Weichert (1963) observed for pine and beechwood a decreasing hysteresis (also noted by Urquhart & Williams, 1925) at increasing temperatures, which disappeared at approximately 348 K (75°C). Engelhardt (1979) was unable to detect any hysteresis between desorption and resorption for his samples at temperatures of 383 K and higher. He also observed a plasticizing of the wood structure at those temperatures, together with an increased water content at saturation. As mentioned earlier, the latter phenomenon was also observed by Swan (1926) at high temperatures. The visible plasticizing of the system indicates a continuing change in the state of aggregation from glassy to rubberlike, and finally to a liquid, all of this in agreement with general polymer behaviour.

In this respect these observations support the view that hysteresis is connected to the solid polymer phase in these systems and disappears gradually as soon as the material weakens and becomes more liquid. In line with this hypothesis is also the general observation that many polymers apparently 'forget' their sorption history when saturation is reached.

3.1.7 Sorption mechanics and models used for isotherm description

After it became known that water does not penetrate the individual crystallites of native cellulose (Katz, 1923), and Urquhart & Williams (1925) determined the water vapour sorption behaviour of cellulose both in its native and mercerized, i.e. non-crystalline, form, the role of the individual anhydroglucose monomers in water sorption became evident. At about the same time (Latimer & Rodebush, 1920) the paramount importance of hydrogen bonding for the behaviour of polar hydrogen-containing molecules became well-established. This again drew attention to the individual polar groups of the starch monomer, -OH and -O-, as the basis for water sorption in starch and cellulose (Urquhart, 1929; Peirce, 1929). Also it was found (Lipatow et al., 1948, in Schierbaum & Täufel, 1962) that hydrophobic substituents at the hydroxyl positions of polysaccharides strongly reduce the water sorption capacity. Later Pauling (1945) extended this concept to polar groups in proteins and it is now well-accepted that the B.E.T. monolayer value (Section 4.2) bears a close correlation to the number of polar groups in the substrate that are capable of forming hydrogen bonds with water.

Using Barrie's (1968) collection of water sorption data for synthetic polymers, van Krevelen & Hoftijzer (1976, page 422) could empirically estimate the contribution of each structural group of the monomer to the water sorption process at different water activities and 298 K. This method may be regarded as an acceptable first estimate for polymers. The results for starch (polyanhydroglucose) are plotted also in Figure 3.1, showing about the correct result for water activities below 0.75. This method predicts that the hydroxyl groups are almost entirely responsible for the water sorption. The contributions of the two ether oxygens in the anhydroglucose monomer may be cancelled with regard to water sorption.

Katz (1917), Sair & Fetzer (1944) and Schierbaum (1960), all fitted the lower part of their sorption isotherms of starch and starch preparations successfully with Freundlich's isotherm equation (Freundlich, 1909). Sair & Fetzer (1944) investigated the sorptive capacities of different starch types and explained the observed differences in terms of more or less *association* between hydrogen-bonded starch chains. Conforming with the findings on cellulose, they concluded water in starch at high humidities to be retained in at least two 'forms': by adsorption and as capillary water. At the end of a

series of papers about mainly phenomenological aspects of starch hydration, also Schierbaum & Täufel (1960, 1962, 1963) arrived at the same mechanisms. In their view, native potato starch binds the first 0.25 kg w./kg d.s. by adsorption and further water up to 0.50 kg w./kg d.s. by capillary condensation; for cereal starches (e.g. wheat) these values are 0.15 and 0.425, respectively. Schierbaum (1960) derived his values for 'adsorbed' water from the isotherm part which fitted the Freundlich equation. This conclusion is very weak as it assumes the sorption mechanisms underlying the Freundlich equation to apply to starch. The Freundlich equation describes essentially a heterogeneous sorption process under certain restrictions as shown by Appel (1973). Schierbaum's high proportion of fit with the Freundlich equation can be explained by his failure to observe the sigmoid shape of the lower part of the isotherm. Sair & Fetzer (1944) could fit their data with the Freundlich isotherm to approximately 0.1 kg w./kg d.s. only. Taylor et al. (1961) measured sorption equilibria for native wheat starch at high water activities (> 0.92) and fitted their results with moderate success to the isotherm equation of Flory and Huggins (Flory, 1953) regarding wet starch largely as a dissolved polymer system. Their results will be considered in more detail in Chapter 6.

In agreement with the general pattern of interpretation of water vapour sorption isotherms of biological materials, the mechanism of adsorption in mono- and multilayers followed by capillary condensation at higher activities is still generally accepted for starch (Nirkko, 1973; Wootton et al., 1974; Stute, 1980). The author and his co-workers (van den Berg et al., 1975), however, rejected capillary condensation as an important mechanism for water vapour sorption. Capillary condensation according to Kelvin's equation presumes rigid capillaries of appropriate dimensions with walls that are impenetrable for the liquid. None of these conditions apply in ordinary (bio)polymers because in the water activity range where the Kelvin equation applies (a_w > 0.4) the polymer structure has already become partially plasticized. Hence the polymer walls are relatively weak and open to the penetrating solvent. This is especially true at high water activities where the isotherm becomes steep and where it is generally assumed that capillary condensation applies. From application of the t-method of de Boer (Lippens et al., 1964; see also: Broekhoff & Linsen, 1970) with the use of the t-curves for water vapour of Hagymassy et al. (1969), van den Berg et al. (1975) supplied evidence that native potato starch during resorption does not show capillary condensation at water activities below 0.99. Their isotherms were fitted with the general B.E.T. equation (Brunauer et al., 1938) and its modification by Guggenheim (1966; Section 4.3). The last equation gave a satisfactory isotherm description up to water activities of 0.7-0.93, depending on the sample. In agreement with Sair & Fetzer (1944) and even earlier for cellulose Urquhart (1929), van den Berg et al. (1975) con-

cluded the water vapour sorption mechanisms of starches to be almost entirely governed by sorption sites, which are the anhydroglucose residues of the starch polymer. These sites build a monolayer by binding one water molecule with two hydrogen bonds. Based on these findings a tentative model for water sorption was formulated briefly. This model will be worked out in further detail in Section 3.6.

3.2 PHASE TRANSITIONS AND CRYSTALLINITY IN RELATION TO WATER CONTENT

3.2.1 General

It is not possible to understand polymer behaviour if the transitions that occur in them are unknown or, more specifically, the temperatures at which these transitions occur and how these temperatures are influenced by the presence of diluents. For the starch-water system these transitions, especially the glass transition, have a drastic effect on the behaviour of the system. Typical states of aggregation for polymers are glassy, rubber-like (weak to stiff), (semi-)crystalline and liquid. For a polymer system only the liquid state is easily comparable with that of small molecules, some special properties (like visco-elasticity) excepted. Hence the most characteristic transitions are the *glass-rubber* transition and the *melting* of crystallites. The melting of the crystal is a first-order phase transition rendering the crystals amorphous (i.e. literally: liquid-like). The glass-rubber transition of amorphous polymers (in short, glass transition) is like a second-order phase transition (Challa, 1973) changing the amorphous polymer from a glass-like into a rubber-like state of aggregation. In many polymers other transitions of less importance can be observed (van Krevelen & Hoftyzer, 1976). In starch, however, nothing is known about them.

Applying general experience of polymer behaviour to partially crystalline starch, it must be assumed that upon heating dry starch the amorphous part changes from a rigid-glassy into a rubber-like state at the glass transition temperature (T_g). For an amorphous polymer, it is known that the transition is accompanied by a strong decrease in elasticity modulus (usually several orders of magnitude) and an increase in thermal expansion coefficient and specific heat. For starch granules as a whole, the mixture of the rigid crystalline part and the rubber-like amorphous part will show a mechanical behaviour characterized as *leathery* and *tough*, perhaps approaching *stiff*. Further heating results in a further weakening and at the melting point gives a viscous liquid (unless this temperature is above the thermal decomposition temperature). At temperatures of approximately 453 K (180°C) and above, dry starch undergoes minor decomposition (e.g. depolymerization, British gum formation). In well-dried native starch the last trace of crystallinity disappears around 493 K (220°C), and then thorough decomposition

takes place (Katz, 1934; own unpublished results). As a result of its relatively strong molecular interactions (due to hydrogen bonds) pure starch polymer can be expected to behave physically rather similar to a nearly crystalline polymer. Therefore *stiff plastical* is possibly the right characterization of the mechanical behaviour of pure starch above T_g.

Water is able to interfere strongly with existing hydrogen bonds: it acts on starch as a *diluent* and *plasticizer* and, when the starch has lost most of its internal association, also as a *solvent*. As a result, water causes a tremendous depression of the glass-transition temperature (T_g), as well as of the melting point (T_m). Starch shares this property with cellulose and many natural polymers. Van Krevelen & Hoftyzer (1976) rightly call this polymer category *hydroplastics*, in contradistinction to the (synthetic) thermoplastics. An illustration of the influence of water on native starch granules is their greater vulnerability to mechanical damage in the dry than in the moist state (van Itallie, 1930; Meuser et al., 1978). Apparently T_g of moist starch is well below room temperature.

Phenomena such as the becoming hard and brittle of many, originally weak and flexible biological products and the immobilization of volatiles upon drying can, at least for a great deal, be attributed to a rise in glass transition temperatures from below to above room temperature. Other typical examples are wave-curling of hair and bending of wood with steam. The importance of the glass transition of cellulose in pulp and paper processing was recently described by Akim (1978). Maier (1972) observed the entrapment of aceton by potato starch film.

A basic problem in establishing quantitatively these transitions for starch is the fact that starches are not pure monodisperse polymers, but mixtures of slightly different polymers with a range in molecular weights and physical arrangements. Because of this, and because small amounts of admixtures are present, no sharp transition temperatures may be expected, but rather temperature ranges. Also the observed temperatures or temperature ranges are always lower than those expected for the pure polymer components (amylose or amylopectin). If water is present, the masss fraction of water or rather mass fraction range in which the transition occurs isothermally is equivalent to a temperature or temperature range at constant composition.

3.2.2 Glass transition

Unfortunately, no measurements of the glass transitions of starches have been found in the literature. Detailed research into the mechano-elastic behaviour of starches with different moisture ratios, together with measurements of specific heats and perhaps volumic masses, would supply more detailed information on these transitions. The only observed quantitative in-

formation available is derived from some results obtained by Muetgeert (1971), when applying Wood's equation (Wood, 1958) for the glass transition temperature of polymer-solvent mixtures. Values derived from Muetgeert's measurements will be compared below with results of a T_g estimation method described by van Krevelen & Hoftyzer (1976) and with values for T_g of amylose derivatives and cellulose reported in the literature.

The effect of diluent plasticizers, especially water, on the T_g of many polymer systems may be expressed effectively (Nielsen, 1962, page 27; Tan & Challa, 1976; Sung et al., 1978) by a semi-empirical equation originally given by Wood (1958) for copolymers:

$$\frac{1}{T_g} = \frac{\omega_p}{T_{g_p}} + \frac{\omega_w}{T_{g_w}} \qquad (3.1)$$

where T_g denotes the glass-transition temperature of the mixture, and subscripts p and w refer to polymer (starch) and diluent (water), respectively; ω_p and ω_w are weight fractions of starch and water. Applying this equation to Muetgeert's findings, data on the glass-rubber transition of starch at room temperature as a function of hydration can be derived.

Ordinary dried starches, as well as other biopolymers, have low specific surface areas, in the order of 1 m^2/g, as obtained by low temperature nitrogen adsorption, which indicates that the substance is not porous for nitrogen molecules (Subsection 2.4.5). Muetgeert, applying techniques of dissolution and solvent-drying, succeeded in transforming defatted maize starch into a dry, very porous compound with a nitrogen specific surface area of more than 100 m^2/g. This high nitrogen specific surface area for the transformed starch implies that the material consists of rigid pore walls of starch with an average thickness of only very few polymer chains and its state of aggregation must be glassy. If, subsequently, water vapour is sorbed onto this porous starch until equilibrium, a drastic decrease in specific surface area down to about 4 m^2/g was observed, starting at approximately 0.10-0.11 kg w./kg d.s. and becoming complete at 0.25 kg w./kg d.s. Figure 3.2 shows this typical behaviour of the transformed starch. This graph points to the gradual weakening and rearrangement of the starch material over the range of hydrations, passing, due to plasticizer action, from a glassy to a rubbery state. The collapse of the structure was established by surface-area measurements, with nitrogen. Such behaviour is not uncommon since it has been observed by Merchant (1957) for cellulose fibres and by Berlin et al. (1970) for casein particles. These materials were all dehydrated by a polar-apolar solvent series. As a general property, these transformed materials must have different sorption isotherms for apolar vapours, depending on their specific surfaces resulting from the transformation, but only one sorption isotherm for water vapour.

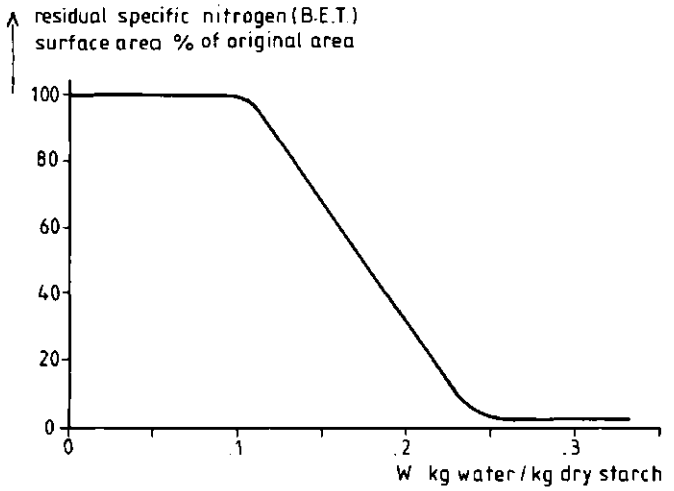


Figure 3.2. Residual nitrogen specific surface area expressed as percentage of the original area for transformed maize starch as a function of hydration. From Muetgeert (1971).

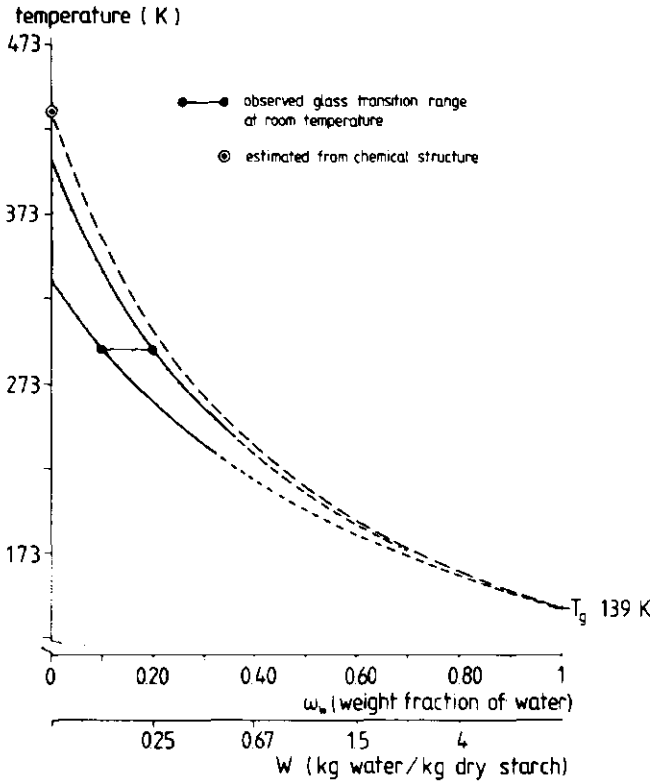


Figure 3.3. Estimated glass-rubber transition temperature range for starch-water mixtures as a function of mass fraction of water on total basis. See text.

Substituting 135 K (-134°C) for the glass-transition temperature of water in equation (3.1), from Muetgeert's results the range 335 K (62°C) - 405 K (132°C) is obtained for the glass-transition temperature of dry amorphous starch. For different weight fractions of water T_g of the water-starch mixture is given in Figure 3.3. Values for T_g belonging to weight fractions of water greater than 0.30 lose their physical significance when additional water in the starch granules freezes. It is clear that beyond the phase separation limit additional plasticizer is ineffective in the further reduction of T_g.

A value for T_g of pure starch (polyanhydroglucose) of 424 K (151°C) was obtained using van Krevelen & Hoftyzer's (1976) method. This method adds empirically determined contributions of groups in the monomer unit and is based on data of a large number of synthetic polymers. This has been shown to work well for the majority of synthetic polymers. When applied to starch, no distinction can be made between amylose and amylopectin or even between cellulose and starch. Hoftyzer (personal communication, 1980) emphasized that the method is only a first approximation. The assumed simple additivity sometimes does not hold and the influence of the mutual distance of characteristic groups is not yet completely understood. Nevertheless, it is certainly the best method available for an approximation. The dashed curve in Figure 3.3 predicts with the thus estimated T_g of pure starch the glass-transition temperatures of starch-water mixtures according to equation (3.1). Taking into regard the nature of the system and the observed data it may be concluded that the theoretical and measured values of T_g are in reasonable agreement.

Table 6 summarizes measured glass-transition temperatures of amylose derivatives, cellulose and cellulose derivatives from the literature and those reported above for starch and amylose. Especially the values of the amylose esters signify a regular series. These values suggest also the correct order of magnitude (424 K) for the T_g of pure amylose (or pure amylopectin).

Just one reference was found relating the glass transition of a polymer to its water vapour sorption behaviour. Brauer & Sweeney (1955) investigated water sorption on thin specimens of polymethyl-methacrylate at different temperatures. Sorption was found to be reversible and nearly independent of temperature below 333 K, which is close to T_g. Specimens reached equilibrium within a relatively short time, thereby sorbing relatively small amounts of water. Above this temperature the sorption capacity increased and equilibrium was very difficult to obtain, which suggested a different sorption mechanism. The analogy between these observations and our problem is limited by the fact that water apparently is no diluent plasticizer for the polymethyl-methacrylate structure.

Table 6. Glass-transition temperatures of starch, amylose, cellulose and their derivatives.

Polymer	T_g(K)	Source
amylose triacetate	440	x
amylose triproprionate	406	x
amylose tributyrate	365	x
amylose valerate (d.e. 2.8)	330	x
amylose hexanoate (d.e. 2.9)	315	x
cellulose	243 - 433*	x
cellulose	490 - 500	+
cellulose tripropionate	400	x
cellulose tributyrate	388	x
cellulose trivalerate	338	x
methylcellulose	423	x
starch	335 - 405	This
amylose (estimated)	424	study

x Source: Polymer Handbook (1976)

\+ Source: Akim (1978)

* Conflicting data (possibly not corrected for the water content of the sample)

3.2.3 Melting transition

From the description given in Subsection 2.5.1 it follows that during gelatinization basically two different processes take place. Starting with water-saturated starch granules just below their gelatinization temperature, these processes are: (a) the gradual loss of crystalline order as visualized by the disappearance of birefringence and the native X-ray pattern, and (b) diffusion of water into the swelling starch granule. The loss of crystalline order during gelatinization can effectively be regarded as the melting of polymer spherulites in a solvent. For the relation between the melting temperature T_m of a polymer and the volume fraction of solvent $(1-\phi)$, Flory (1953) derived the following expression:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_{m,u}} \cdot \frac{v_u}{v_w} \cdot \left((1-\phi) - \chi(1-\phi)^2 \right) \qquad (3.2)$$

where T_m^0 denotes the melting temperature of pure polymer in the absence of solvent; $\Delta H_{m,u}$ is the molar enthalpy of fusion per monomer unit; the ratio (v_u/v_w) divides the molar volume of the monomer unit by that of the solvent

(here: water); ϕ denotes the volume fraction of polymer in the mixture, and χ is the Flory-Huggins polymer-solvent interaction parameter (Section 4.5).

Various references (Katz, 1930; Collison & Chilton, 1974; Lelievre, 1973, 1976; Donovan, 1979, 1980; a.o.) studied gelatinization temperatures of native starch as a function of hydration. However, as a result of the use of different techniques, sometimes different starches and the fact that gelatinization of a population of starch granules occurs over a temperature range of several degrees, their results are rather divergent. Lelievre (1973, 1976) studied the loss of birefringence of native wheat starch, and Donovan (1979) applied differential scanning calorimetry (DSC) to investigate potato starch gelatinization. Both applied equation (3.2) to fit their observations. Marchant & Blanshard (1980) recently reviewed this topic and compared the results of Lelievre (1976) and Donovan (1979) with previously unpublished data of Zobel et al. (1965, in Marchant & Blanshard, 1980). Also recently Donovan & Mapes (1980) reported again on phase transitions of some hydrated native starches and Nägeli-treated potato starch. The latter results show that acid-treated starch has shifted its gelatinization temperature range as compared with its native form, which is in line with the expectation that such treatment leads to a less defective crystalline order.

For the present purpose it may suffice to reproduce the summarized results of Marchant & Blanshard (1980) to which is added an own estimate of the melting temperatures of potato (B type) starch crystallites. The same estimation method of van Krevelen & Hoftyzer (1976) used earlier for the glass-transition temperature can be applied with other values to estimate the melting point of polymers. This value for polyanhydroglucose is 533 K. Using Flory's equation (3.2) together with this value and the gelatinization temperature (endotherm peak value: 346.5 K) as reported recently by Donovan & Mapes (1980) for water-saturated Nägeli-treated potato starch, the melting point curve was calculated. The water content (0.65 kg w./kg d.s.) of the sample gelatinized under saturation conditions was averaged from the data of Zobel et al. (1965, in Marchant & Blanshard, 1980) and Donovan (1979). This is the hydration level for potato starch beyond which no further decrease in gelatinization temperature takes place. This moisture ratio must be close to the saturation point (at $a_w = 1$) for gelatinized starch. Figure 3.4 shows these combined results indicating an area of temperature-moisture ratio combinations where gelatinization occurs. An accurate comparison of the three melting point curves for starch crystallites is further complicated by the different parameters (see Table 7) employed by the different authors for curve calculation. Especially χ and the volumic mass value, which is incorporated in both the molar volume ratio and the volume fraction, are derived from different sources. The melting points for pure starch used by Donovan (1979) and by Zobel are too low and consequently their enthalpy of fusion

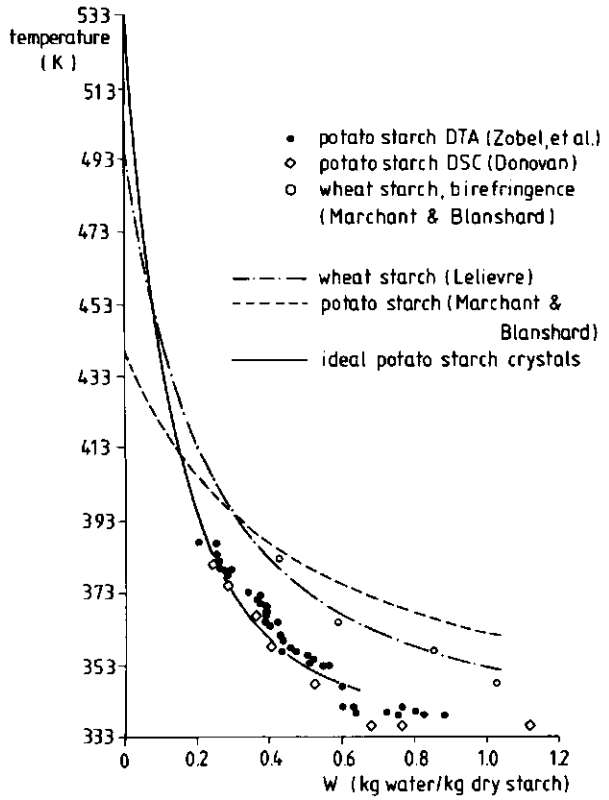


Figure 3.4. Change in melting temperatures of starch crystallites (gelatinization) as a function of hydration. Combined experimental and theoretical results from different sources. Adapted from Marchant & Blanshard (1980). The curve for potato starch as derived by Marchant & Blanshard, using the results of Donovan (1979) indicates the stage where gelatinization is ultimately finished. See text.

Table 7. Different parameters in equation (3.2) used for curve calculation in Figure 3.4 by different authors.

	Lelievre (1976)	Donovan (1979), Marchant & Blanshard (1980)	Zobel et al. (in Marchant & Blanshard, 1980)	This study
χ	0.5	0.0875	-	0.77
T_m^o [K]	495	441	426	533
$\Delta H_{m,u}$ [kJ/mol]	25.1	56.5	62.4	14
volumic mass of starch [kg/10^{-3}m^3]	-	1.55	-	1.65

value turned out too high. Because the last trace of crystallinity of native potato starch experimentally disappeared at approximately 493 K during decomposition of the sample, it may be assumed that the real value for the melting point of pure starch is between this temperature and the one estimated with the method of van Krevelen & Hoftyzer (1976). When compared with the estimated T_g^o for pure starch (Section 3.2.2), for the important ratio T_g^o/T_m^o a value of 0.80 for starch is calculated. This value may be expected for polymers with a strong internal association (van Krevelen & Hoftyzer, 1976).

Noteworthy is also that Flory's equation (3.2) predicts a rise in melting points at further increasing hydration, which leads to a predicted melting point for water just above its boiling point (!). Apparently, Flory's model has little predictive value at very high levels of hydration, but there it follows just the common shape of melting point-composition diagrams for low molecular compounds. Nevertheless, it may be concluded that Figure 3.4 supplies the expected behaviour of the melting points of starch crystallites as a function of hydration with reasonable accuracy. Probably Lelievre's curve describes the final melting of the A polymorph better here, while our curve represents better this behaviour for the B-starch polymorph. The correctness of Lelievre's curve is also supported by a good fit to some data points reported by Katz (1930) for wheat starch.

3.2.4 Starch crystals

This section is to survey briefly some main trends in the development of our knowledge about the structure of starch crystals with special reference to the specific role of water in that structure. We shall emphasize the B type, for which a new crystal structure has been proposed in the course of this project (Cleven et al., 1978).

In Section 2.4 it was concluded that native starches contain amorphous and crystalline parts that are intimately mixed and not distinguishable. Furthermore, the crystals have a hexagonal arrangement. In passing it can be noted that hexagonally arranged configurations fitting the dimensions of ice are not uncommon for biopolymers in the presence of water, because this enables a good wetting behaviour and sometimes gives rise to specific biological functions (Warner, 1967, 1978). The type of interaction of water and starch crystals can neither be compared with that in cellulose where water only penetrates the amorphous parts and not the crystallites (Howsmon, 1954), nor with that in protein crystals, the original structure of which can almost never be repaired after complete removal of water. Drying and wetting under mild conditions is known to be reversible for the starch crystals, which show a small volumetric increase of the crystalline unit cell

upon hydration. In both of these respects the interaction is to some extent comparable with that of certain zeolithes. For example, van Reeuwijk (1974) observed for chabazite a volumetric swelling of the unit cell of 1.15% during the uptake of approximately 20% water, while B-starch unit cells swell nearly 5% during the uptake of about 25% water (Subsection 3.2.5).

Several proposals for the crystal structures of the A, B and V type polymorphs have been made. Reviews of the published data of those structures were given by Badenhuizen (1949), Marchessault & Sarko (1967), Marchessault & Sundarajan (1976), Sarko (1975), French & Murphy (1977) and briefly by Banks & Greenwood (1975) and Rees (1977). The proposals for B-starch were summarized by Cleven et al. (1978). A first visual impression of the major model proposals for starch and amylose inclusion complexes can be obtained from Rees (1977, page 57). Of these proposals only the structure of V-amylose is considered fully elucidated. Katz & Derksen (1930) already reported that two forms of V-amylose exist: an *anhydrous* form (V_a) and a *hydrated* form (V_h), the crystalline unit cell of the latter having a slightly higher volume (Zobel et al., 1967). The transition of anhydrous V-amylose into the hydrated form occurs at $a_w \sim 0.6$ (Zaslow & Miller, 1961). From a molecular point of view this transition is realized through a rotation of the helix over 30^0 and localization of water at the helix exterior (Zaslow et al., 1974). In contact with liquid water a rapid change of V-amylose into B-amylose was observed by Zaslow & Miller (1961). The so-called anhydrous form is by no means entirely devoid of water. This polymorph contains at least one water molecule per anhydroglucose unit. As suggested by Suggett (1975), this water is perhaps located inside the V-amylose helix, hydrogen-bonded by the glucosidic oxygens of the amylose chain, meanwhile still leaving sufficient space for the complexing agent. More water is unlikely to be present inside the helix which at its interior has a rather apolar character.

The A type polymorph has hardly been studied as compared to the B type. For the latter, the first proposals of crystal unit cells date back to the twenties. The steady increase in size of the proposed crystal unit cells for B-starch over the years is striking. This is probably due to improved X-ray techniques. Furthermore, the lattice plane spacings of the hydrated B-polymorph as published in various references show some variation. The major problems involved in the elucidation of the crystal structures of starches have already been given in Subsection 2.4.3. The lattice plane spacings for hydrated B-starch as published by Kreger (1951) agree well with those of Cleven et al. (1978). The latter precisely standardized their spacings determination with some corundum as an internal standard added to the sample.

It was generally assumed that A and B type starch crystals are built up of single helices until Kainuma & French (1972), as a result of packing analy-

ses of spatial models, suggested that a double helix could fit the structural dimensions of B-starch better than the wider single helical arrangements generally do. This idea was worked out by Wu & Sarko (1977, 1978; Wu, 1977) for both polymorphs A and B by comparing X-ray data with results of computer-simulated models of the molecular structure. Their proposals are structures built up by right-handed six-fold double helices, B hexagonal and A orthogonal with a slightly distorted hexagonal packing, containing in hydrated form approximately 3 (or 3.5) and 0.67 water molecules per anhydroglucose monomer respectively. These double helical arrangements as proposed by Wu & Sarko (1978) are not entirely convincing. Their assumed glucosidic bridge of 105^0 is somewhat unlikely (Greenwood, 1979). Another problem is how a single left-handed helical structure like V-amylose can so easily develop out of or into a right-handed double helical structure, such as is commonly observed in practice during gelatinization or at hydration. Furthermore, the role of water as an integral part of the crystal structure remains vague in the double helix proposals. Finally, the agreement between observed and calculated lattice plane spacings could be closer. Brant (1976) pointed to serious weaknesses in computer simulations of molecular conformation energy studies.

Studying carefully the X-ray powder pattern of hydrated Nägeli-treated potato starch, Cleven observed a small but significant new diffraction maximum at 3.16 nm (Cleven et al., 1978). Also, during hydration the 0.37 nm diffraction maximum was found to develop relatively faster than other reflections together with a shift in the diffraction maxima towards greater lattice plane spacings, indicating an expansion of the crystal unit cell during water uptake, stopping at approximately 0.25 - 0.30 kg w./kg d.s. Perhaps hinted by a suggestion of Favejee (1935) the 0.37 nm reflection, which is the height of an ice tetrahedron, was related to structured water inside the crystal unit cell. Moreover, Cleven observed that wetting of dry starch with methanol developed the structure as visualized by X-ray, but without the 0.37 nm diffraction maximum. Combination of these new findings with Kreger (1951)'s fibre axis direction led to the proposal of a new fairly large-sized crystal unit cell for hydrated B-starch with a close agreement between observed an calculated lattice plane spacings. Figure 3.5 gives a diagram of the basal plane of the crystal unit cell with its hexagonal arrangement. Compared with the crystal unit cell dimensions given by Kreger (1951), this new cell doubles and triples the basal plane width and the fibre axis, respectively. The shaded hexagons accommodate columns of water molecules, structurized like *cubic ice*, hydrogen-bonded to each other and to the surrounding starch helices. These helices are accommodated in the open hexagons. Molecular model building confirmed that the most probable left-handed sixfold helix (Brant, 1976) nicely fits into the hexagonally arrayed structure. Figure 3.6 shows one helix with almost the height of the crystal unit

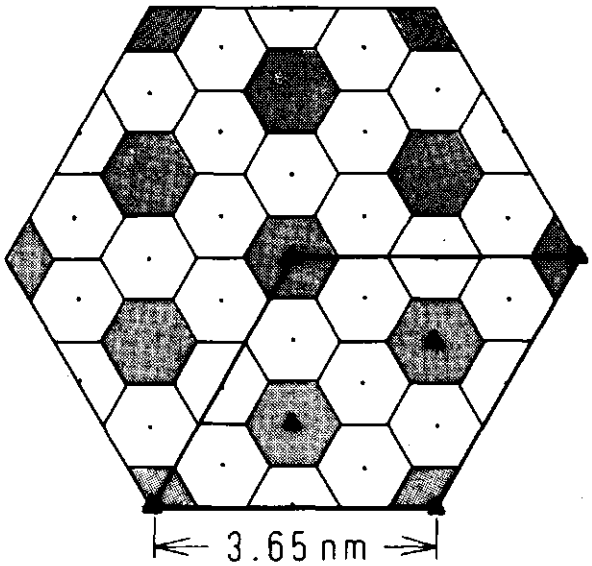


Figure 3.5. Basal plane diagram of the hexagonal crystal unit cell as proposed for hydrated B type starch crystals by Cleven et al. (1978). The open hexagons represent cross-sections of starch helices and the shaded hexagons contain structurized water.

cell (3 pitches), hydrogen-bonded to a column of cubic ice according to the proposal of Cleven et al. (1978). Remarkable is the fact that the height of the crystal unit cell (fibre axis c = 3.15 nm) is about equal to its hexagon side times $\frac{1}{2}\sqrt{3}$ ($3.65 \cdot \frac{1}{2}\sqrt{3} = 3.16$ nm), which indicates that many reflections in the X-ray pattern are near-identical. Evidently this further complicates the X-ray pattern interpretation. According to this model a fully hydrated B-starch crystal is estimated to contain about 2.5 water molecules per anhydroglucose monomer, being almost one in the structured water column and approximately one and a half bridging the polar groups between the monomers. For the latter there is ample space in the model. The volumic mass of dry crystalline B-starch in this model is 1 200 kg/m^3. The density relations of the hydrated starch are described in further detail in the next sections.

The most probable single helix for B-amylose (Brant, 1976) much resembles the commonly accepted V-amylose structure. From the observed easy polymorphic changes it might be concluded that also the A type structure has a

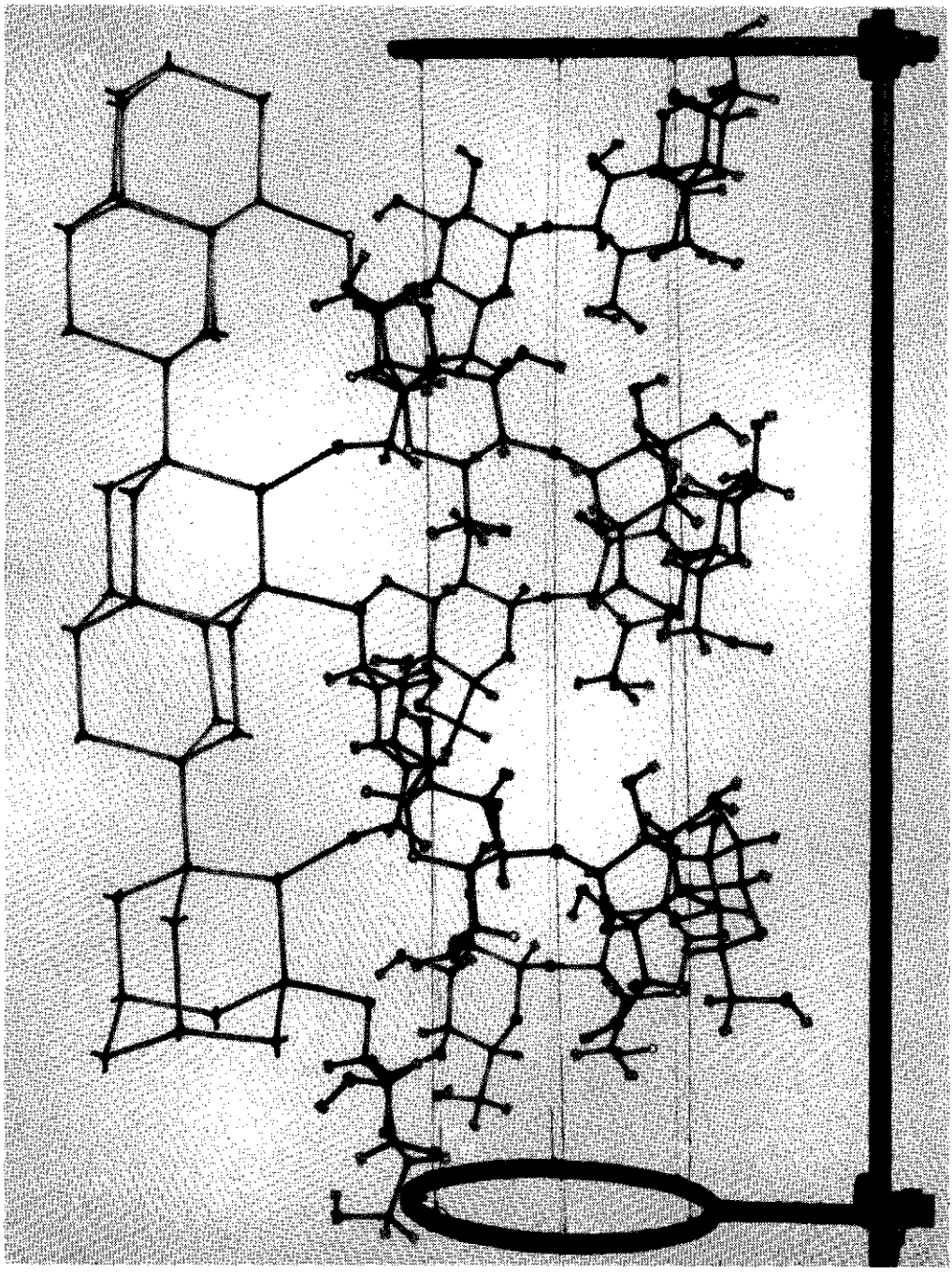


Figure 3.6. Most probable six-fold helix, hydrogen-bonded to a column of cubic ice. This structure fits well into the crystal structure for B-starch, the basal plane of which is shown in Figure 3.5.

close resemblance to those configurations. It is commonly assumed that the major difference between A and B type crystal structures is that the latter contains more water of crystallization (Banks & Greenwood, 1975). Blackwell et al. (1969) suggested for hydrated B-amylose that the hydroxyl groups linked to carbon atoms (2) and (3) form a hydrogen bond between two neighbouring monomers of the chain and the remaining hydroxyl group at carbon atom (6) forms an interchain bond between helical turns involving a water molecule, i.e. (6)-OH-H_2O-OH-(2). Whereas in A-amylose the latter bridge is directly between the adjoining helical turns. Guilbot et al. (1961) concluded from X-ray measurements that the first 9% water in A-starch is essential for the crystalline arrangement. Deuteron magnetic resonance signals of deuterated water in native starches of potato (B type) and wheat (A type) are split as a result of anisotropic motion (Hennig & Lechert, 1977; Hennig, 1977) of the water molecules in the system of radially oriented crystallites. Hennig (1977) also reports that native potato starch contains more uniformly ordered water than native wheat starch. Furthermore, Hennig & Lechert (1977) state that water must be regarded as an essential component of the crystallinity of the B-starch structure. These observations and conclusions are supported by our findings.

Generally speaking, it can be concluded that water molecules evidently are integral parts of the starch crystal polymorphs A, B and V, the amount of water varying for the different types. These amounts of *water of crystallization* are estimated roughly at 0.1, 0.25, 0.1 and 0.2 kg w./kg d.s. for the pure crystals of the A, B, V_a and V_h modifications respectively.

3.2.5 Partition of water over amorphous and crystalline parts

The X-ray measurements of Cleven et al. (1978; plus unpublished results) show that the crystal-plane spacings of native potato starch increase slightly during hydration from zero water content up to approximately 0.30 kg w./kg d.s. Favejee (1935) observed the same behaviour for native wheat starch. This points to a swelling of the starch crystals due to the uptake of water molecules. It was possible to assess the shift of the crystal-plane spacing from the available X-ray data (X-ray diffractograms for different moisture ratios and densitograms of Guinier-de Wolff photographs for fully hydrated samples) for the X-ray diffraction maxima near 0.52 nm and 1.58 nm, viz. peaks 9 and 3, respectively in the numbering of diffraction maxima as adopted by Cleven et al. (1978). The results are shown in figure 3.7. Other peaks are too broad or too small for a reliable assessment. Comparison of the spacing at high water content and the spacing at zero water content (obtained by linear extrapolation to zero hydration) gives for peak 9 a shift from about 0.515 nm to 0.522 nm. This linear increase of 1.4% corresponds to a volumetric expansion of approximately 4.3%. For peak 3, the observed

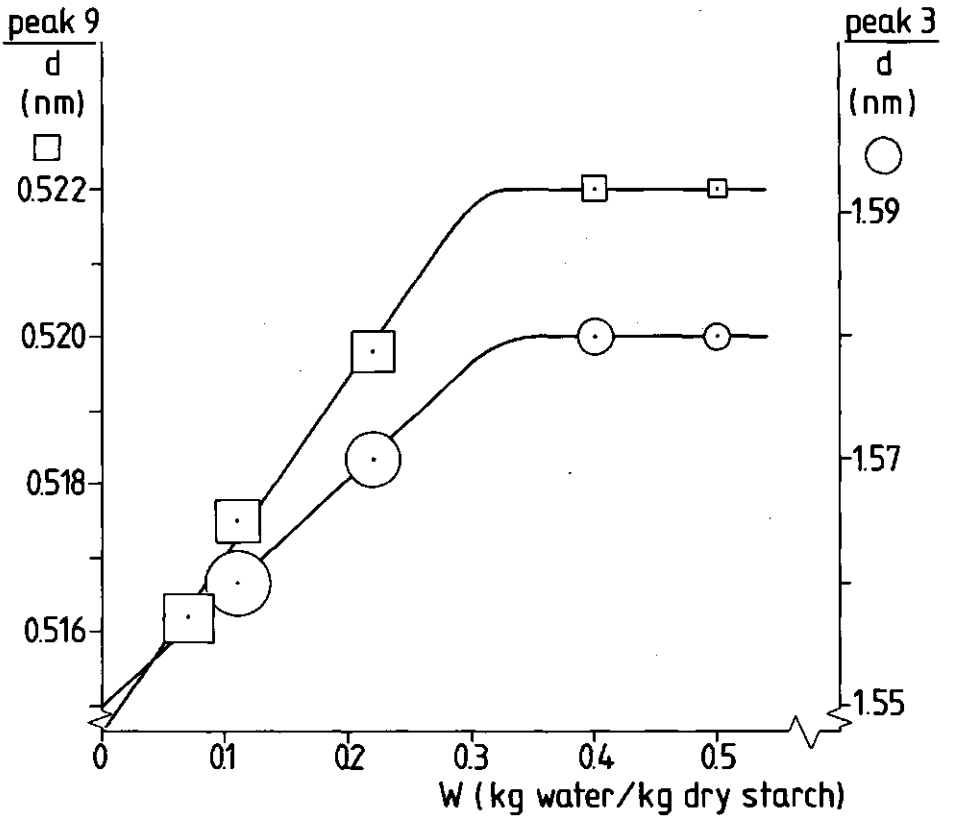


Figure 3.7. Relation of shift of lattice-plane spacings of native potato starch crystals to moisture ratio (mass of water to mass of dry starch). X-ray diffraction maxima near 0.52 nm and 1.58 nm. Size of squares and circles indicate estimated error.

increase from about 1.55 nm to 1.58 nm gives linearly 1.9% and volumetrically 5.8%. At about the same moisture ratio (0.25 - 0.30 kg w./kg d.s.) at which the peaks stop shifting, full development of X-ray intensity (i.e. peak sharpness) is observed (Cleven et al., 1978, Figure 2). For wheat starch quantification is more difficult as no such large peaks occur in the A type X-ray pattern.

In the B type unit cell, peak 3 stems from the (001) crystal plane of the basic structure and peak 9 from a combination of crystal planes (300), (002) and (211), all giving the same peak (Cleven et al., 1978). From stereometric considerations it is possible that, upon incorporation of foreign molecules into an orderly crystal lattice, which swells accordingly, one crystal plane is displaced more than others, but due to the mixed nature of peak 9 and the lack of great accuracy of these results no detailed conclusions about this directional aspect can be reached from these results. From the average of both crystal planes it can be concluded that completely dry B type starch crystals swell volumetrically by 5% during hydration, and that this swelling is complete at a moisture ratio of about 0.3 kg w./kg d.s. From these X-ray data and considering the volumic masses of water, of starch under wet conditions and moisture-free B type starch crystals, a more or less quantitative picture can be obtained of the partition of water molecules over the amorphous and crystalline parts of native potato starch during water uptake.

Normally, when air-dry starches (0.16 - 0.24 kg w./kg d.s.) take up water, they swell more or less proportionally to their volumetric water uptake. More detailed data about the volume of starch containing different moisture ratios are given in section 3.3. At full hydration of potato starch the partial specific volumic mass of the starch component is 1 650 kg/m^3. Pure moisture-free B type starch crystals, according to Cleven et al. (1978), were calculated to have 1 200 kg/m^3, which leaves a volume of 0.273 m^3 available for water per m^3 of starch crystals. This again gives a moisture ratio of 0.227 kg w./kg d.s. for fully hydrated B type starch crystals and a volumic mass of 1 473 kg/m^3. From their model Cleven and the author estimated that there is space in the crystal lattice for approximately 0.25 kg w./kg d.s., which gives a volumic mass of 1 500 kg/m^3. Both values for the volumic mass agree well with experimental values (Subsection 3.3.2), which corroborates the conclusion that at ordinary hydration levels there is virtually no difference in density between amorphous and crystalline starch parts.

The picture developed here suggests that in dry starch the first water up to about 0.25 kg w./kg d.s. distributes itself in proportion to mass ratio over the amorphous and crystalline parts of the starch granule. Immediately beyond this level (up to 0.3 kg w./kg d.s.) the crystalline parts take up

their last water molecules and then stop swelling. Almost certainly further water is taken up entirely into the amorphous parts which swell from this level exactly proportionally with the volume of water taken up (Subsection 3.3.2).

3.3 VOLUME RELATIONS OF STARCH AND WATER

3.3.1 General aspects

Hydrated starch is a mixture of water and dry starch, both of which have their own density, or more correctly, volumic mass. Its reciprocal is the mass volume, commonly referred to as specific volume. It is instructive for the understanding of the water-dry starch interaction to examine the specific volume of the starch as a function of its hydration by various methods. However, before analysing this, some general remarks on the volumic mass of polymers with any type of voids have to be made. The ultimate view developed here for starch deviates somewhat from current views on this matter (e.g. de Willigen & de Groot, 1967). In particular, the action of water as a plasticizing diluent (Subsection 3.2.2) has so far not been duly accounted for.

At the very onset we should realize that the volumic mass or mass volume of a substance is a typically *macroscopic* physical property. When dealing with particles having pores of near-molecular dimensions, these notions can no longer be interpreted in a simple way.

A volumic mass is usually determined from a combination of measurements of mass and volume, the latter appearing the more difficult to determine accurately. To obtain the volume of an irregularly shaped substance, methods of immersion into a liquid or a gas have been employed. As in the case of water and starch, both the fluid and the polymer consist of atoms, molecules and/or chains of monomers with sizes of the same order of magnitude. Hence it is impossible to obtain an unambiguous measure for the volume (and thus the volumic mass) of the pure polymer. When two fluids or a fluid and a solid both consisting of particles of different dimensions and shapes are mixed, as a rule an *apparent compression* is observed. A simple illustration of this is the mixing of spheres of two sizes. A stack of closely cubically-packed identical spheres in vacuum will have an overall volumic mass of about 0.74 times the volumic mass of the individual sphere. When these spheres are subsequently mixed with smaller spheres of identical material, the overall volumic mass will increase and, depending on the size ratio between the different spheres, it may well exceed 0.90 times the individual-sphere volumic mass. So, if spheres of different sizes are mixed *compression* is observed even in the absence of specific interaction. The same occurs upon mixing of fluid molecules with a dry polymer containing voids of molecular dimensions.

The following theoretical cases for the measurement by immersion of volumic mass or mass volume can be distinguished:

1. The fluid medium does not enter the pores at all. The volume measured is the *external* volume, and the obtained density will be the *outer, apparent* volumic mass of the porous body.

2. The medium fills the pores completely. A general condition for this to be possible is that the pore diameter far exceeds the diameter of the fluid molecules. The *internal* volume of the compact substance is measured and one obtains the *true* (macroscopic) volumic mass of the substance.

3. The medium only partly fills the pores. Some intermediate value of volumic mass is obtained between cases 1 and 2.

4. The medium fills the pores and is moreover compacted at the surface of the compact substance. This volumic mass exceeds the *true* volumic mass of case 2.

5. Medium molecules fill all the pores and moreover partly penetrate the surface of the 'compact' substance. The value obtained for the density exceeds also the *true* volumic mass of case 2. This may occur if the substance is either porous for the auxiliary fluid medium or if it has a very rough surface with cavities able to contain molecules of the medium. The difference with case 2 is virtually only one of surface definition, namely a difference of surface roughness on a molecular scale. This case 5 was employed for example by Heertjes (1938) in his interpretation of this density measurements with some natural fibres.

6. The medium acts as a plasticizing diluent for the (polymer) substance. In this case, upon mixing the dry, originally rigid, polymer with the auxiliary fluid, the polymer softens and it is moulded and spatially rearranged into a more dense form. Thus the mixture of both components is rearranged in space and the voids existing in the dry rigid polymer matrix that were previously inaccessible are deformed and subsequently filled by the molecules of the fluid. Also in this case the obtained volumic mass exceeds the *true* volumic mass of case 2. This measured value should be considered as the *true* volumic mass of the mixture *under the prevailing conditions*, i.e. soaked in the plasticizing diluent.

In Subsection 3.3.2 it will be shown that starch and water are relatively best represented by case 6. This is supported by the observed glass transition (Subsection 3.2.2).

3.3.2 Specific volume of starch-water mixtures

In the volumes of literature on starch relatively little attention is paid to the mass volume and almost none in relation to its level of hydration. Moreover, as will be shown, the general picture of published starch mass volumes is obscured by the varying methods of measurement used, leading to different results (e.g. Dengate et al., 1978; El-Saied, 1979; Nara, 1979). The obtained value for the volumic mass of a starch sample is rather sensitive to its moisture content. Therefore, the latter quantity should be specified accurately when reporting volumic masses. Unfortunately some research workers (e.g. El-Saied, 1979) take no notice of this and so increase the confusion.

In total four references were found that deal with starch volumic masses measured at a series of different moisture contents up to saturation. Obviously, not incorporated in this are the well-known starch tables, used in commercial starch recovery. These tables all report density values for aqueous slurries of water-saturated, native starch. For one of these references, Kurilenko & Jakowkina (1959), the Russian original could not be traced and only a brief abstract was obtainable. Another reference, Fish (1957), reports on potato starch gel with different moisture ratios. The volumic mass was measured in a density gradient column with carbon tetrachloride and chloroform. As the gel is a modification of native starch, with possibly a slightly deviating volumic mass, Fish's data will be used only for comparison; moreover, Fish (1957, page 48) made a small error in the calibration of his density gradient column* and did not take into account possible effects of starch gel retrogradation.

In the third reference, de Willigen & de Groot (1967) report on careful pycnometric measurements of native potato starch at different hydrations using paraffin oil. For our further interpretation mainly the density values of de Willigen & de Groot (1967) will be used, together with our own results. The last reference (in Japanese) is that of Nara et al. (1968) which was briefly reviewed by Nara himself (1979). It reports on volumic masses of 7 different native starches measured at different hydration levels in a density gradient column (probably at 25°C). Figure 3.8 presents the summarized literature values for the volumic mass of potato starch as a function of moisture ratio.

In general, several different values for the volumic mass of dry and air-dry starches can be found in the literature. It is noteworthy that the older

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* He used for the sugar crystal volumic mass = 1 590 kg/m^3 instead of the correct value of 1 564 kg/m^3.

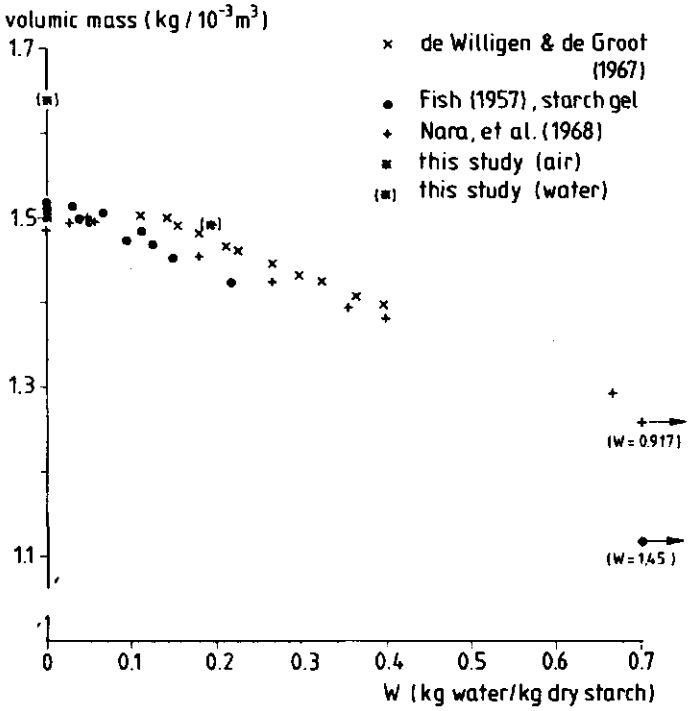

Figure 3.8. Comparison of available values of volumic mass (density) as a function of hydration. See text.

literature, roughly before 1950, reports values of 1 620-1 650 kg/m³ for pure (dry) starch, whereas the literature thereafter usually reports values of 1 480-1 530 kg/m³. Some examples are: Saare (1897) stated that numerous investigations on potato starch of different origins always gave the same specific weight. A volumic mass of 1 650 kg/m³ at 17.5°C is obtained when water is used as the medium. Samec & Blinc (1941) used Parow's value (Parow, 1907, 1928) of 1 648 kg/m³, which at the time was generally accepted. Leach & Schoch (1961) measured 1 511 kg/m³ for dry native potato starch under xylene at 30°C. Their pycnometric method (Schoch & Leach, 1964) is referred to for standardization, which is recommendable provided the method is extended with a procedure for proper deaeration of sample and auxiliary medium. The Handbook of Chemistry and Physics (all recent editions) gives for starch a volumic mass of 1 530 kg/m³ without any specification (presumably maize starch). For rough estimation purposes a value of 1 500 kg/m³ is widely accepted.

Already Rodewald (1896) established the important influence of the nature of the auxiliary medium for the measurement. He measured for dry wheat starch 1 625 kg/m³ under water and 1 429 kg/m³ under petroleum-ether. These values could both be confirmed by our own measurements with different auxiliary

fluids. Table 8 summarizes the most important ones of these results for native potato starch and its main fractions, amylose and amylopectin. These fractions were obtained by the industrial separation process of AVEBE and selected on the basis of purity criteria.

Table 8. Volumic masses in kg/m³ of native potato starch and its fractions, obtained with different measuring fluids at 293 K (20°C). Moisture ratios of the samples (kg water/kg dry starch) are given in brackets. Samples measured were air-dried and oven-dried for 20-24 h at 398 K (125°C) in a ventilated stove.

Method of measurement	Native potato starch (BDH)	Amylose (AVEBE)	Amylopectine (AVEBE)
Beckman Air Comparison Pycnometer	1 502 (∿ 0)	1 466 (∿ 0)	868 (∿ 0)
(air)	1 492 (0.205)	1 470 (0.1423)	874 (0.0996)
25 ml liquid pycnometer (paraffin oil)	1 498.9 (∿ 0)	1 438.8 (∿ 0)	875.4 (∿ 0)
25 ml liquid pycnometer (dioxane)	1 551.6 (∿ 0)	-	-
25 ml liquid pycnometer	1 639.3 (∿ 0)	1 645.1 (∿ 0)	1 654.7 (∿ 0)
(water)	1 493.0 (0.1926)		

From Table 8 it follows that inert gas and most organic liquids fill up a major part (probably most) of the ordinary starch pores, as in case 3. Dioxane, having two mutually compensating dipoles and being capable of forming hydrogen bonds, has some specific interaction* with the starch, which results in the relatively highest volumic mass for organic liquids. Water clearly acts as a diluting plasticizer; it leads to the highest volumic mass. This action is especially clear from the values obtained with the amorphous amylopectin (= cold water soluble), where gases and organic liquids apparently are not able to penetrate into the starch polymer network.

* A preliminary experiment measuring the heat of immersion calorimetrically revealed an important endothermal heat effect of more than 3.5 kJ/g native potato starch.

Preliminary measurements with helium (usually considered to approach case 2 best) gave volumic mass values up to 1 270 kg/m^3. This indicates that the free space in the amylopectin is inaccessible to air or paraffin oil (Table 8). However, helium was found to penetrate the sample only very slowly and equilibrium could not be reached with the air comparison pycnometer within an acceptable measuring time, so that the obtained values in this instance are not reliable. Certainly they must be higher for helium.

All traced literature values on the volumic mass of starch are compiled in Appendix 1. Relevant specifications of the measuring method, if available, are added. Considering the different behaviour of starch when immersed in different organic liquids or in water, most values in Appendix 1 agree reasonably with each other. Differences presumably result from differences in moisture and fat content, possible natural variation, possible differences in the pre-treatment of the starch samples, and different methods of measurement and neglect to apply corrections to observed values. In practice this means that one has to be very careful in selecting a measured volumic mass value for a specific purpose. For a given starch sample, different purposes may require different volumic mass values.

For starch, no systematic research into the influence of the nature of the measuring fluid on the volumic mass has been published. For cellulose and its derivatives, extensive investigations into this influence were carried out decades ago (e.g. Davidson, 1927; Heertjes, 1938; Hermans, 1946). A similar picture emerges when comparing starch with cellulose, in that the highest volumic mass is observed in water. For the plasticizing action of water on these carbohydrates, the work of Campbell & Russel (1935, in Hermans, 1946, page 88) is of particular interest here. They showed that for cellulose it is possible to arrive at the *same* volumic mass in water and organic liquids if, after preliminary swelling with water, the moisture in the fibre is stepwise replaced by organic liquids through a polar-apolar series, e.g. by using first methanol, then ethanol, and finally benzene. Under these conditions, the same volumic masses (viz. the value in water) were found in all liquids. This observation is in good agreement with case 6 if it is assumed that the densest structure of the polymer, created by the diluent plasticizer (water), persists (becomes 'frozen in') during dehydration in another liquid medium. And it follows that this dehydration must be down well below the level of hydration where the glass-rubber transition in the amorphous part of the polymer takes place. The results of Russel & Campbell and the observations of Muetgeert (Subsection 3.2.2) are in good agreement. They reveal different aspects (concerning volumic mass and specific surface area) of the same basic phenomenon, namely the glass-rubber transition of the amorphous carbohydrate polymer.

Among the values for volumic mass obtained with inert liquids and gases, those for paraffin oil are characteristic (case 3, possibly approaching case 2). The corrected data of de Willigen & de Groot (1967), whose measurements are considered to be very accurate, together with some own measurements cover most of the interesting range of hydrations. To represent the interaction between water and dry starch, it was found most illustrative to plot the mass volume at *constant amount of dry starch* against the sorbed moisture ratio. As the temperature coefficient for expansion of starch between 289 K and 298 K is 0.0003989 per degree centrigrade (Rodewald, 1896) for wheat starch, no expansion correction was made in our own measurements that were all obtained at 293 K (20°C). Figure 3.9 gives these results. If plotted in this way, water and starch are considered as a mixture to which water is added. When no further specific interaction between the components takes place the process is additive and the slope of the curve must become 1.0028 (the mass volume of pure water at 298 K in $m^3/10^3$ kg). In Figure 3.9 only the last three data points (> 0.3 kg w./kg d.s.) conform with this slope. Extrapolation of this part of the curve to the ordinate axis gives the value for the specific volume of starch under water: 0.604 $m^3/10^3$ kg. Its reciprocal, the volumic mass is 1 656 kg/m^3, which is surprisingly close to Saare's original value of 1 050 kg/m^3! Also Lamm (1934) found 0.6 $m^3/10^3$ kg for the partial specific volume of starch in solution. The starch structure apparently assumes its maximum volumic mass only at moisture contents exceeding 0.3 kg w./kg d.s. At lower levels of hydration, the starch contains some empty space that is accessible to water; for completely dry native potato starch this empty space amounts to even about 10.5% of its total volume. From Figure 3.9 this empty space can be read as the difference between the experimental curve and the extrapolated straight line.

Unfortunately no volumic mass values of comparable accuracy are available at moisture levels between 0.01 and 0.1 kg water/kg dry starch. However, inspection of the comparable curves for celluloses (Hermans, 1946), and for wool (Heertjes, 1938), together with Figure 3.8, strongly supports the correctness of the portions of the curve at those moisture levels. The last measuring point of Nara et al. (1968) shows a wide departure from their given linearization. It can be shown, however, to be located very close to the extrapolated line in Figure 3.9 at the same moisture ratio (0.917 kg w./kg d.s.). At this point of hydration, free water is already extant outside the starch granules. It can be concluded that the values for the volumic mass of potato starch slurries (at this temperature), as given in the well-known starch tables, must all be located on this same straight line. Hence, it is no longer necessary to measure these many values for volumic mass of commercial starch slurries as has been done in the past (Appendix 1). For starches other than that of potato, the measurements of Nara et al.

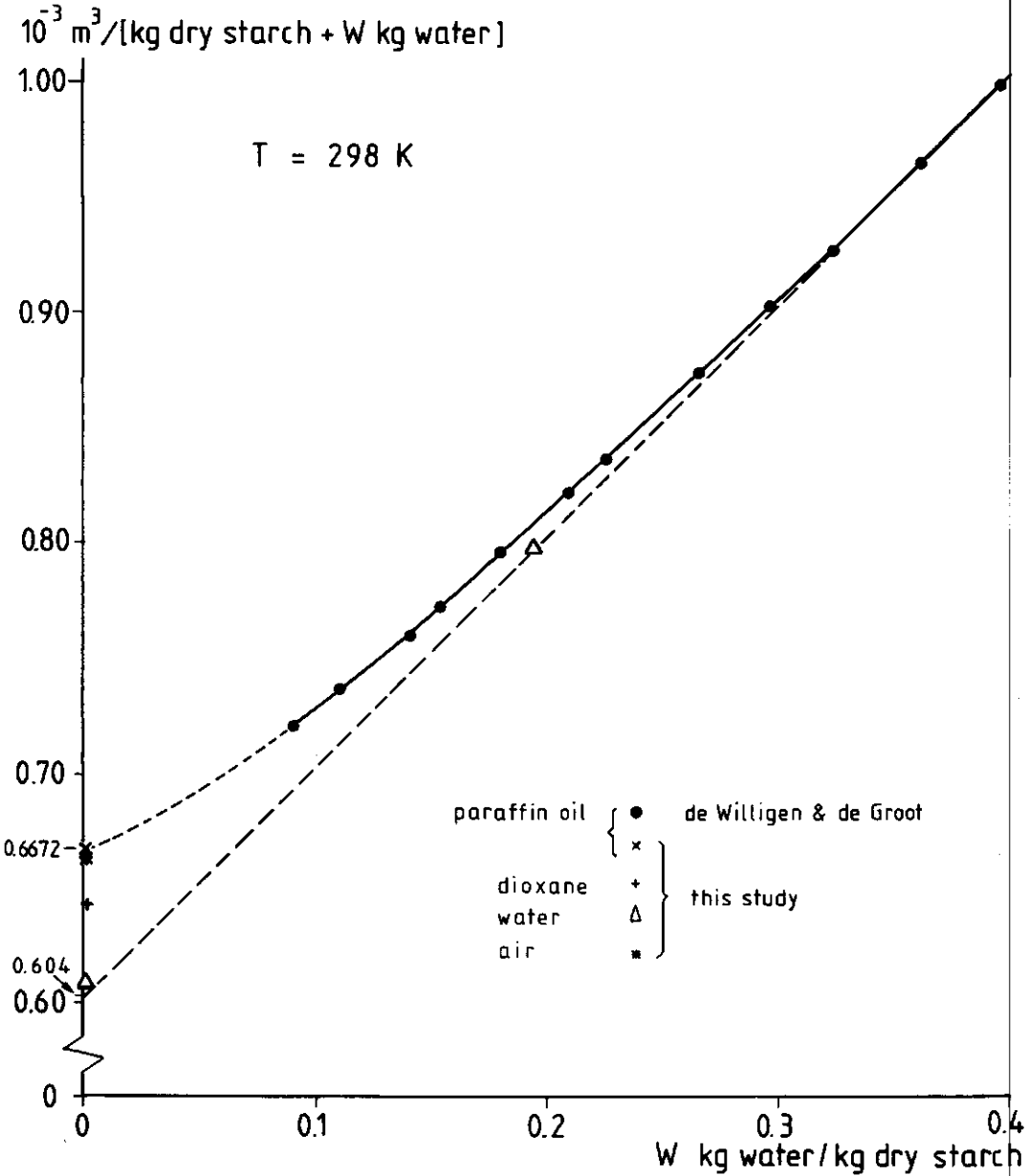

Figure 3.9. Mass volume at constant amount of dry substance for native potato starch-water mixtures as a function of hydration. See text.

(1968) indicate a comparable relation between volumic mass and level of hydration.

Contraction of a dried biological material upon wetting (for completely dry native potato starch about 10.5% by volume on dry starch basis) is generally observed. In the past it has often been interpreted in terms of compression of the water component, sorbing onto a surface. De Willigen & de Groot (1967) concur on this point. If compression of water occurs, the slope of the curve in figure 3.9 gives the volumic mass of the first water attached to the dry starch, which can be expressed as $\left(\frac{\partial\ Va}{\partial\ W}\right)^{-1}$. This gives a value in excess of 2 000 kg/m^3. This value for volumic mass of the sorbed water cannot have physical significance. Inspection of the sorption isotherm (van den Berg et al., 1975) and estimation of the swelling pressure show that even at 0.03 kg w./kg d.s. this pressure decreases to below $2.5 \cdot 10^5$ kPa. Water compressed to $3 \cdot 10^5$ kPa shows only 10% decrease in volume. The maximum volumic masses for water have been observed as $25 \cdot 10^5$ kPa, at which pressure esoteric ice polymorphs with volumic masses of 1 650 kg/m^3 can be found (Subsection 2.1.3). It is more logical to explain the obtained results in terms of the plasticizer influence of water on the starch polymer.

3.3.3 Volumic relations of crystalline and amorphous parts

Relating the obtained relation between volumic mass and hydration with starch crystallinity, the possible differences in volumic mass between crystalline and amorphous parts of native starch will be investigated. For this topic, workers generally assume a significantly higher density for the crystallites of starch than for the amorphous parts (e.g. Leach & Schoch, 1961; Nara, 1979). This assumption is based on general experience with polymers having crystalline and amorphous parts and some older proposals for starch crystalline structures. Commonly, the analogy is drawn with cellulose, which in its native form is about 70% crystalline and consists of cellulose-I crystallites embedded in amorphous parts. As mentioned before, in accepting this analogy it is seldom realized that there exist very distinct differences between native starch crystals and most other polymer crystals, especially with regard to water.

It is known (Subsection 2.4.3) that native starch crystals do contain water for their mere existence, contrary to cellulose crystallites. When taking up water, starch crystals (as monitored by their X-ray pattern) *develop* showing 5% swelling during the uptake of about 0.25 kg w./kg d.s. (Subsection 3.2.5). Apparently, the crystals in their dry state are porous and less dense than when hydrated. For the B type starch crystal, as found by Cleven et al. (1978), the calculated volumic mass as a function of hydration is given in figure 3.10, together with the observed volumic mass for whole na-

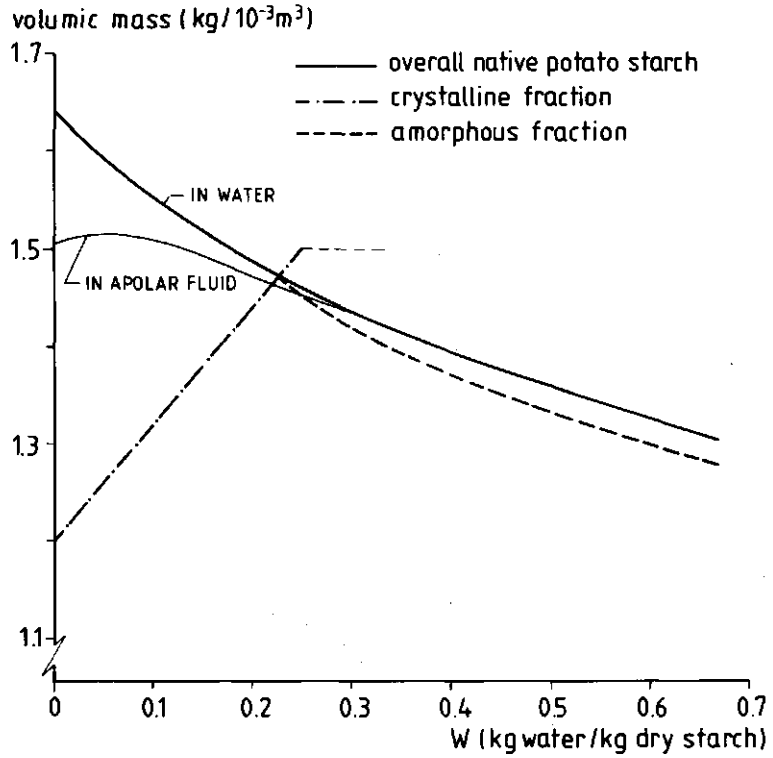

Figure 3.10. Volumic mass of (overall) native potato starch and its crystalline and amorphous fractions as a function of hydration. See text.

tive potato starch (data from Figures 3.8 and 3.9). Here we assume that the crystals take up their maximum mass of water (0.25 kg w./kg d.s.) and remain as such during further water uptake in the overall starch. Assuming a crystallinity of 30%, as measured for potato starch (Subsection 2.4.3), the volumic mass of the amorphous fraction as a function of hydration was obtained at moisture levels beyond approximately 0.23 kg w./kg d.s., the level at which masses of crystalline and amorphous parts equalize. At lower hydration levels the meaning of this reconstruction is somewhat doubtful because of the complicated specific starch-water interaction and the somewhat tarnished concept of volumic mass of the separate components at these low moisture ratios. As noted in Subsection 3.2.5, a remarkable property of the starch model developed here is that in ordinary air-dry starch (for potato starch 0.20 - 0.25 kg w./kg d.s.) crystalline and amorphous parts of the native granule do have about the same volumic mass. This is probably one of the origins of the great difficulty to distinguish between them.

Nara (1979), in his attempt to reconstruct the same relation, presents an-

other view. His reasoning, however, is based upon the crystallinity model of cellulose, together with the assumption that starch crystallites do not contain water. He further does not pay attention to the different values for volumic mass as obtained with water and inert solvents and gases. This is an unfortunate disregarding of the true nature of the specific interaction between starch and water.

Differences in volumic mass between potato starch and other types of starches are most probably small. Several data given in Appendix 1 support this view. It would be interesting to study more systematically volumic masses of pure starches of different X-ray types, especially the A and B types. For such comparative studies, not only water contents but also contaminants, especially natural fats (volumic mass about 930 kg/m^3), in the starch should be taken into account. Observed differences in volumic mass between native wheat starch (A type) and native potato starch (B type) can be explained partially by differing fat contents. Because the major part of common native starches has an amorphous nature, it is very difficult to detect possible differences in volumic mass between pure starch crystallites this way. But anticipating the day when sufficiently large, pure crystals of different starch types become available for measurement, the author doubts whether important differences in volumic mass actually exist between these crystals. The uptake of water into native starch crystals with apparent lack of clear discontinuities, the relative ease with which different crystalline forms convert into one another without important changes in properties and the physical nature of the starch granules in which crystalline and amorphous parts are not distinguishable all support this view.

From this section the author concludes that the proportion of empty space in dry native potato starch is 10.5%; that empty space is gradually filled with water upon hydration. This space consists most probably of pores of molecular dimensions and smaller and is partly located inside the crystallites. During water uptake the pores inside the amorphous parts collapse gradually when the amorphous part of the starch polymer matrix is plasticized by the increasing amount of water. This collapse is complete at a moisture content of 0.3 kg w./kg d.s. At that stage the starch crystallites also contain their maximum amount of water.

3.3.4 Volume and temperature

Volumic masses at temperatures other than room temperature as a function of hydration were not found in the literature, but for water-saturated native potato starch de Willigen & de Groot (1967) reported some results important for practice with an interesting analysis of the temperature-volume relationships. This is generalized below.

Applying the second law of thermodynamics to a swollen native starch grain in water (think for example of an immersed piece of cross-linked gel with limited swelling), it follows for the dependence of a small reversible change of the pressure P of this system with temperature T that:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{-\partial Q}{\partial V}\right)_T \qquad (3.3)$$

Here S and V denote the system entropy and system (grain) volume respectively, and ∂Q is the reversibly exchanged heat. As under these circumstances the starch grain system can only imbibe or release water, during this swelling or shrinking the entropy change is almost entirely determined by the redistribution of water over the system and not by conformational changes of the polysaccharide. Consequently, the heat effect ∂Q approximately equals the involved heat of water sorption. Assuming the isothermal quotient $\left(\frac{\partial Q}{\partial V}\right)_T$ to be constant, equation (3.3) can be simplified after integration at constant volume into:

$$P = P_{ref} - K_P \ln\left(\frac{T}{T_{ref}}\right) \qquad (3.4)$$

where P_{ref} and T_{ref} are an (arbitrary) reference pressure and temperature of the system; K_P is a constant with the dimension of pressure. For the system starch grains in water at low gel pressures it may further be assumed that the system volume is about proportional to the (inner) system pressure which is set by the cross-linked macromolecule. This changes (3.4) into its volume analogy:

$$V = V_{ref} - K_V \ln\left(\frac{T}{T_{ref}}\right) \qquad (3.5)$$

where V_{ref} and K_V are both constants with the dimension of volume.

De Willigen & de Groot (1967) measured heats of immersion of native potato starch at different hydrations in a relative way and plotted these results against the volume contraction during hydration which were calculated from their volumic mass measurements (Subsection 3.3.2). From their linear plots de Willigen and de Groot (1967) showed that for native potato starch hydration the isothermal quotient $\left(\frac{\partial Q}{\partial V}\right)_T$ is constant, as was also reported by Kurilenko & Jakowkina (1959). Subsequently, de Willigen & de Groot (1967) determined mass volumes and water contents of the same sample saturated with water at three temperatures (273.2, 298,2 and 318.2 K) covering the range between freezing point and gelatinization temperature. As saturation water contents the values 0.504, 0.418 and 0.355 kg w./kg d.s. were reported at these temperatures. Their data give according to equation (3.5) indeed a linear relation with the function:

$$V = 0.005723 - 0.000824 \ln T \qquad (3.6)$$

where V is the volume (m^3) of 1 kg of pure native potato starch in water and T is the absolute temperature. For simplicity T_{ref} was taken to be 1 K. So 0.005723 m^3 may be seen as the reference volume of 1 kg starch extrapolated to 1 K.

The temperature dependence of the volume of starches is important for practice. For instance, an increase of the temperature of commercial separation of wet starch slurries from 293 K (20°C) to 318 K (45°C) will decrease the amount of water adhering to the starch by about 10%, thus decreasing the drying expenses and increasing the purity of the recovered starch product.

3.4 HEAT OF INTERACTION OF WATER AND STARCH

3.4.1 General

Since the sorption of water by starch is a spontaneous process, it is accompanied by a *decrease* in free energy G. Also there is a *decrease* in entropy S caused by trapping vapour molecules at active sorption sites, in a thin surface layer or in a 'solid' solution. Thus, the enthalpic change during this process must be *negative* (exothermic).

At high water activities, the molar heat evolved upon sorption from the vapour phase equals the enthalpy of condensation, indicating that under these conditions water vapour sorption is comparable with condensation. The enthalpy of sorption increases with decreasing water activities, but is never more than $1\frac{1}{3}$ times the enthalpy of condensation, which indicates that the nature of the binding process is physical (*physisorption*). The *excess* or *net enthalpy of sorption*, defined as $\Delta H_{exc} = \Delta H_{sor} - \Delta H_{cond}$, can both be measured directly and estimated indirectly. As *direct* methods differential thermal analysis (DTA) and immersion calorimetry have been applied. *Indirectly* the enthalpy can be obtained from sorption isotherms at different temperatures, applying the equation of Clausius-Clapeyron. In the following subsections results from both methods will be briefly reviewed and compared and subsequently interpreted in terms of the expected molecular model of sorption.

3.4.2 Results from direct methods

Collison & Dickson (1971) measured heats of *dehydration* (or *evaporation*) of native wheat and potato starch as a function of hydration by DTA. Although the observed heat values are somewhat higher (approx. 72 kJ/mol water) than might be expected, their finding of a constant heat of dehydration at mois-

ture ratios lower than approximately 0.14 kg w./kg d.s. is noteworthy. Also Oleneva & Chizhov (1973) measured heats of evaporation of different gelatinized starch pastes, but their results contain only two data points in the comparable moisture range. For the heat of evaporation close to zero water content, Oleneva & Chizhov (1973) measured 66 kJ/mol water.

Various references in the literature report on measurements of the heat of *immersion* (or *wetting*) of starches. These heats of immersion were measured at the given temperature as direct calorimetric heats which originated upon mixing of starch samples of different water contents with excess water. This gives ΔH_{exc} expressed per kg dry starch as a function of moisture content. The older data were reviewed by Schierbaum & Täufel (1962) together with their own results for native potato and wheat starch as a function of hydration. Since then heats of immersion were reported by van den Berg et al. (1975) for native potato starch, by Yamada (1979) for wheat starch and flour and by Nara (1979) for native starches from potato, sweet potato, wheat, manioc and maize. The reported heats of immersion for potato starch in the different references agree approximately. Expressed on starch basis, the heat of immersion decreases with hydration from approximately 125 kJ/kg dry starch for absolutely dry starch towards zero heat effect at about 0.40 kg w./kg d.s. The other starches all show the same trend with a little lower excess enthalpy for the dry starches ranging from 100 to 120 kJ/kg dry starch. A later series of measurements on 5 native starches by Weldring (to be published) corroborates this trend.

With respect to the crystal structure in native starch, one finding by Nara (1979) is particularly interesting. Nara determined heats of wetting for starches both in the native and mechanically damaged form. The latter was obtained from grinding in a ball mill for 42 h and exhibited the X-ray pattern of an amorphous substance. The dry amorphous starches all had an identical heat of immersion of 125.4 kJ/kg dry starch (zero water content), which, except for potato starch, is significantly higher than that of the native starches. This might point to a somewhat lower density of active sorption sites for native starches (due to their partial crystallinity) as compared with the amorphous forms. Generally the starches with the highest sorption capacities at $a_w < 0.5$ also show the highest heats of immersion. In line with this are some preliminary observations that heating of native starch at temperatures beyond 373 K lowers both the heat of immersion and the sorption capacity (Subsection 3.1.4). Subsequent wetting and drying at near ambient temperatures restores the original heat of immersion value for the heated samples. This observed argument between trends in heats of immersion and sorption capacity at lower water activities directly supports the basic role of active sites in the sorption process.

At low water activities starch behaves as an almost inert physical (ad)sorbent onto which physisorption takes place. When thermodynamic equilibrium is attained, the first derivative of the heats of immersion with respect to the moisture ratio corresponds to the *differential net enthalpy of sorption*. At higher water activities where the sorbent is plasticizing, the observed enthalpy will also contain a contribution from the weakening of the polymer structure. However, since the glass-rubber transition involves only a minor enthalpy change, this contribution may in first instance be neglected. While taking the derivative, van den Berg et al. (1975, Figure 3) observed that the first steep part of the heats of immersion curve between 0.02 and 0.10 kg w./kg d.s. can be approximated by a straight line which indicates that all water in this range (up to approx. 0.9 water molecules per anhydroglucose residue) is sorbed with an equal sorption enthalpy. The results of Schierbaum & Täufel (1962) and Nara (1979) agree with this; so does the already mentioned constant heat of dehydration reported by Collison & Dickson (1971). The differential net enthalpy of sorption as a function of hydration, thus obtained, is shown diagrammatically in Figure 3.11 (A) and will be discussed in Subsection 3.4.4. Also incorporated in this figure is the result (B) obtained from the B.E.T.-isotherm analysis anticipating a later analysis in terms of sorption models.

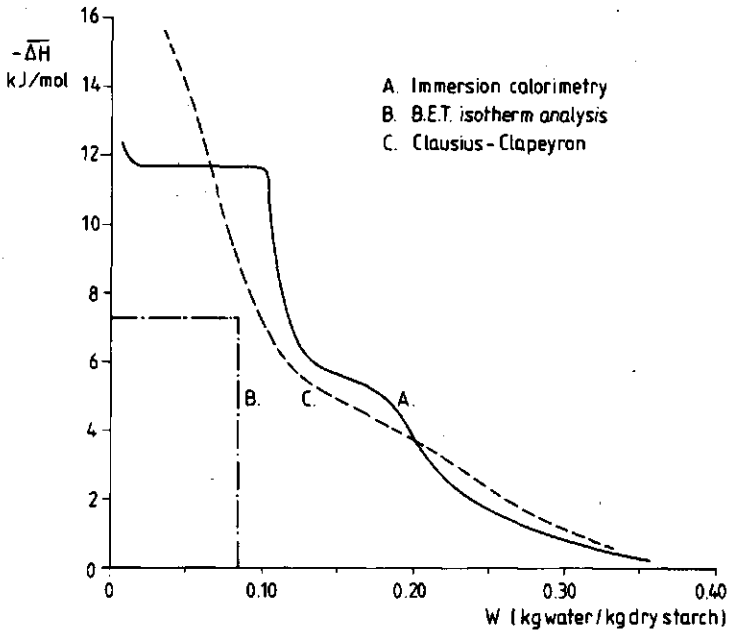

Figure 3.11. Molar excess enthalpies for sorption of water by native potato starch at 293 K as a function of hydration. A, the differential net enthalpy of sorption derived from immersion calorimetry; B, the net enthalpy of sorption from isotherm analysis with the B.E.T. model of sorption; C, the net isosteric enthalpy of sorption obtained with the Clausius-Clapeyron equation. See text.

3.4.3 Results from indirect methods

Figure 3.11 also gives (C) the net isosteric enthalpy of sorption for native potato starch as calculated from resorption isotherms measured at three temperatures (van den Berg & Leniger, 1976) using the Clausius-Clapeyron equation which reads:

$$\left(\frac{\partial \ln a_w}{\partial T^{-1}} \right)_w = \frac{\Delta H_{is}}{R} \qquad (3.7)$$

where ΔH_{is} is the molar net *isosteric* enthalpy of sorption which theoretically differs by only RT from the (molar) net enthalpy of sorption. This relation is derived for condensing systems from the second law of thermodynamics, thereby neglecting the molar volume of the condensed (or sublimed) vapour as compared with that of the original vapour and assuming the vapour phase to behave perfectly.

Theoretically it is somewhat doubtful whether the Clausius-Clapeyron equation may be applied as such to the system under investigation. Apart from the hysteresis mentioned in Subsection 3.1.6, a major objection is that the actual sorption process does not strictly meet the isosteric condition. At a constant moisture ratio, generally with changing temperatures, a redistribution of sorbed molecules will take place over sites, subsequent layers or in voids, thus leaving the total sorbed amount constant but not its distribution. Less relevant for the application of the Clausius-Clapeyron equation but important for the magnitude of the heat effect is whether at low activities we deal here with a gas-solid (sublimation) or a gas-liquid (condensation) equilibrium. The latter is certainly the case at higher activities, where the picture is further complicated by plasticizing of the sorbent structure. In practice the Clausius-Clapeyron analysis of sorption isotherms is generally thwarted by the quality of the equilibrium data, because substantial heat effects are derived from observed small differences in sorption.

In conclusion it may be stated that for these systems the Clausius-Clapeyron analysis merely supplies an acceptable first order approximation of the net enthalpy of sorption. This is shown in Figure 3.11 where the values derived with this analysis give the correct magnitude but with a distinct difference in the shape of the curve. A thorough study to assess the theoretical value of the Clausius-Clapeyron equation for water vapour sorption by polymers would be beneficial for all who deal with this area.

3.4.4 Conclusions with respect to the model of sorption

Deriving the enthalpy of sorption from measured heats of immersion is clearly the most sensitive of the presented methods. The functionality (Figure 3.11) derived in this way shows two shoulders, indicating a distinction between the first, the second and further sorbed molecules at a sorption site. With respect to the model of sorption the following picture emerges:
Starting with dry starch, the first 2 per cent of water are sorbed heterogeneously with a falling differential net enthalpy of sorption. Water between 0.02 and approximately 0.10 kg w./kg d.s. is sorbed almost homogeneously with a constant excess enthalpy of sorption of about 11.7 kJ/mol water. This water fills the active sites with one water molecule ('monolayer') up to a stoichiometric ratio of approximately 0.9 water molecule per anhydroglucose monomer. Further water sorbed between 0.10 and approximately 0.19 kg w./kg d.s., i.e. 1.7 water molecules per anhydroglucose monomer, accommodates in a second layer and is sorbed nearly homogeneously with an excess enthalpy of sorption of approximately 5.2 kJ/mol water. In this range of water contents water diversifies its action and begins to plasticize the starch structure. The homogeneous-type (ad)sorption may be explained from the identical polar groups of the starch polymer and perhaps their partial similarity with the water molecule. Water beyond 0.20 kg w./kg d.s. is sorbed with a gradual decreasing excess enthalpy of sorption which eventually becomes negligible. The discrimination between the two sorbed layers will be the basis of a model of sorption to be described in subsection 4.6.1.

Some results of a further thermodynamic analysis are shown in Figure 3.12. This diagram gives a combination of the thermodynamic excess functions as a function of hydration: Gibbs free energy, enthalpy, and entropy of sorption for the (native potato) starch-water system. The differential net Gibbs free energy of sorption was calculated from the resorption isotherm, the differential net enthalpy of sorption stemmed from measured heats of immersion as described before, and the differential net entropy of sorption was calculated from the difference.
A comparable analysis for maize starch and some starch preparations, but using enthalpies estimated from isotherms at different temperatures by means of Clausius-Clapeyron's equation, was published before by Masuzawa & Sterling (1968) and Morsi et al. (1967). The magnitude of the latter results is comparable with ours but shows somewhat different shapes for the enthalpy and entropy functions. However, in some cases one shoulder in the monolayer range was also observed.

The sorption entropy in Figure 3.12 becomes strongly negative in the monolayer range, indicating strong immobilization of sorbed molecules in the first layer. Immediately beyond this level of hydration ($\sim$ 0.10 kg w./kg

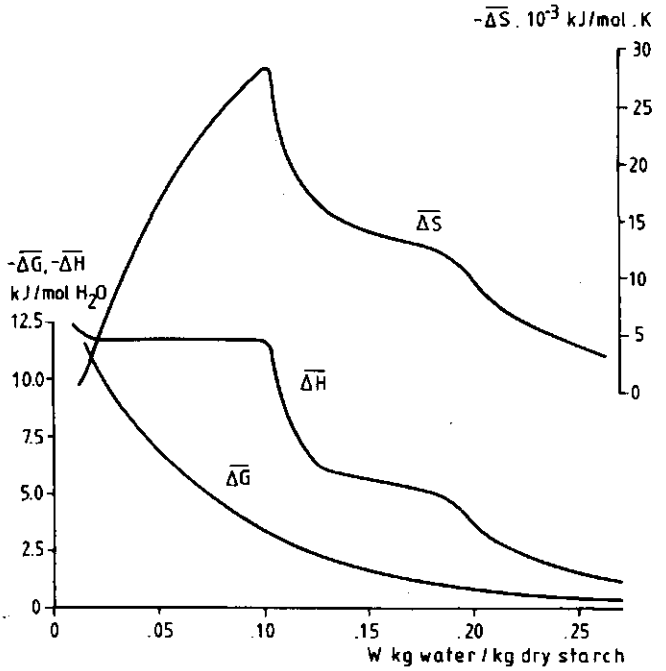

Figure 3.12. Differential thermodynamic functions for sorption of water vapour by native potato starch at 293 K as a function of hydration. ΔH_{exc} (left ordinate), the differential net enthalpy of sorption; ΔG (left ordinate), the differential net Gibbs free energy of sorption; ΔS (right ordinate), the differential entropy of sorption (van den Berg et al., 1975).

d.s.) the sorbed molecules have a much increased number of configurations which points to the onset of a second layer of sorbate molecules. Although less clearly, a third layer is indicated to begin at 0.19-0.20 kg w./kg d.s. Using an equation by de Boer (1953) for the adsorption time:

$$\tau = \tau_0 \cdot \exp\left(\frac{\Delta H}{RT}\right) \qquad (3.8)$$

where τ_0 is the oscillation time of adsorbed molecules and ΔH is the molar enthalpy of adsorption, the average lifetimes of molecules in the first and second layer can be roughly estimated. Taking, somewhat arbitrarily, $\tau_0 = 10^{-14}$ (de Boer, 1968, page 35) for an average molecule in the first and second layer, sorption times of $9 \cdot 10^{-5}$ and $6 \cdot 10^{-6}$ s. are calculated. These values have the same order of magnitude as the relaxation times of water molecules in ice ($2 \cdot 10^{-5}$ s. at 273 K).

The magnitudes of the sorption enthalpies (55.8 kJ/mol and 49.3 kJ/mol for the first and the second layer respectively) are close to the bond energy of two hydrogen bonds (20-25 kJ/mol). This points to hydrogen bonding as a

realistic sorption mechanism at a molecular level. For the crystalline part of B type native starch, this observation agrees directly with the postulated ice-like structured water molecules. However, also in the amorphous parts of dry starch sufficient room is available (Section 3.3) to accommodate water molecules between polar-groups, thereby forming new hydrogen bonds with them. Due to the relative immobility of the polymer, which is loaded with hydroxyl groups, these first water molecules generally may be expected to behave somewhat *ice-like*. Further water will gradually become more mobile and eventually give rise to the observed changes of the starch polymer structure like swelling and glass transition.

3.5 SOME OTHER ASPECTS OF STARCH-WATER RELATIONS

3.5.1 Introductory remarks

In the literature a variety of papers can be found dealing with the interactions of water and starches as well as comparable carbohydrate systems applying other than thermodynamic techniques. This section touches briefly on this interesting area of research with the aim to supply more background information on the starch-water system.

3.5.2 Diffusion of water in starch

Since there are only very low activation energies involved, generally the rate of physical (ad)sorption processes is quite fast. The rate controlling step is likely the *diffusion* of the (ad)sorbate molecules towards or from the sorption sites or (in exceptional cases) the heat equilibration of the system. Under ambient conditions mass diffusion is much slower than heat transmission. Some remarks about kinetics relevant to the measurement of sorption isotherms are included in Chapter 5.

The diffusion of water in potato starch gel (amorphous) as a function of hydration has been studied by Fish (1957, 1958), who derived diffusion coefficients by applying non-steady state slab-diffusion theory to thin slabs of gel undergoing small steps in resorption and desorption. Beyond the moisture ratio of 0.15 kg w./kg d.s. Fish (1957) observed a somewhat anomalous diffusion behaviour. Here the initial part of the experimental graph of the relative uptake or loss of water, when plotted versus the root of time, deviates from the expected linearity. Such behaviour is not uncommon for water-polymer systems (Barrer & Barrie, 1958) and can for a major part be attributed to a change in mobility of the polymer. At a high level of hydration the diffusion coefficient of water in starch gel does not decrease significantly with decreasing water content until this value reaches about 0.31 kg w./kg d.s. Figure 3.13 shows the smoothed results for 274 and 298 K obtained by

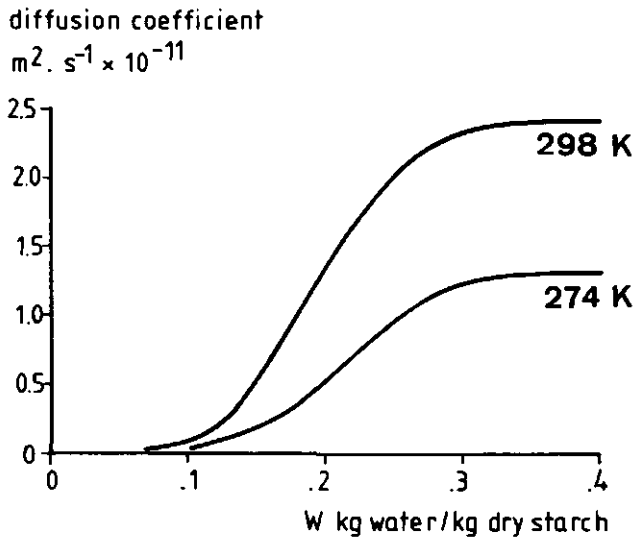

Figure 3.13. Diffusion of water in potato starch gel, from Fish (1958).

Fish (1958). In the hydration range below 0.15 kg w./kg d.s. the log of the diffusion coefficient as a function of hydration is linear over more than three decades (Fish, 1957). A similar composition dependence of the diffusion coefficient has been found for many food materials (Bomben et al., 1973).

At high levels of hydration the diffusion of water in starch is similar to bulk diffusion. Basler & Lechert (1974) used pulsed NMR to investigate water diffusion in maize starch gels with moisture ratios beyond 1 kg w./kg d.s. and found the water molecules to diffuse uniformly and unrestrictedly with the same activation energy as in bulk water. They also reported that the swollen starch grain boundaries are no barriers to diffusion.

At lower hydration levels (below approx. 0.30 kg w./kg d.s.) it must be assumed that the majority of the water molecules in starch are transported by surface diffusion, the molecules hopping from site to site. Results from volumetric measurements (Section 3.3) leave literally no room for any speculation about pore or Knudsen diffusion mechanisms to occur in starch at low hydration levels. Also Vollmer (1954), after investigating water vapour transport under different atmospheric conditions through paper sheets, i.e. thin layers of crude cellulose, concluded to the mechanism of surface diffusion.

3.5.3 Spectroscopic results

From investigations of the hydration behaviour of several polysaccharides, starch not included, by means of infrared spectroscopy, Kleeberg & Lück (1979) generally concluded that upon hydration at a water activity of about 0.5 the number of hydrogen bonds of the water directly with the carbohydrate becomes a minority. From that hydration level onwards increasing amounts of water are present that have hydrogen bond interactions comparable with those in liquid water. In general, the vibrational state of carbohydrates at low water contents differs markedly from that in more dilute solution.

From measurements of the dielectric constant of potato starch gel and the assumption that the immobilized water fraction has the same dielectric constant as the organic material at microwave frequencies, de Loor & Meyboom (1966) concluded to approximately 0.16 kg of 'bound' water per kg starch. Water present in excess of this was thought to be liquid-like. Dielectric absorption spectra of wheat starch (Guilbot et al., 1960) and maize starch (Nagy et al., 1972) determined at different levels of hydration showed discontinuities in the growth of peak areas at approximately 0.09 and 0.15 kg w./kg d.s., which they attributed to transitions in water binding mechanisms.

From deuteron magnetic resonance (DMR) spectra of a starch-based product Tait et al. (1972) concluded that the first 0.07 kg w./kg d.s. is solid-like or irrotationally bound. They obtained a similar value for the B.E.T. monolayer value of the same product. Water sorbed in excess of 0.07 up to 0.20 kg w./kg d.s. was restricted in its rotational frequency by a factor of 10^4-10^5 as compared to that in pure liquid water. Above about 0.20 kg w./kg d.s. the relaxation behaviour of the water molecules in starches is no longer uniform (Tait et al., 1972; Hennig & Lechert, 1974). Beyond that hydration level the transversal relaxation time of pulsed NMR measurements (Hennig & Lechert, 1974) shows two ranges of proton mobility indicating the presence of an increasing amount of much less restricted water molecules. Upon still further hydration beyond 0.30 kg w./kg d.s. Lechert & Hennig (1976) observed signals of liquid water being present in the sample. Calorimetric measurements carried out with the same sample showed that this liquid-like water is also able to freeze (Lechert & Hennig, 1976).

Combining NMR and dielectric results from a variety of hydrated biopolymer systems, Kuntz (1975; Kuntz & Kauzmann, 1974) suggested generally three water environments for biopolymers, namely: 'irrotationally bound' water, 'bound' water, and bulk water, with approximate correlation times in the ranges of microseconds, nanoseconds and picoseconds, respectively. In practice, however, the time scales of the various water motions are difficult to

separate (Kuntz, 1975). Applying this scheme to the NMR results mentioned before, it may be concluded that in starch hydration the first water environment corresponds to the first 0.07 - 0.10 kg w./kg d.s. The second environment ends somewhere between 0.20 and 0.30 kg w./kg d.s. These boundaries cannot be defined rigorously, partly because they are influenced by the total level of hydration. For instance, NMR signals indicate that the first category of water increases slightly with hydration. This observation may have several explanations. (i) It is generally consistent with sorption theory. The first layer is not saturated as soon as the monolayer sorption value is reached but sorbing of the first molecule at a site is a dynamical equilibrium process proceeding over the whole range of activities. However, (ii) it may be explained also by new sites becoming available for sorption as hydration (and swelling) proceeds. Another (iii) explanation could well be that the nature of bonding of the first molecule is influenced by further molecules sorbing on top of or close to it, which is made visible by the NMR signal.
When viewed as a whole, the picture of the water-starch interaction derived from NMR results is rather consistent with the picture derived from the sorption enthalpies (Section 3.4).

3.5.4 Unfreezable water

Some direct information is supplied by determination of the unfreezable water fraction of the water-starch system. In line with the calorimetric results mentioned before (Lechert & Hennig, 1976), DTA measurements showed for potato starch the first 0.320 - 0.327 kg w./kg d.s. to be unfreezable down to 93 K (Young, 1970, in Duckworth, 1971). Own preliminary measurements confirmed this: we found a value of approximately 0.33 kg unfreezable (down to 120 K) water per kg dry native potato starch. Stoichiometrically the same moisture ratio corresponds with three water molecules per anhydroglucose residue (or active site). This value is remarkably similar to the hydration of some other systems. In general the correlation length (or persistence length) in liquid water is of the order of three to four molecular diameters. It is therefore not surprising that similar values are also encountered in a system of quite different nature, namely monoglyceride-water bilayers. Here, water layers of 1 nm thickness (about three molecular diameters) do not show freezing behaviour (Larsson, 1981). A problem in making this comparison is that we don't know whether the three water molecules at a starch site are piled on top of each other or laterally spread over the site.

3.5.5 Summary

Based on the results described in the Sections 3.4 and 3.5, a schematic sum-

mary of the behaviour of water in the water-starch system is given in Figure 3.14. As mentioned before, some of the indicated boundaries are not as sharp as is suggested by the diagram, because most transitions proceed fairly continuously over the range in mass fractions of water. Also most of the compared results were derived from different investigations of different starch samples, which may cause some dispersion. The enthalpic transitions agree remarkably well with the averaged NMR results. The irrotationally bound water and that bound with greatly restricted rotation are identical with the first and second sorbed layers, respectively. So are the fractions of water with two ranges of proton mobility (0.20 - 0.30 kg w./kg d.s.) and that beyond the second layer where the excess sorption enthalpy becomes almost zero. Four methods (A, C, D and E) in Figure 3.14 indicate roughly the monolayer water content as it is also derived from the B.E.T. method (Brunauer et al., 1938; Section 4.2) and four methods (A, B, C and E) indicate whereabouts bulk-like liquid water occurs in the system (beyond approx. 0.30 kg w./kg d.s.).

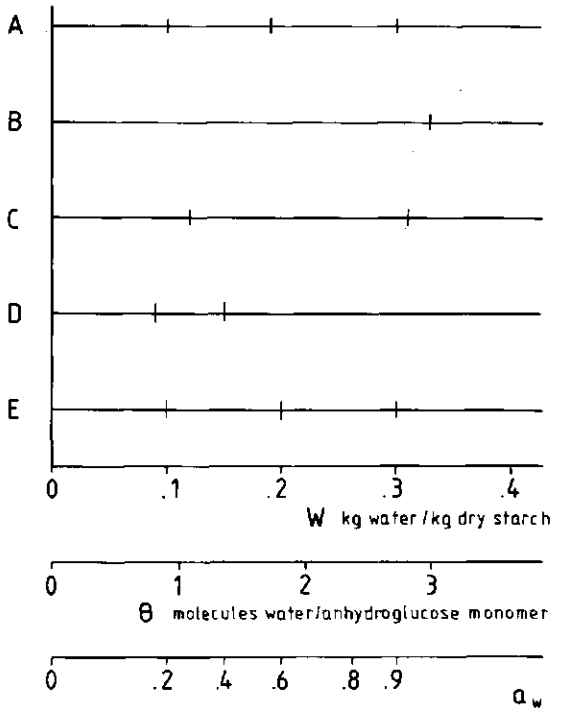

Figure 3.14. Averaged water contents of transitions in the behaviour of water in the water-starch system as observed by different methods. A, sorption enthalpy (immersion calorimetry); B, unfreezable water (DTA); C, diffusion coefficients; D, dielectric absorption; E, rotational freedom of molecules (NMR). The scale of a_w at the abscissa was taken from an isotherm for native potato starch averaged for hysteresis.

3.6 SORPTION OF WATER VAPOUR BY STARCH

Based on the collected results in the previous sections, this section attempts to describe in more detail the process of sorption of water vapour on initially dry starch with emphasis on the state of equilibrium. The analysis will lead to a model of sorption which will serve as the basis of further analysis. This analysis will use some existing theories as well as some theories to be developed. For the general purpose of interpretation the sorption isotherm may be schematically divided into three parts corresponding approximately to the three *classes* or ranges of sorbed water indicated before (Subsections 3.4.4 and 3.5.3). The sorption isotherm shown in Figure 3.15 is schematically divided in these classes. The distinction between these classes necessarily cannot be sharp but is merely indicative of the nature of the majority of the water molecules present in that class.

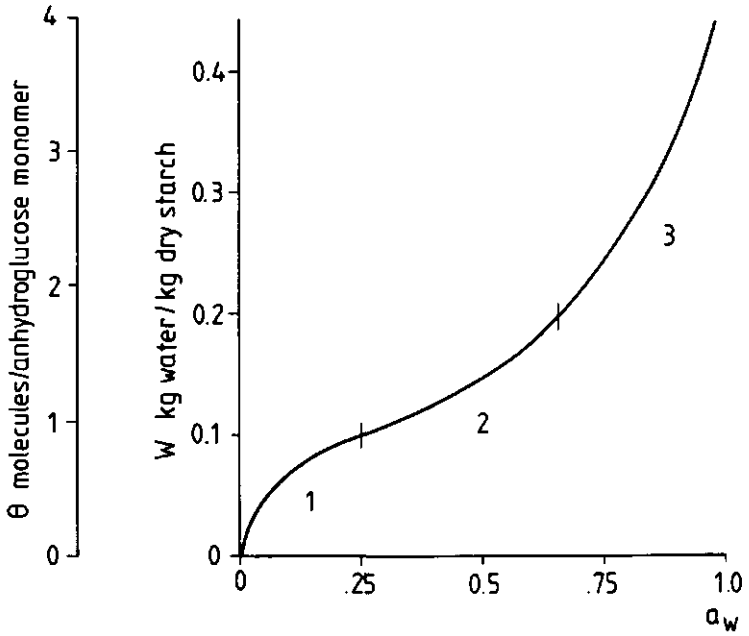

Figure 3.15. Idealized isotherm for water vapour sorption on starch schematically showing the three classes of sorbed water that are distinguished in the text.

Beginning with dry starch, the sorption in these three classes at ambient temperatures may be characterized as follows:

- *Class 1* water ranges to approximately 0.10 kg w./kg d.s., roughly corresponding to a water activity of 0.20. It represents strongly sorbed and immobilized water which behaves in many respects as part of the starch solids. In terms of sorption we encounter localized physical adsorption of small po-

lar molecules at polar sorption sites, located in a fairly rigid polymer structure. Stoichiometrically the sorption sites can be identified with the anhydroglucose monomers of the starch polymer and class 1 water almost forms a completed monolayer (0.11 kg w./kg d.s.). The first approximately 0.02 kg w./kg d.s. is sorbed heterogeneously with a sorption enthalpy exceeding that which corresponds to two hydrogen bonds per water molecule. Further water in this class is sorbed almost homogeneously with an enthalpy close to that of two hydrogen bonds per water molecule. In reality the picture of the sorption process is complicated by the facts (i) that the anhydroglucose monomers contain each three hydroxyl groups available for hydrogen bonding with water when the structure is swollen, and (ii) that in native starch the polymer structure is partly crystalline. Water molecules may well form hydrogen bridges between different monomers compensating simultaneously more than one free polar group. The ordered domains in the polymer structure start to develop a crystalline pattern during the uptake of water in this range, indicating the straightening out of a lattice that is deformed in the dry state. In these crystallites water molecules can form specific structures (Subsection 3.2.4). During the uptake of class 1 water, starch shows only minor swelling (Figure 3.9). Therefore most of this water is accommodated in void spaces of the dry polymer matrix with an ensuing increase in the volumic mass of the system. The experimental isotherm in this range of hydration can be well described by the simple B.E.T. isotherm equation (Brunauer et al., 1938).

- Water in *class 2* is sorbed with a decreasing sorption enthalpy upon increasing moisture content. The shoulder in the enthalpy function up to approximately 0.19 kg w./kg d.s. (Figure 3.12) suggests as an overall picture the formation of a more or less homogeneously sorbed second layer of sorbate molecules with an average sorption enthalpy somewhat lower than that corresponding to two hydrogen bonds per water molecule. According to a more detailed analysis, however, class 2 water diversifies in its effects because of its plasticizing action on the initially rigid polymer structure. This action induces an increase of the chain mobility which gradually takes place with hydration over the entire class 2. The majority of the water molecules in this class sorb in the vicinity of the first molecules in new holes or at newly created sites, both of which are freed for water sorption by the swelling and gradual weakening of the sorbent structure. The entropy function indicates a strongly increased number of configurations (or mobility) for these water molecules. It is likely that instead of rupturing one or two hydrogen bonds between polymer chains the water molecules in this class establish two to four new bonds, thus gaining an average net result of somewhat less than two hydrogen bonds per water molecule. In native starch this water is supposed to distribute uniformly (in proportion to their relative masses) over crystalline and amorphous parts of the starch; it further or-

ders the crystals of the former part with only a little volume expansion and causes substantial swelling of the amorphous part. During the uptake of this water the whole system swells considerably although not yet fully in proportion to the sorbed volume. Part of the water in this class can also take part in and/or accelerate certain chemical and biochemical reactions, thereby acting as a reactant or as a solvent. Somewhat arbitrarily and a little depending on the type of starch, the upper boundary of this class of constituent water is set at about 0.20 kg w./kg d.s., which corresponds approximately with a_w = 0.65. Class 2 water forms an almost *continuous* transition from the first to the third class of water, which is also reflected by the course of most system properties as a function of hydration.

- *Class 3* extends to saturation and contains a majority of almost freely moving water. Initially, up to about 0.30 kg w./kg d.s. the binding energy further decreases but beyond this value the enthalpy of sorption roughly equals the enthalpy of condensation of bulk water. Also at about this hydration level, in native (B type) starch the crystals are saturated so that all further water is taken up by the amorphous parts, which are now likely to behave like swelling gels. Although this is not practiced here, class 3 water might be further divided into water below and beyond about 0.30 kg w./kg d.s. (see also Figure 3.14). Beyond 0.30 kg w./kg d.s. the system swells exactly proportional to the imbibed volume. Water in class 3 has many properties very similar to those of bulk water. Apparently the greater part of this water is free of restrictive interaction with the solids. It can be thought to be mechanically entrapped in the void spaces of the now fully weakened amorphous parts of the swollen starch network. Therefore the amount of class 3 water is largely determined by the network elasticity and the density of cross-links. For instance, native potato starch, having a specific grain structure with presumably many cross-links, can take up roughly 0.5 kg w./kg d.s. at saturation. On the other hand, the same sample, after complete breakdown of the crystalline native structure through gelatinization and freeze-drying, can hydrate to more than 0.70 kg w./kg d.s. (van den Berg et al., 1975, Figure 2). In class 3 the isotherm for water vapour sorption rises steeply. The high part of this curve can be approximated with the simple Flory-Huggins isotherm equation which models a polymer solution system (Taylor et al., 1961). Not seldom the water in this class is named 'capillary' water. However, this term disregards the true nature of the gel-like system in which there exist no rigid capillaries of the size predicted by Kelvin's equation.

Although it is physically somewhat difficult to use the term 'phase' in this connection, in a water-saturated native starch two phases (at least) can be distinguished, namely a solid phase of more or less perfect hydrated crystals (or crystallites) embedded in a gel-like phase of hydrated amorphous

starch. However, as no more specific information is available on the size and shape of starch crystallites, we can only speculate about the presence of possible phase boundaries. At low levels of hydration not exceeding one water molecule per anhydroglucose unit only one solid phase can be distinguished.

With respect to the water sorption mechanism of starch no single mechanism accounts for the observed overall behaviour. Rather a combination of mechanisms is needed. Briefly summarizing, it is concluded that *class 1* water (0 - 0.10 kg w./kg d.s.; see figure 3.14) fills the available sorption sites with about one *localized* water molecule per site. This 'monolayer', except for the first 0.02 kg w./kg d.s., is almost *homogeneously* sorbed with an average binding energy which exceeds that which corresponds to two hydrogen bonds per water molecule. In many respects this water behaves as a part of the solid. *Class 2* water (0.10 - 0.20 kg w./kg d.s.) roughly forms a second 'layer' of molecules that are also (nearly) *homogeneously* sorbed with an average binding energy that is somewhat less than that of two hydrogen bonds. This water is more mobile and plasticizes the amorphous parts of the initially rigid starch polymer structure. In native starch (partially crystalline) class 1 and 2 water develop the crystalline pattern upon its penetration into the crystals. *Class 3* water (beyond 0.2 kg w./kg d.s.) approaches with its properties gradually that of bulk water. Initially it terminates the plasticizing of the amorphous polymer structure, but beyond 0.30 kg w./kg d.s. a gel-like system exists. In the case of native starch the crystallites are embedded in the gel-like structure, but beyond this water content they do not take up further water.

4 SORPTION THEORIES

4.1 INTRODUCTION

In Section 3.6 it was concluded that the process of water sorption by starches is basically governed by two mechanisms, viz. localized (ad)sorption, almost homogeneous in nature, and formation of a gel. In addition there is the complication of the plasticizing of the (polymer) sorbent structure during the (re)sorption process. For starch (and other polymers) this picture is not entirely new. Already Katz (1933) concluded that the first sorbed water in a swelling biopolymer forms 'hydrates' whereas further imbibed water is about homogeneously distributed throughout the system forming a 'solid' solution. He based this conclusion mainly on his former research results (Katz, 1917-1919) and some juveniled parts of Nägeli's old 'micelle' theory (Section 2.4). Some later developments in the general theory of water sorption by polymers were reviewed by McLaren & Rowen (1952) and Howsmon (1954) and more recently by Kuntz & Kauzmann (1974). However, since the plasticizing of the polymer structure was not considered specifically, both sorption mechanisms were sometimes considered competitive, in other cases one of them was assumed to predominate. Generally this plasticizing behaviour and the observed hysteresis led to great complications in the modelling of water sorption by starch and other biopolymers.

A compilation of existing sorption theories (covering altogether 77 isotherm equations) which over the years were somehow connected to water sorption of biological materials was composed earlier (van den Berg & Bruin, 1978). None of these theories adequately covers the system under investigation. A satisfactory sorption theory in this case should contain both mentioned mechanisms of sorption together with the hysteresis and temperature effect. The resulting isotherm equation should only contain parameters having a clear physical meaning. On the ideal sorption theory, however, it was stated by Young & Crowell (1962, page 157): '*the perfect sorption theory which takes all factors into account would lead to an isotherm equation of such complexity that it could not fail to describe any isotherm shape. Such an equation would also be quite useless because none of its constants could be evaluated unequivocally*'. From a mathematical point of view it is easy to fit any number of experimental data points to a sigmoid curve. For instance, some suitable exponential function with one or more logarithms and sufficient parameters will always be able to describe the experimental curve with good accuracy. The usefulness of a theory depends mainly on the motives of the user. For example, in the case that only a mathematical description is needed to calculate drying processes, the user is more interested in an

equation that describes the observed isotherm and can be solved analytically than in the correctness of the underlying sorption theory. In the present study a physically more satisfying approach is followed with respect to the adoption and further elaboration of relevant sorption theories. However, for obvious reasons a practical *limitation* of four is set to the *number of parameters* in the sorption isotherm equation. Furthermore, all parameters must have a clear physical meaning. It is realized that any attempt to describe the relation between mass fraction of water and water activity as the compounded outcome of the complicated interactions between water and starch, with an isotherm equation containing at most *four* parameters, will always remain a simplification in so far that not all structural and interaction details can be covered.

Based on the two mechanisms (homogeneous localized (ad)sorption and polymer solution formation), the Langmuir (1918) and B.E.T. (Brunauer et al., 1938) theory and the Flory-Huggins theory (Flory, 1953) together with some of their modifications will be used in this study. In a sense it is general practice to interpret water sorption isotherms of foods in terms of the B.E.T. model. In our case, however, the choice of the model is based on an independent analysis of the sorbent nature. For most other food systems the unmodified B.E.T. model seems not so well justified since usually many different polar groups are available for water sorption. The use of the B.E.T. equation in food practice is mainly based on the empirical observation that the B.E.T. monolayer value corresponds roughly with the water content that is connected with the longest shelf life of the product.

Furthermore it must be admitted that the B.E.T. premises (Section 4.2) are a very poor model of the rather complicated water-starch interaction. Especially the neglect of lateral interactions between sorbed molecules is a serious error. Nevertheless, the B.E.T. isotherm equation describes the low part of the experimental isotherm well and it was shown before that modification of the equation extends this range considerably (van den Berg et al., 1975). A general difficulty of the interpretation of the water-starch sorption behaviour with the B.E.T. (or any other surface sorption) model is that in this case we do not have more insight in the real sorption surface except that it consists of the anhydroglucose monomers which according to stoichiometric analysis act as individual sorption sites. Some modifications of the Langmuir and B.E.T. theory which add favourably to the model in physical significance and (hopefully) to its isotherm-fitting ability will be discussed in the following Sections 4.3, 4.4 and 4.6. It will be pointed out that the distinction between multilayer sorption in the B.E.T. model and formation of a simple (Raoult) solution is not very sharp as far as the mathematical formulation is concerned. Therefore, the B.E.T.-like approach to multilayer sorption is in fact more general than suggested by its premis-

es. This means also that one may never draw conclusions to the fulfilment of the premises of a sorption model solely at the basis of the agreement of the observed isotherm data with the model equation. Section 4.5 presents a discussion of relevant polymer solution theories. An attempt to account for swelling of a sorbent with a homogeneous surface by means of a fluctuating number of sorption sites is presented in Subsection 4.6.3. The last section (4.7) of this chapter describes some interesting sorption models in the literature and outlines some mutual relations. All models discussed in this chapter are of a general nature. Also the new ones have probably a wider field of application than merely the water-starch system.

4.2 SORPTION THEORIES OF LANGMUIR AND BRUNAUER, EMMETT AND TELLER FOR HOMOGENEOUS SURFACES

Using kinetic arguments, Langmuir (1918) derived his classical monolayer isotherm equation (case I) for localized adsorption of molecules from an ideal gas onto an arbitrary lattice arrangement of identical, independent and indistinguishable adsorption sites on a surface. (Langmuir used the word: elementary adsorption places.) This equation can be written as:

$$\frac{N}{N_s} = \frac{C_L a}{1 + C_L a} \tag{4.1}$$

where N is the number of the sorbed molecules; N_s is the number of sorption sites; C_L is the Langmuir adsorption constant which depends on the nature of the interaction between adsorbate and sorbent and the temperature and a is the thermodynamic relative activity of the sorbing gas or vapour (Subsection 2.1.5). The ratio N/N_s in implicit equations will be named θ, the degree of occupation of sorption sites.

In the same paper, Langmuir extended his treatment to the case that adsorption sites can hold more adsorbed molecules (his case IV), which he thought to be spread out over the place (or site) instead of being piled up on top of each other. For the further discussion, however, this distinction makes no essential difference. For this case (IV) Langmuir derived:

$$\frac{N}{N_s} = \frac{\sigma_1 m + 2\sigma_1\sigma_2 m^2 + 3\sigma_1\sigma_2\sigma_3 m^3 + \ldots\ldots}{1 + \sigma_1 m + \sigma_1\sigma_2 m^2 + \sigma_1\sigma_2\sigma_3 m^3 + \ldots\ldots} \tag{4.2}$$

where $\sigma_1, \sigma_2, \sigma_3$ ... are the relative lifetimes (adsorption times) of the first, the second, the third etc.... molecule on a site and m is the number of moles of gas striking the adsorption sites per second; m is proportional to a.

For a following case, case VI in the Langmuir classification, 'adsorbed films more than one molecule in thickness' (later by Brunauer et al. (1938) considered as piles of molecules on one sorption site), Langmuir applied the same equation (4.2) stating literally:
'*We should expect the relative life, σ_1, of molecules in the first layer to be very different from that in the second and subsequent layers. There may be a small difference between σ_2 and σ_3, but as the number of layers increases still further the values of σ should remain practically constant. If σ_1 and σ_2 are different, but all subsequent values of σ (i.e., σ_3, σ_4, etc.) are equal to σ_2, then ...* equation (4.2) *... finally takes a very simple form and shows that at very low pressures N is proportional to m, but at pressures close to saturation N begins to increase rapidly and becomes infinite when saturation is reached.*'

Putting $\sigma m = Ca$ and $\sigma_2 m = a$, mathematical transformation shows that Langmuir had in mind an equation for the sorption isotherm which can take the following form:

$$\frac{N}{N_S} = \frac{Ca}{(1 - a)(1 - a + Ca)} \qquad (4.3)$$

where C is a constant depending on the interaction of the first adsorbed molecule with the adsorption site.

Equation (4.3) was later rederived by Brunauer, Emmett & Teller (1938) (B.E.T.) for multimolecular adsorption onto independent sites in basically the same way as Langmuir (1918) did, assuming the adsorbed molecules beyond the first one to have bulk liquid properties. The B.E.T. equation in our notation reads:

$$\frac{N}{N_S} = \frac{W}{W_1} = \frac{C_B a}{(1 - a)(1 - a + C_B a)} \qquad (4.4)$$

where W is the amount of gas adsorbed; W_1 is the amount of gas adsorbed when all sites contain one molecule, often named completed *monolayer*, and C_B is the B.E.T. adsorption constant which will be specified later. A first analysis shows that (4.4) can also be written as:

$$\frac{N}{N_S} = \frac{C_L a}{1 + C_L a} + \frac{a}{1 - a} \qquad (4.5)$$

where $C_L = C_B - 1$. Equation (4.5) clearly describes multimolecular adsorption as Langmuir's case I (4.1) to which a term is added for *multilayer* formation. This second term deserves special attention since it is mathematically equivalent to Raoult's law (Raoult, 1888), which equals solvent activity (as

measured through vapour pressure depression) and solvent mole fraction in the case of an ideal solution. For water as the solvent it reads:

$$a_w = x_w = \frac{N(w)}{N(w) + N(s)} \qquad (4.6)$$

where x denotes mole fraction and N is the total number of molecules; w denotes water and s the solute. Introducing into (4.6) the mass fraction of water on a dry basis or moisture ratio, W (kg water/kg dry solute):

$$W = \frac{N(w) \cdot M_w}{N(s) \cdot M_s}$$

where M denotes molecular weight, one arrives at:

$$\frac{W}{M_w/M_s} = \frac{a_w}{1 - a_w} \qquad (4.7)$$

Bringing the ratio of molecular weights in (some) connection with the monolayer value W_1, we may compare the second term of B.E.T.'s isotherm equation directly with Raoult's law.

For further discussion it is interesting to note that Langmuir did not assume the molecules adsorbed beyond the first one to have bulk liquid properties; it suffices that they are *identical*. As will be shown in Section 4.3 in the isotherm equation this makes a difference that is mathematically accounted for by another constant adjusting the gas activity *a*.

Since Brunauer et al. (1938) forwarded their B.E.T. theory, it has gained great importance. It has become without exaggeration the most widely used tool for the estimation of specific surface areas of nearly all kinds of solid substances, including foods and other biological materials. The B.E.T. equation fits the lower parts ($a<0.35$) of most experimental sorption isotherms reasonably well, so that two numerical constants suffice to describe the lower part of the isotherm. Also for further theoretical developments, such as for example the *t*-plot for porous adsorbents, the B.E.T. model played a crucial role. However, in almost any case the amount adsorbed at activities exceeding 0.4 is less than that predicted by the B.E.T. equation.

Basically the B.E.T. model for sorption is simple: perpendicular piles of molecules sorbed onto identical sites that are independent of each other, in dynamic equilibrium with an ideal gas. The B.E.T. theory has with reason been severely criticized (see e.g. Young & Crowell, 1962), but in general it is a useful compromise between theory and practice. The model gives a valuable first picture of the phenomenon of localized sorption that cannot yet

be replaced by a much better alternative. The shortcomings of the B.E.T. model are particularly obvious when it is being applied to sorption of water vapour to complicated swelling biopolymers such as starch. However, it is difficult to improve the model without impairing its simplicity, which is one of its major attractions. Ross (see Hiemenz, 1977, page 307) perhaps summarized the discussion pro or contra the B.E.T. model effectively by comparing it to a 'master chef who concocts a palatable dish out of an old shoe'. For some, the end result is what matters: a palatable dish, for others, the starting material dominates their opinions: the old shoe. In the present study it will be tried to take a balanced viewpoint between these two extremes.

Concerning the sorbent it is emphasized that the B.E.T. model does not define the spatial arrangements of sorption sites. Both *ad*sorption and *ab*sorption are included. This was realized by Cassie (1945, 1947) who derived equation (4.3) for systems (like ours) where absorption is more likely the case than adsorption. It should also be realized that accepting W_1 in (4.4) as a measure of the specific surface area is only an abstraction of reality since only the number of sorption sites is counted. Although the words *monolayer* and *multilayer*(s) are in use for the first molecules and the second and following molecules sorbed onto the active sites, respectively, they do in fact suggest too much.

Because *kinetic* arguments are in essence not relevant to equilibrium conditions which are described by the isotherm equation, it is more elegant to derive these equations by means of statistical thermodynamics.* In this way, Fowler & Guggenheim (1939, page 426) rederived (4.1) and so did Hill (1946) with (4.3). Also Cassie (1945) already used a statistical argument. From this derivation it follows for the B.E.T. constant that

$$C_B = \frac{q_1}{q_\ell} = \frac{j_1}{j_\ell} \exp\left(\frac{H_1 - H_\ell}{RT}\right) \qquad (4.8)$$

where q_1 is the partition function of the first molecule sorbed on a site; q_ℓ is the same of the molecules sorbed beyond the first one and set equal to the partition function of a molecule in bulk liquid; H_1 is the molar enthalpy of sorption of the molecules sorbed in the first layer; H_ℓ is the same

---

* The basis of statistical thermodynamics was laid by J.W. Gibbs and Boltzmann in the previous century and applied to sorption systems by R. Fowler in the thirties. For a general introduction the reader is referred to Hill (1960). Basic for the application to sorption systems like the one under consideration is that due to the neglect of side interactions between sorbed molecules, the sorption system may be thought to be separated into small individual subsystems (sorption sites). The individual contributions of these subsystems can be approached statistically and added subsequently.

for condensation of bulk liquid. The ratio of reduced partition functions or accommodation factors j_1 and j_ℓ, that is independent of temperature, is not easy to evaluate and usually set unity. This ratio is entropic in nature and will rceive some further attention in Subsection 4.6.2. In the B.E.T. model of sorption the influence of temperature is accounted for by C_B only; this dependence stems from the exponential in (4.8). It also appeared that the statistical derivation leading to the Langmuir and B.E.T. equations strictly applies only to sorption of monoatomic molecules.

4.3 MODIFICATION OF MULTILAYER PROPERTIES, THE GUGGENHEIM, ANDERSON AND DE BOER THEORIES

The assumption that the sorbed molecules in the B.E.T. theory have 'condensate' (bulk liquid) properties gives rise to an infinite spreading pressure at the relative gas activity of unity. This is a serious shortcoming of the B.E.T. theory (Hill, 1960), which several workers in this field have tried to correct. One obvious approach is outlined in this section.

Applying the B.E.T. isotherm equation to the description of experimental isotherms, Anderson (1946) observed a considerably improved fit to relative activities of about 0.7 by just multiplying the activity by another constant, less than unity, thus obtaining an equation which reads in our notation:

$$\frac{W}{W_1} = \frac{C_B K a}{(1 - Ka)(1 - Ka + C_B Ka)} \qquad (4.9)$$

Following the kinetic B.E.T. theory, Anderson interpreted the parameter K nearly correctly as exp (H_d/RT), where H_d is defined by:

$$H_d = H_2 - H_\ell \qquad (4.10)$$

where H_2 is the molar enthalpy of sorption of the second and following molecules on a sorption site and H_ℓ is again the same for condensation of bulk liquid.

In a fundamental discussion of localized multilayer sorption Guggenheim (1966) offered the theoretical basis for this modification. He did not heed Anderson's paper, nor the constant K in (4.9). Guggenheim's derivation will be briefly repeated here, somewhat adapted in notation and further extended in order to elucidate the physical meaning of the constants.

Derivation of the isotherm equation by statistical thermodynamics is most efficiently carried out by working with the grand canonical ensemble, con-

sidering the sorption system as consisting of identical active sites (distinguishable and independent), isothermal and open with respect to the sorbing vapour. The grand partition function for this system reads (Hill, 1960; Guggenheim, 1966):

$$\Xi\ (\mu,\ N_s,\ T) = (1 + \lambda q_1 + \lambda^2 q_1 q_2 + \lambda^3 q_1 q_2 q_3 + \ldots)^{N_s} = (\xi)^{N_s} \qquad (4.11)$$

where λ is the absolute activity of the sorbate as given in equation (2.4); q_i is the partition function of a single molecule sorbed in the ith layer; ξ is the grand partition function expressed per sorption site. The strict relation between the statistical mechanical conception and the thermodynamic conception of the system is given by the *characteristic* function which can be written as:

$$\Xi\ (\mu,\ N_s,\ T) = \exp\left(\frac{\pi_s N_s a}{kT}\right) \qquad (4.12)$$

where π_s is the surface pressure of the sorbed vapour and a the surface occupied by one sorbed molecule. The isotherm equation follows directly from the ratio N/N_s. The average number of sorbed molecules $\bar{N}$ in the system is estimated from its statistical expectation:

$$\bar{N} = \lambda\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{N_s,T} \qquad (4.13)$$

which gives the sorption isotherm equation in its most general form:

$$\frac{N}{N_s} = \frac{q_1\lambda(1 + 2q_2\lambda + 3q_2q_3\lambda^2 + 4q_2q_3q_4\lambda^3 + \ldots)}{1 + q_1\lambda(1 + q_2\lambda + q_2q_3\lambda^2 + q_2q_3q_4\lambda^3 + \ldots)} \qquad (4.14)$$

With these key-equations, using various assumptions about the relations between the partition functions of the single sorbed molecules in the different layers, the B.E.T. equation and most of its obvious modifications are readily obtained.

The assumption introduced now is the approximation originally suggested by Langmuir (1918) (Section 4.2), reading in this notation:

$$q_2 = q_3 = q_4 = \ldots\ldots = q_m \qquad (4.15)$$

This assumption is based on the consideration that, except for the first layer, a sorbed molecule is held only by other sorbed molecules. Introducing a parameter C_G by putting:

$$q_1 = C_G q_m \qquad (4.16)$$

and combining this with (4.14) and (4.15) one obtains:

$$\frac{N}{N_s} = \frac{C_G \lambda q_m}{(1 - \lambda q_m)(1 - \lambda q_m + C_G \lambda q_m)} \tag{4.17}$$

Applying the equilibrium condition:

$$\lambda_{sorbate} = \lambda_{gas} \tag{4.18}$$

and subsequently relating the absolute gas activity to its pressure p (see e.g. Hill, 1960):

$$\lambda_{gas} = p \cdot \exp\left(\frac{\mu^0}{kT}\right) \tag{4.19}$$

where μ^0 is the standard thermodynamic potential of a single gas molecule; λq_m can be written as:

$$\lambda q_m = p/g \tag{4.20}$$

with

$$g = \frac{\exp\ (-\mu^0/kT)}{q_m}$$

g and C_G are constants that are characteristic of the nature of interaction between sorbent and sorbate. They depend on the properties of the gas, but are independent of the gas pressure. Combining (4.20) and (4.17) gives:

$$\frac{N}{N_s} = \frac{C_G \cdot \frac{p}{g}}{(1 - \frac{p}{g})(1 - \frac{p}{g} + C_G \cdot \frac{p}{g})} \tag{4.22}$$

Writing:

$$g = p^0/K \tag{4.22}$$

where p^0 denotes the saturation vapour pressure of the sorbate at isotherm temperature, we obtain an equivalent of the Anderson equation (4.9) which reads in our notation:

$$\frac{N}{N_s} = \frac{C_G Ka}{(1 - Ka)(1 - Ka + C_G Ka)} \tag{4.23}$$

The constants in this equation are:

$$C_G = \frac{q_1}{q_m} = \frac{j_1}{j_m} \exp\left(\frac{H_1 - H_m}{RT}\right) \tag{4.24}$$

and

$$K = \frac{p^0}{g} = \frac{q_\ell}{q_m} = \frac{j_\ell}{j_m} \exp\left(\frac{H_\ell - H_m}{RT}\right) \tag{4.25}$$

Both de Boer (1953) and Guggenheim (1966) found g in nearly all experimental cases of physical adsorption to exceed p^0, implying that $K < 1$ although positive. Moreover, Guggenheim (1966) noted that:

$$g/C_G = p_h \tag{4.26}$$

where p_h is the vapour pressure at which half of the sites are occupied with one sorbate molecule.

Equation (4.23) can be rewritten as:

$$\frac{N}{N_s} = \frac{(C_G-1)Ka}{1 + (C_G-1)Ka} + \frac{Ka}{1 - Ka} \tag{4.27}$$

which can be compared with (4.5). By analogy, the Langmuir constant C_L equals $(C_G-1)K$ in the first term of equation (4.27). The second term, describing the formation of multilayers in the G.A.B. model, has the mathematical form of Raoult's law for a non-ideal solution. For water this reads:

$$a_w = \gamma_w x_w = \gamma_w \cdot \frac{N(w)}{N(w) + N(s)} \tag{4.28}$$

where N is the number of molecules of water (w) or solute (s) and γ_w is the activity coefficient of water in the mixture which is directly related to its molar *excess Gibbs free energy*. Equation (4.28) is easily modified into:

$$\frac{W}{M_w/M_s} = \frac{a_w/\gamma_w}{1 - a_w/\gamma_w} \tag{4.29}$$

where W is again kg water per kg dry substance.

Combining the molecular weight ratio with the monolayer value and the reciprocal activity coefficient with K which is related to the molar *excess enthalpy* (4.25), we see the resemblance between (4.29) and the second term of (4.27).

When compared with the B.E.T. model this sorption model as given by (4.23) discriminates between *multilayer* and *condensate* properties for molecules sorbed on top of the first molecule at a site. C_B has become C_GK. Therefore, this theory must be considered to be a *more general* model for localized homogeneous sorption of which the B.E.T. model is the limiting case for

$g = p^0$. This more general model may carry equally well the names of Anderson (1946) who originally proposed it, of de Boer (1953, chapter 5) who derived (5.18) kinetically and gave it considerable attention, and of Guggenheim (1966). Clearly all three authors worked independently. In the present study this sorption model is further referred to as the Guggenheim, Anderson and de Boer (G.A.B.) model of sorption. It is interesting to note that also Brunauer (Brunauer et al., 1969) following his original (1938) kinetic theory, extended his B.E.T. equation the same way, but referred only to Anderson (1946).
On comparing both models it is found that the constants N_s (or W_1) and C in both the B.E.T. and G.A.B. model contain nearly the same physical information with comparable accuracy, but the G.A.B. equation gives a much improved mathematical description of experimental isotherms together with energetic information on the averaged multilayer. It was concluded before (van den Berg et al., 1975; van den Berg & Leniger, 1976) that the G.A.B. model must be preferred to the B.E.T. model as a procedure for experimental isotherm analysis.

Recently the more general character of the G.A.B. model was also realized by some other workers. Dent (1977) referring to Anderson (1946), and Gascoyne & Pethig (1977) referring to Guggenheim (1966) and Anderson (1946), rederived it statistically. These two studies also applied the G.A.B. isotherm to water vapour sorption on biopolymers, as was done before by Berendsen (1975) and the author (van den Berg et al., 1975; van den Berg & Leniger, 1976). Some years after its original proposal by Anderson (1946) this equation was already in use to describe water vapour sorption isotherms of food materials (Karel, personal communication, 1978). In section 4.7 the G.A.B. theory is shown to be directly related to the theory of Hailwood & Horrobin (1946) which was developed with special reference to water sorption by polymers.

4.4 LIMITATION OF THE NUMBER OF SORBED MOLECULES PER SITE

The simple B.E.T. model for homogeneous adsorption discussed in section 4.2 assumes sorption to proceed indefinitely. Another obvious modification of this model, also already mentioned by Langmuir (1918) in his cases IV and VI, is therefore limitation of the number of sorbed molecules per site. This limitation may be due to sterical restrictions. In their original paper, Brunauer et al. (1938) derived for the case of limitation to n sorbed layers:

$$\frac{N}{N_s} = \frac{C_B a[1 - (n+1)a^n + na^{n+1}]}{(1 - a)[1 - a + C_B a - C_B a^{n+1}]} \qquad (4.30)$$

Equation (4.30) follows directly from the statistical thermodynamic derivation by replacing in (4.14) the infinite series by a limited number of terms. This was first shown by Hill (1946). Lunde & Kester (1975) gave a mathematical generalization of this summation over the subsequent sorbed layers. At low sorbate activities, (4.30) numerically equals (4.4), the simple B.E.T. equation, but (4.30) shows an improved fitting capability for experimental sigmoid isotherms up to relative activities 0.6-0.7. In the case of the water-starch system a physical limitation of the number of sorbed layers, which is obviously the case, might be caused by steric reasons due to limited swelling of the system volume.

Assuming a decrease in probability of escape out of the nth layer as more of the surface is covered with n layers, Pickett (1946) proposed a simplified version of (4.30):

$$\frac{N}{N_s} = \frac{C_B a(1 - a^n)}{(1 - a)(1 - a + C_B a)} \qquad (4.31)$$

This equation generally leads to a comparable or slightly improved fit of sigmoid isotherms compared with (4.30). Rounsley (1961) rederived and applied (4.31) at moisture sorption isotherms of several biopolymers and observed comparable results. He did not refer to Pickett (1946), neither to Hill (1946) who pointed out serious weaknesses in Pickett's modification.

An interesting modification in line with the described models for sorption is the limitation of the number of sorbed layers combined with the more general G.A.B. sorption model (Section 4.3). Introduction of the averaged multilayer assumption into the derivation of (4.30) yields directly:

$$\frac{N}{N_s} = \frac{C_G Ka[1 - (n+1)(Ka)^n + n(Ka)^{n+1}]}{(1 - Ka)[1 - Ka + C_G Ka - C_G(Ka)^{n+1}]} \qquad (4.32)$$

or, if combined with Pickett's model, it yields:

$$\frac{N}{N_s} = \frac{C_G Ka[1 - (Ka)^n]}{(1 - Ka)(1 - Ka + C_G Ka)} \qquad (4.33)$$

As far as this author is aware, these two equations have not yet been published. With regard to the description of experimental isotherms both equations may be expected to apply well as they have four adjustable parameters, N_s, C_G, K and n, all with a clear physical meaning.
Equation (4.32) will be investigated as fitting equation in Chapter 6.

4.5 THEORY OF POLYMER-SOLVENT INTERACTION

This section briefly summarizes the polymer-solvent interaction theory of Flory & Huggins (Flory, 1953), together with a modification of it by Hill & Rowen (1952) designed to account for a more specific interaction between polymer and solvent than is contained in the Flory-Huggins theory. Both approaches may apply to the system under study.

Flory (1941, 1942) and Huggins (1941, 1942) independently applied volume statistics to the concept of a quasi-crystalline lattice as a model for a polymer solution, i.e. an amorphous polymer above its glass transition temperature mixed with a solvent. A lattice site can contain either a solvent molecule or a polymer segment, assuming equal volumes for both. Introducing some simplifications, Flory and Huggins derived a useful expression for the entropy of mixing. Assuming furthermore the heats of interaction between polymer segments and solvent molecules to be independent of the polymer configuration in the mixture, an enthalpy term χ was formulated and added in order to obtain the Gibbs free energy of mixing. χ is called the Flory-Huggins interaction parameter. Theoretically χ equals ε/kT, with ε denoting the interchange energy of a solvent molecule and a polymer segment. Later it appeared that χ also contains an entropic part, independent of temperature. Consequently χ has a semi-empirical nature. The derivation is not given here since it is presented well in Flory's handbook (Flory, 1953). Elucidating is also the basic derivation by Guggenheim (1952), who correctly mentions that the theory was designed essentially for non-polar interactions.

For the solvent activity in a polymer solution the Flory-Huggins equation reads for water as the solvent:

$$a_w = (1 - \phi)\cdot\exp\left[\left(1 - \frac{v_w}{v_p}\right)\phi + \chi\phi^2\right] \qquad (4.34)$$

where v is the partial molal volume, and the subscripts w and p stand for solvent (water) and polymer, respectively; ϕ denotes the volume fraction of polymer. Because the ratio v_w/v_p for the starch-water system is smaller than the reciprocal D.P. it is entirely negligible with respect to unity, which further simplifies (4.34). This reduced equation contains only one parameter, χ, for values > 0.5 it predicts phase separation, starting at extreme dilutions.

Taylor et al. (1961) applied (4.34) to sorption equilibria at high humidity of wheat starch (a_w > 0.92) and dextrans. A χ-value of 0.84 was found to describe the highest moisture range. The results of Taylor et al. (1961) will be used for comparison purposes in Chapter 6.

Rowen & Simha (1949) applied (4.34) to sorption equilibria in the cellulose-water system and were able to describe the isotherm at high water activities (> 0.8) with χ = 1.25. Molyneux (1975), reviewing water sorption behaviour of synthetic polymers, gives comparable results for some polymers containing polar groups. As expected, the theory does not account for the specific interaction between the polymer and the first water molecules. Mathematically this is also clear because (4.34) predicts only type III isotherms of the B.D.D.T. classification (Brunauer et al., 1940). At first sight, an improved isotherm description may be expected when the monolayer water is not counted in the water fraction. The thus corrected Flory-Huggins equation (4.34) is given in Section 6.4. Generally equation (4.34) and its published modifications have found remarkably little application in the area of water vapour sorption of biopolymers and foods, especially when compared with B.E.T.-like equations.

For elastic network gels with only a limited uptake of solvent, the total free energy of the system contains also a contribution preventing unlimited swelling. At a solvent activity of unity, this term balances the general mixing term (Flory & Rehner, 1943; Flory, 1953, page 576). Applying rubber elasticity theory and assuming isotropic swelling behaviour of the gel, Hill (1960) showed that the corrected solvent activity may be approached by:

$$a = (1 - \phi) \exp\left[\phi + \chi\phi^2 + \frac{1}{Z}\left(\phi^{1/3} - \frac{\phi}{2}\right)\right] \qquad (4.35)$$

where Z denotes the average number of statistical polymer segments per chain element between the network junctions. The effect of the correction becomes negligible for long chain elements (or low concentration of network junctions). In starch, however, especially its native form with its many hydrogen bonds and its limited swelling capacity, a high concentration of active network junctions may be expected. The correction itself implies important simplifications that have to do mainly with the restraint in end-to-end distances of polymer chains and their distribution within the network. Other authors have derived similar correction terms (see Prins, 1965, 1967). However, when applied to the starch-water system differences between these terms are much smaller than other deviations from the theoretical model. These deviations are (i) the changing state of aggregation of the starch polymer from glassy to rubbery, (ii) the non-isotropic swelling (Subsection 2.5.1) of starch in water, (iii) the non-additivity of the volumes of starch and water below 0.3 kg w./kg d.s., (iv) the probably changing number of effective joints in the amorphous part of the network during hydration as part of the hydrogen bonds is gradually exchanged by water bridges, together (v) with the general shortcomings of the Flory-Huggins theory to account for more specific polymer-solvent interactions such as hydrogen bonds. As all these deviations are more pronounced at lower water activities (approximate-

ly < 0.75), successful prediction of the sorption isotherm may not be expected in this area. Moreover, also (4.35) describes only isotherms of type III of the B.D.D.T. classification.

Hill & Rowen (1952) tried to remedy the latter shortcoming by incorporating into the outlined polymer-solvent interaction theory the concept of homogeneous localized sorption of solvent molecules onto the polymer segments which form a monolayer. This theory is added in order to make this brief review more complete. Unfortunately the present author became aware too late of this interesting combined theory to be able to incorporate it in his testing programme. Preliminary estimations confirmed Rowen(1958)'s finding that sigmoid isotherms can be predicted by this model. In their communication, Hill & Rowen (1952) announced a more detailed account, which to our knowledge has never appeared. In a later communication Rowen (1958) showed the influence of the parameters in some simulations. Apparently the idea of Hill & Rowen has been forgotten, since the only literature reference to it was found in a brief sentence in the review by Barrie (1968) on water in polymers.

In the model of Hill & Rowen the average volume available to a polymer segment increases towards that of a pair of a polymer segment with a solvent molecule. In a further state of mixing the general Flory-Huggins theory is followed. For isotropic swelling polymer gels in water, the Hill-Rowen isotherm equation reads:

$$\ln a_w = \frac{1}{\beta}\left[\frac{\gamma'}{\theta+\gamma'}\left(1-\frac{1}{2Z}\right)+\frac{\gamma'}{\theta_1+\gamma'}\ln\left(\frac{\theta-\theta_1}{\theta+\gamma'}\right)+\chi'\left(\frac{\theta_1+\gamma'}{\theta+\gamma'}\right)^2 + \frac{1}{Z}\left[\left(\frac{\gamma'}{\theta+\gamma'}\right)^{1/3}-\frac{1}{2}\left(\frac{\gamma'}{\theta+\gamma'}\right)\right]\right] \qquad (4.36)$$

where θ denotes $\frac{N}{N_s}$ and $\theta_1 = \frac{N_1}{N_s}$, in which N_1 is the number of solvent molecules sorbing localized onto the polymer segments forming ultimately a monolayer; β denotes the volume ratio of a statistical polymer segment to a sorbate molecule; $\gamma' = ZN_c\beta/N_s$, where N_c represents the number of polymer chains in the network, and χ' is the adjusted Flory-Huggins interaction parameter. The term $\frac{\gamma'}{\theta+\gamma'}$ has the character of ϕ.

The last term, $\frac{1}{Z}\left[\left(\frac{\gamma'}{\theta+\gamma'}\right)^{1/3}-\frac{1}{2}\left(\frac{\gamma'}{\theta+\gamma'}\right)\right]$, is the limited swelling correction term. The last part of this term was not given by Hill & Rowen (1952), but has been added by analogy to (4.35), analogous to the arguments of Prins (1967). The influence of Z decreases progressively with increasing values of Z, becoming negligible at values Z > 10. For these values of Z the entire limited swelling correction term starts to become negligible. For unlimited

swelling Hill & Rowen (1952) give the following equation:

$$\ln a_w = \frac{1}{\beta}\left[\frac{\gamma'}{\theta+\gamma'}\left(1 - \frac{1}{Z}\right) + \frac{\gamma'}{\theta_1+\gamma'} \ln\left(\frac{\theta-\theta_1}{\theta+\gamma'}\right) + \chi'\left(\frac{\theta_1+\gamma'}{\theta+\gamma'}\right)^2 \right] \qquad (4.37)$$

Comparison shows that the simple Flory-Huggins equation (4.34) is a special case of (4.37) for $\theta_1 = 0$. The C_B parameter from the B.E.T. theory in this model is expressed as:

$$(C_B)^\beta = \left(\frac{\theta_1}{1-\theta_1}\right)^\beta \left(\frac{\theta+\gamma'}{\theta-\theta_1}\right)^{\gamma'(\theta+\gamma')/(\theta_1+\gamma')^2} \cdot \exp\left[\chi'\left(\frac{2(\theta-\theta_1)}{\theta+\gamma'} - 1\right) - \frac{\gamma'}{\theta_1+\gamma'}\right] \qquad (4.38)$$

This equation is an auxiliary relation between θ and θ_1. It must be used to solve θ_1 before pairs of θ - a_w values can be obtained from (4.36) or (4.37) for different parameters.

Two possible theoretical modifications of this model deserve mentioning here in order to bring it closer to the starch-water system. One is to correct for the lack of volume additivitly in the early stages of sorption as observed in the starch-water system (Section 3.3). This could be done by simply cancelling the increase in segment volume due to localized sorption, since the free volume in dry starch equals approximately the volume of a water monolayer. The second modification would be an adjustment for the increasing number of sorption sites during the sorption process, for example along the lines briefly indicated in Subsection 4.6.3.

4.6 SOME OTHER SORPTION THEORIES FOR HOMOGENEOUS SURFACES

4.6.1 Modification for the first two sorbed molecules per site unequal and different from further sorbed molecules

In the Langmuir and B.E.T. theories and their modifications mentioned so far the first sorbate molecule at a site is assumed to have properties different from the next molecules sorbing at the same site. Irrespective of their number at a site, all latter molecules in the model have identical properties. The enthalpy of water sorption by (native potato) starch as derived from immersion calorimetry (Section 3.4) indicates that, when compared with the first sorbed molecule, the second molecule sorbing at a site has a significantly decreased binding energy. However, this energy for the second molecule is still clearly distinguishable from that of further sorbing molecules. The assumption of the second sorbate molecule at a site behaving differently from the others can be accounted for in still another modification of the B.E.T. theory. This modification is described below and combined with the G.A.B. and the B.E.T. models with a limited number of sorbed layers. Ob-

viously more of such combined models are possible, for example with also the third molecule at a site having deviating properties, but the isotherm equations thus derived usually contain five or more adjustable parameters, a number exceeding the limits set for this study.

Following the statistical derivation of the simple B.E.T. equation, in analogy with (4.15) we introduce the following assumption for the partition functions of the individual sorbate molecules at a site:

$$q_1 \neq q_2 \neq q_3 = q_4 = \ldots\ldots = q_\ell \qquad (4.39)$$

where q_1, q_2, q_3, ... etc. are the partition functions of the first, second, third, ... etc. sorbate molecules and q_ℓ is the partition function of a bulk liquid molecule. Combination with the general isotherm equation for homogeneous (ad)sorption (4.14) yields:

$$\frac{N}{N_s} = \frac{q_1\lambda[1 - 2q_\ell\lambda + (q_\ell\lambda)^2 + 2q_2\lambda - q_2q_\ell\lambda^2]}{(1-q_\ell\lambda)[1 - q_\ell\lambda + q_1\lambda(1-q_\ell\lambda) + q_1q_2\lambda^2]} \qquad (4.40)$$

Let again as in the B.E.T. model: $q_1 = C_B q_\ell$, and writing analogously for the partition function of the second molecule:

$$q_2 = C_{TB} q_\ell \qquad (4.41)$$

we obtain for the isotherm equation:

$$\frac{N}{N_s} = \frac{W}{W_1} = \frac{C_B a_w(1 - 2a_w + a_w^2 + 2C_{TB}a_w - C_{TB}a_w^2)}{(1 - a_w)(1 - a_w + C_B a_w - C_B a_w^2 + C_B C_{TB} a_w^2)} \qquad (4.42)$$

C_{TB} can be expressed as:

$$C_{TB} = \frac{q_2}{q_\ell} = \frac{j_2}{j_\ell} \cdot \exp\left(\frac{H_2 - H_\ell}{RT}\right) \qquad (4.43)$$

where H_2 is the molar enthalpy of sorption for the second sorbate molecule at a site.
Comparison of equations (4.42) and (4.4) shows that the simple B.E.T. equation is a boundary case of this new isotherm equation (4.42) for $C_{TB} = 1$ (or $q_2 = q_\ell$).

Introduction of the same assumption (4.39) but now written as:

$$q_1 \neq q_2 \neq q_3 = q_4 = \ldots\ldots = q_m \qquad (4.44)$$

into the G.A.B. model of sorption gives with (4.14) again an expression like

(4.40) with q_m instead of q_ℓ, namely:

$$\frac{N}{N_s} = \frac{W}{W_1} = \frac{C_G Ka_w[1 - 2Ka_w + (Ka_w)^2 + 2C_{TG}Ka_w - C_{TG}(Ka_w)^2]}{(1 - Ka_w)[1 - Ka_w + C_G Ka_w - C_G(Ka_w)^2 + C_G C_{TG}(Ka_w)^2]} \qquad (4.45)$$

In this case the constant C_{TG} is expressed as:

$$C_{TG} = \frac{q_2}{q_m} = \frac{j_2}{j_m} \cdot \exp\left(\frac{H_2 - H_m}{RT}\right) \qquad (4.46)$$

In the limit of $C_{TG} \to 1$ isotherm equation (4.45) turns into (4.23).

Another obvious modification can be obtained by the combination of (4.39) with the B.E.T. model with a limited number (n) of sorbed molecules per site (Section 4.4). This leads to the following isotherm equation:

$$\frac{N}{N_s} = \frac{W}{W_1} = \frac{C_B a_w[1 - 2a_w + a_w^2 + C_{TB}a_w(2 - a_w - (n+1)a_w^{n-1} + na_w^n)]}{(1 - a_w)[1 - a_w + C_B a_w(1 - a_w + C_{TB}a_w - C_{TB}a_w^n)]} \qquad (4.47)$$

Again by putting $C_{TB} = 1$ it can be shown that isotherm equation (4.30) is a special case of this model (4.47).

The model isotherm equations (4.45) and (4.47) both have four adjustable constants with a clear physical meaning. They will be considered as fitting equations in Chapter 6. The equivalent of the sorption model pertaining to isotherm equation (4.32), extended with assumption (4.44), will not be considered since it contains already five adjustable constants. This isotherm equation reads:

$$\frac{W}{W_1} = \frac{C_G Ka_w[1 - 2Ka_w + (Ka_w)^2 + C_{TG}Ka_w(2 - Ka_w - (n+1)(Ka_w)^{n-1} + n(Ka_w)^n]}{(1 - Ka_w)[1 - Ka_w + C_G Ka_w\{1 - Ka_w + C_{TG}Ka_w - C_{TG}(Ka_w)^n\}]} \qquad (4.48)$$

4.6.2 The combined sorption theory of Guggenheim, Anderson and de Boer with an entropic multilayer correction

In Section 4.2 the Langmuir and B.E.T. models of sorption were briefly discussed. In the B.E.T. theory the parameter C_B (analogous to C_L in the Langmuir model) can be considered as a compounded parameter which contains all possible enthalpic and entropic contributions. By setting the ratio of accommodation factors, j_1/j_ℓ, in (4.8) unity it is assumed that entropic contributions can be neglected with respect to the enthalpic ones. This assumption is not unreasonable since the enthalpy of interaction for the first molecule is much greater than the product of temperature and entropy. Espe-

cially at low coverages the accommodation factors are relatively invariant. The literature at this point is somewhat confused. Depending upon the particular system, Kembal & Schreiner (1950) estimated that the accommodation factor ratio may deviate considerably (10^{-5} - 10) from unity. As the B.E.T. equation fits experimental isotherms usually up to $a_w \sim 0.35$ (in the case of starch here W is approx. 0.15 kg w./kg d.s.), the numerical value of C_B is predominantly determined by the first one or two molecules sorbing on a site.

The more general G.A.B. model of sorption (Section 4.3) assigns to its multilayer part more realistic properties, different from those of the bulk liquid. This results in the two parameters C_G and K. By analogy to the parameter C_B in the B.E.T. model, the parameter C_G is almost enthalpic in nature. Also in practical cases the numerical value of C_G is determined mainly by the low activity part (roughly $a_w < 0.4$) of the experimental isotherm, while the parameter K is more determined by the isotherm part at a higher activity range (roughly $0.4 < a_w < 0.75$). When compared to C_G the parameter K must contain much more entropy because the second and third layers have a considerably lower interaction enthalpy with the sorbent, whereas their interaction entropy is more important. At higher θ the number of configurations and steric factors such as packing and coordination are likely to play a significant role. This entropy effect can be accounted for by dividing K into an enthalpy and an entropy parameter. We may assume the accommodation factors in (4.25) to be proportional to the total number of realization possibilities (Ω) of their state, so that:

$$\frac{j_\ell}{j_m} \sim \frac{\Omega_\ell}{\Omega_m} = \exp\left(\frac{S_\ell - S_m}{R}\right) \tag{4.49}$$

where S is the molar entropy belonging to the state indicated by the index. Combining this result with (4.25), for the new K' can be written:

$$K' = \exp\left(\frac{S_\ell - S_m}{R}\right) \cdot \exp\left(\frac{H_\ell - H_m}{RT}\right) = E \cdot K \tag{4.50}$$

where K is the parameter of the G.A.B. equation (with neglected accommodation factors).

Introduction into the G.A.B. model of the parameter K' instead of the original K in the multilayer part of the model remedies the originally neglected entropy contribution in this part of the model. This correction was not introduced into the monolayer part because it is relatively less important there. Also it may be argued that this new parameter should be different in the monolayer part because of the neglected entropy part of C_G. In practice, the adjustment magnitude of C_G will partially cancel the effect of this correction since E may not be expected to deviate very much from unity.

Replacing K in the second (multilayer) term of (4.27) by K' as given by (4.50) leads directly to:

$$\frac{N}{N_S} = \frac{W}{W_1} = \frac{(C_G - 1 + E)Ka_w}{(1 - Ea_w)(1 - Ka_w + C_G Ka_w)} \qquad (4.51)$$

which is equivalent to:

$$\frac{W}{W_1} = \frac{(C_G - 1)Ka_w}{1 - Ka_w + C_G Ka_w} + \frac{Ka_w}{1 - Ka_w} + \frac{(E - 1)Ka_w}{(1 - Ka_w)(1 - Ea_w)} \qquad (4.52)$$

in which the effect of the entropy correction is given in a separate term. As may be expected for the limit $E \to 1$ (4.51) changes into the G.A.B. isotherm equation (4.23).

4.6.3 Initiation of a sorption theory with a variable number of sorption sites

Depending on their nature many swelling (ad)sorbents cannot be expected to have a constant number of sorption sites (or sorption surface) during the entire sorption process. Rather, the number of sites exposed to the vapour will increase upon swelling. For instance, during the uptake of water in dry starch, interchain hydrogen bonds are gradually replaced by water bridges and sorbate molecules penetrate the newly created holes. The 'walls' of these holes presumably contain ample possibilities for further hydrogen bonding, thus *creating* new sorption sites. To our knowledge, in the literature a sorption theory accounting for a variable number of sorption sites has not been elaborated yet.

A start of such a theory is briefly presented here as a possible modification of the sorption theory described before, namely a model of sorption onto homogeneous surfaces with a variable number of sorption sites. The outlined theory rather gives access to a *family* of isotherm equations, and no specific theoretical isotherm model is derived. One example equation which is possibly applicable to the present system is given. The specific features of each particular equation of this family depend on the relation between the number of sorption sites (N_S) and other characteristics of the sorption process. This specific relation may be derived from assumptions or measurements and is later introduced into the model. Usually such relationships will somehow link N_S to N or λ indirectly via polymer properties, but as a start we presume (like in the B.E.T. model) that N and N_S are independent system variables.

The new theory starts from the same premises as the B.E.T. theory, except that the number of sites is not constant but variable. The sorption system

is divided into two parts, one with a constant number of sites N_{so} (corresponding to the initially available number of sites in the empty sorbent) and a part with a varying number of sorption sites N_{sv} (initially zero). The following treatment applies to the variable part. In order not to introduce further heterogeneity in the sorption process, the assumption is retained that the newly formed sorption sites in the variable part are identical and indistinguishable from those in the constant part of the sorption system. Later the new result for the variable part is added to the already known result for the non-variable part of the system.

The variable part of the sorption system can be considered as an 'extended' grand canonical ensemble which, in addition to being open to changes in energy and the number of sorbed molecules, is also open to some reservoir containing sorption sites. Under equilibrium conditions the number of sorption sites is balanced by some surface pressure (or 'sorption site creation function') ι, which is a property of the sorbent and should not be confused with the (surface) spreading pressure of the sorbate. The extended grand canonical partition function for this (one component) system, basically a two-dimensional lattice gas sorbed localized at a variable surface, reads:

$$\Upsilon(\mu,\iota,T) = \sum_{N_{sv}=0}^{N_{sv}=max} \Xi(\mu,N_s,T)\cdot\exp\left(\frac{\iota N_{sv}}{kT}\right) \qquad (4.53)$$

Here $\Xi(\mu,N_s,T)$ denotes the 'ordinary' grand partition function of a non-variable sorption system with N_s sites, as given by (4.11) and (4.12). The new ensemble in generalized form was described and analysed by Hill (1956, chapter 3). It presents a *special* case since its characteristic function is *zero*. Another relation between N_{sv} and ι (in our case unknown) is necessary to describe the system.

An alternative approach, physically perhaps somewhat more realistic, is to consider the (variable) sorption sites as another component in a (two-component) system where one component is now sorbing onto the other. The sorbate is again considered as a surface phase sorbed at indistinguishable 'site molecules' that are distributed (provisionally at random) in the volume of the variable part of the system. The former surface pressure function ι now equals the thermodynamic potential of the surface sites. We may write for the grand partition function of this new grand canonical ensemble, which is open to both components:

$$\Xi(V,\mu,\iota,T) = \sum_{N=0} \sum_{N_{sv}=0} Q(N,N_{sv},V,T)\cdot\exp\left(\frac{\mu N}{kT}\right)\cdot \exp\left(\frac{\iota N_{sv}}{kT}\right) \qquad (4.54)$$

Here $Q(N,N_{sv},V,T)$ is the canonical partition function of the same system at given N and N_s. This system is almost identical to another case briefly out-

lined by Hill (1960, section 7.3), in which gas molecules of different size adsorb upon each other. The characteristic function for this system reads:

$$\Xi(V,\mu,\iota,T) = \exp\left(\frac{p_s V}{kT}\right) \tag{4.55}$$

where the term $p_s V$ is (in our case) the total volume-pressure energy of the sorption sites, analogous to the term pV for a perfect gas. The average number of sorption sites is given by:

$$\bar{N}_{sv} = kT\left(\frac{\partial \ln \Xi}{\partial \iota}\right)_{V,\mu,T} = q(o)\cdot\xi'\cdot\exp\left(\frac{\iota}{kT}\right) \tag{4.56}$$

where q(o) is the partition function of an individual empty sorption site and ξ' is the partition function per individual sorption site in the new system. This function ξ' is comparable to ξ in (4.11) but it now contains in each term a contribution of the site proper.
The average number of sorbed molecules $\bar{N}$ is given by:

$$\bar{N} = \lambda\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{V,\iota,T} \tag{4.57}$$

which gives (see also Hill, 1960, page 139):

$$\bar{N} = q(o)\cdot\exp\left(\frac{\iota}{kT}\right)\cdot\lambda\cdot\left(\frac{\partial \xi'}{\partial \lambda}\right)_T \tag{4.58}$$

Combining equations (4.56) and (4.58) we obtain as a preliminary relation for the isotherm equation:

$$\frac{N}{N_{sv}} = \theta_v = \frac{\lambda}{\xi'}\left(\frac{\partial \xi'}{\partial \lambda}\right)_T \tag{4.59}$$

Since λ does not contain any property of the sorption site this contribution in ξ' can be divided out and the partition function per site ξ' in (4.59) reduces to ξ of the pure sorbate, as in equation (4.11). This leads for the degree of coverage θ directly to the general isotherm equation (4.14) with the difference that N_s is now the variable number N_{sv}. For N_{sv} a relation must be introduced subsequently.

At this point the fixed and the variable part of the sorption system can be combined and θ_{new} for the whole system is given by:

$$\theta_{new} = \frac{N}{N_{so} + N_{sv}} \tag{4.60}$$

In the case of an increasing number of sites N_{sv} is positive, but for a decreasing number it is negative. In order to obtain an isotherm equation,

further specific assumptions concerning the sorption model have to be introduced, for example leading to a B.E.T.- or G.A.B.-type model, together with some function relating N_{sv} to the sorption characteristics. Obviously, an increasing number of sites gives a positive deviation of θ_{new} as compared to θ of a fixed system and conversely. One equation that according to its form may belong to this family of isotherm equations is (4.51).

Unfortunately for the starch-water system a possible relation between N_{sv} and N (or any other sorption characteristic) is speculative. The most realistic speculation about this relation may be derived from the data on the specific surface area of activated starch reported in Figure 3.2. The main increase in number of sorption sites presumably takes place during the weakening of the starch structure. Therefore a likely function for N_s in starch might be some inverse relation of the observed specific surface area function. For the present purpose, however, we satisfy ourselves with a more simple relation for the number of sites. To this end, the conditions of the general G.A.B. model of sorption are combined with the following relation for N_{sv}:

$$N_{sv} = S' \cdot (1 - Ka_w) \cdot N \qquad (4.61)$$

where S' is a swelling constant which brings in proportion the site creation action and the term $(1 - Ka_w)$ counterbalances partly the linear effect of N since it may be assumed that the site creation process is progressively inhibited with increasing water activity. Finally the system becomes a polymer solution.
Based on these assumptions, equations (4.60), (4.61) and (4.23) can be combined and we find the following expression for N/N_{so}, which equals θ in the non-variant system:

$$\frac{N}{N_{so}} = \frac{C_G Ka_w}{(1 - Ka_w)(1 - Ka_w + C_G Ka_w)} \left[1 + \frac{N}{N_{so}} \cdot S' \cdot (1 - Ka_w)\right] \qquad (4.62)$$

Using again (4.23) for N/N_{so}, we arrive at the isotherm equation:

$$\frac{N}{N_{so}} = \frac{W}{W_1} = \frac{C_G Ka_w [1 - Ka_w + (S'+1) C_G Ka_w]}{(1 - Ka_w)(1 - Ka_w + C_G Ka_w)^2} \qquad (4.63)$$

Another form of (4.63) shows directly its difference from the G.A.B. isotherm equation (4.23):

$$\frac{W}{W_1} = \frac{C_G Ka_w}{(1 - Ka_w)(1 - Ka_w + C_G Ka_w)} + \frac{S' \cdot (C_G Ka_w)^2}{(1 - Ka_w)(1 - Ka_w + C_G Ka_w)^2} \qquad (4.64)$$

This four-parameter equation will receive attention in Chapter 6, but should

be considered as just one example out of a variety of isotherm equations that can be obtained by the method outlined in this subsection.

4.7 SOME OTHER ISOTHERM EQUATIONS BASED ON COMBINED MECHANISMS OF SORPTION

In the literature several isotherm equations based on combined mechanisms have been proposed specifically to describe water vapour sorption equilibria of polymers with polar groups. As pointed out before, combination of sorption mechanisms is a justified approach for the interpretation and description of water vapour sorption equilibria of biopolymers. This section aims to show that some valuable background information is obtained by comparing some of the published isotherm equations with the sorption theories presented in the previous sections of this chapter. The choice made out of published sorption theories was determined mainly on the basis of their localized sorption character and their specific relation to water vapour sorption on polymers.

Probably the first proposal for a water vapour sorption model by polymers was made by Peirce (1929), who studied the cellulose-water system. Peirce considered the sorbed water to be present in two distinct classes, which he designated somewhat erroneously as 'phases'. Water in the first class closely associates with the sorption sites, i.e. the anhydroglucose monomers of cellulose, whereas water in the second class is sorbed in a looser fashion to all available surfaces. Peirce (1929) further assumed that the evaporation equilibrium is governed only by the vapour pressure and the surface fraction covered by the second class of water. His isotherm equation reads:

$$a_w = 1 - \exp\left[-K_p\{9W - 1 + \exp(-9W)\}\right] \qquad (4.65)$$

where K_p is the only adjustable constant. Equation (4.65) could describe accurately the isotherm data obtained by Farrow & Swan (1923) for gelatinized starch film over the range $0.1 < a_w < 0.8$. Smith (1947) improved Peirce's model, but his corrections had an ad hoc character. Generally, (4.65) belongs to a category of isotherm equations that are rather successful in describing sigmoid experimental isotherms with a small number of parameters. This after all interesting category also contains the well-known *polarization* theory isotherm (de Boer & Zwikker, 1929; Bradley, 1936) and its modifications together with the semi-empirical isotherm equation of Henderson (1952) and its various descendants. The latter are widely utilized in drying and storage in the field of agricultural engineering. Directly linked if not belonging to this category by their mathematical form are the early *potential* theory isotherm (Polanyi, 1916), the Harkins & Jura (1944) isotherm, the fundamental *slab adsorption* theory of Frenkel, Halsey and Hill (Hill, 1952; Young & Crowell, 1962), and also the isotherm equation of Kühn (1964).

The Frenkel-Halsey-Hill theory can be regarded as another important theoretical approach to physical adsorption, which is complementary to that of Langmuir and B.E.T. Unpublished results showed that both the Harkins & Jura equation and the Henderson equation describe sorption isotherms of starch well in the middle a_w range (0.25 - 0.8). This category of isotherm equations is not further considered in this study.
The picture of the sorption process as given by Peirce (1929) is far from correct, but his view that sorbed water in a (bio)polymer system occurs in *two types* (of high and low affinity respectively) proved to be a Leitmotiv in further theory development.

Following perhaps Katz (1917-1919, 1933) who proposed the same from his study of swelling, Hailwood & Horrobin (1946) postulated the sorbed water to exist in two independent 'states', namely (i) 'hydrates' of different order with definite units of the polymer molecule, and (ii) water in 'simple' solution between the polymer molecules. The hydrates were assumed to be mutually independent, which is equivalent to the Langmuir and B.E.T. assumption of neglecting lateral interactions. Assuming further an ideal solid solution of hydrates and dissolved water, at equilibrium for the absolute activity of the hydrate of order i may be written:

$$\lambda_{Hi} = \lambda_p \cdot \lambda_{dw} \cdot K_1 \cdot K_2 \cdot \ldots\ldots \cdot K_i$$

where index p indicates dry polymer and dw stands for dissolved water; K_1, K_2 ... indicate the corresponding equilibrium constants for the hydrates. Setting $\lambda_{dw} = ka_w$, eventually the following general equation was derived:

$$c(w) = \frac{ka_w}{1 - ka_w} + \frac{ka_wK_1 + 2(ka_w)^2K_1K_2 + \ldots\ldots\ldots}{1 + ka_wK_1 + (ka_w)^2K_1K_2 + \ldots\ldots} \qquad (4.66)$$

where c(w) is the concentration of water molecules per mole of polymer; k is a constant relating the activities of water in the solid phase and the vapour phase, and K_1, K_2, etc. are equilibrium constants for the formation of hydrates. Hailwood & Horrobin (1946) subsequently restricted the sorption process to monohydrates only, which reduces the second term of (4.66) to a Langmuir term. Rewritten in our notation, the isotherm equation reads:

$$w \cdot \frac{M_p}{M_w} = \frac{K_1ka_w}{1 + K_1ka_w} + \frac{ka_w}{1 - ka_w} \qquad (4.67)$$

where M_p denotes the molecular weight of the polymer and M_w the molecular weight of water. Equation (4.67) is mathematically identical to the G.A.B. isotherm (4.27). Perhaps more interesting is the fact that (4.67) and its derivation conform directly with the analysis of the second term as in terms of Raoult's law in non-ideal version (4.29), describing in essence a solu-

tion process. Also J.J. Hermans (see P.H. Hermans, 1946, page 188) proposed a combination of the isotherm equations of Langmuir and Raoult for the interpretation of sigmoid water sorption isotherms without any reference to the B.E.T. equation nor to the Hailwood & Horrobin equation.

Hailwood & Horrobin (1946) as well as others (D'Arcy & Watt, 1970; Kuntz & Kauzman, 1974) applied the Hailwood-Horrobin equation (4.67) successfully to experimental isotherms of various polymers over a wide range of water activities, in conformity with the experiences with the G.A.B. model of sorption. The fact that different physical sorption models lead to the same isotherm equation suggests a wider applicability of the equation for the type of systems under study. Enderby (1955), interested in the correct form of the isotherm of water on cellulose at low water activities, successfully applied a simplified version of (4.67) containing a Langmuir term added to a linear one. Riedel (1961), studying water in beef, combined a Langmuir term with an empirically adapted Raoult term.

Still another isotherm equation in this development was proposed by D'Arcy & Watt (1970) as a series development:

$$W = \sum_{i=0}^{i=n} \frac{K_i' K_i a_w}{1 + K_i a_w} + C a_w + \frac{k' k a_w}{1 - k a_w} \qquad (4.68)$$

where K_i', K_i, C, k' and k denote constants. This isotherm equation is based on stoichiometry of the keratin(wool)-water system and the assumption of the simultaneous independent sorption processes. Because in keratin (a protein) different polar groups are acting as the primary sorption sites, the first (Langmuir) term is replaced by a sum over n available site types i. This is comparable with the different hydrates of Hailwood & Horrobin (1946) and is essentially equivalent with the introduction of *heterogeneity*. The second linear term is seen by D'Arcy & Watt (1970) as approaching a Langmuir expression when $K_i a_w \ll 1$, valid for weak sorption sites. The third term again describes secondary sorption, i.e. the formation of multilayers. Assuming the occurrence of only one type of site with high affinity for water, the isotherm equation with its five adjustable parameters is able to describe various experimental isotherms accurately. Unfortunately D'Arcy & Watt (1970, 1978) pay little attention to the detailed physical interpretation of these parameters, reducing their equation in this respect to a mere fitting tool. For example the monolayer water content is evidently incorporated in K_i', C and k'.

After the polymer-solvent interaction theories became more mature in the early forties, Barrer (1946) was perhaps the first to propose a combination of the sorption mechanisms of localized adsorption and polymer solution theory for isotherm description. From his experience with rubber-apolar solvent

systems, Barrer (1946) proposed to describe the wool-water isotherm with an equation containing a Langmuir term together with a polymer-solvent mixing term, assuming non-zero enthalpy of mixing. Unfortunately results were not given.

A more rigorous and very detailed approach was followed by Tomka (1973), investigating the casein-water system. By combining classical heterogeneous localized sorption theory, corrected for lateral interactions with polymer-solvent theory according to Flory-Huggins, and correcting the result with a contribution for polymer chain deformation, Tomka (1973) derived finally a set of equations. This set contains an isotherm equation which may be applied only when two auxiliary boundary conditions are fulfilled. The model contains seven physically significant parameters and fits (as may be expected) the entire experimental sorption isotherm of casein accurately. It may be seen as a nice attempt to approach the *perfect* sorption theory mentioned in Section 4.1. This sorption model falls well beyond the scope of this study. In his theory, Tomka (1973) did not heed the simpler model of Hill & Rowen (1952) as outlined in Section 4.5.

5 EXPERIMENTAL

5.1 MEASUREMENT OF ISOTHERMS FOR WATER VAPOUR SORPTION

5.1.1 General

An authoritative handbook surveying the available techniques for determination of isotherms for water vapour sorption and their theory was published by Gál (1967). The same author also reviewed more recent developments in some later publications (Gál, 1975, 1978). For biological materials it is generally found not to be simple to obtain reliable isotherms. Experience is a prerequisite and even then results may be scattered between samples of the same nature and even between identical samples assayed at different places. Convincing illustrations of the former can be found in the survey of Heiss (1968) for many types of foods. A more specific example of the latter, concerning a starch sample, was supplied by the results of the international ring test investigation by Multon (I.N.R.A. Nantes, personal communication 1972-1974). Also Figure 3.1 for native potato starch is illustrative in this respect. In this ring test eleven research laboratories (in the U.S.A. and Western Europe) collaborated in measuring the resorption isotherm of an identical pure sample of native manioc starch at 298 K. All used the same method to determine the mass fraction of water (I.S.O., 1968). Nevertheless a wide dispersion of results was obtained. At a water activity of 0.5 absolute differences amounting to as much as 0.2 in a_w and 0.04 kg w./kg d.s. in mass fraction of water were observed. A figure with the summarized results of this test was published recently by Wolf et al. (1980, Figure 3). The isotherm measured in the sorption balance of the author was satisfactorily located inside a narrow band of isotherms together with those of Chen (Food and Agricultural Engineering Dept., Amherst, Massachusetts), Kapsalis (U.S. Army Laboratories, Natick, Massachusetts) and MacKenzie (then at the Cryobiology Research Institute, Madison, Wisconsin).

When a sample equilibrates under atmospheric conditions the rate limiting factor is the diffusion of water through the gas phase. Therefore, modern techniques prefer the use of an evacuated atmosphere in which the inert gas pressure (at room temperature) is at most about 200 Pa, a small fraction of the water vapour pressure. In this way the equilibration time of about one month (as was needed by Rakowski, 1911) can be reduced to about one day. Under such high vacuum conditions the transfer of the heat of sorption becomes the rate-controlling step. Preliminary measurements indicated that in our sorption balance, where the sample in an aluminium foil cup is suspended on a quartz spring, the sample temperature may well jump about 20 degrees centigrade as a reaction to a large step in water activity. Comparable observa-

tions were made by Bluestein (1971). Hence the isotherm determination is not strictly *isothermal*. However, these temperature jumps are not significant as no temperatures are reached which are known to influence the sorption characteristics of starch. Also the directions of the temperature jumps during resorption and desorption with regard to hysteresis and temperature effect work out to retard the attainment of equilibrium. In desiccators where the contact between the weighing jar and the porcelain plate causes a better heat conductance the jumps in temperature are smaller.

5.1.2 Sorption balance

A specially constructed set-up with six McBain sorption balances was used for the measurement of most of the isotherms reported in this study. For a detailed description of the equipment the reader is referred to Weldring et al. (1975). To this former description one corrective remark must be added which is based on a renewed interpretation of data observed in the low moisture range. At water activities below 0.29, where saturated lithium chloride solutions are used for equilibration, the accuracy claimed by Weldring et al. (1975) is a little too high. Under the experimental condition that these salt slushes were not well stirred, it is now estimated that the claimed maximum deviation in mass fraction of water of ± 0.001 kg w./kg d.s. is about ±0.0015 - 0.0020 with a slight systematic upward deviation during resorption measurements and a downward one during desorption measurements. The slight irregularities below a_w = 0.3 which were observed before (van den Berg et al., 1975) might partially be explained by this effect.

The sorption equilibria were measured with the same sample starting from dryness by increasing a_w in successive steps. As a criterion for the attainment of equilibrium two weight determinations were taken at least 16 hours apart differing no more than the estimated reading error. This resulted in an equilibration period of 20 to 70 hours per measuring point. This time depended on the step size and the moisture range. In nearly all cases, 95 per cent of the total response was reached within three hours. The value of zero moisture of a sample (Subsection 3.1.2) was determined before and after measurement of the isotherms.

5.1.3 Desiccator method

Some resorption isotherms (native potato starch at different temperatures, amylopectin and amylose) were determined with the conventional technique of vacuum desiccators with saturated aqueous salt solutions to control the water activity. Following our general experience, the data for the water activity of these solutions were taken from the tables of Greenspan (1977), Acheson (1965) and Young (1967). Because the tables of Greenspan (1977) be-

came available only after a first series of measurements was finished and preliminarily reported (van den Berg & Leniger, 1976), some of these data could be corrected. Subsequently they were combined with later results and included in the present study. For the isotherm at 293 K a small systematic difference (namely a slightly higher value for the mass fraction of water of about 0.002 kg w./kg d.s. in the middle range) was found when compared with the same isotherm measured with the sorption balance. Most probably this resulted from the greater step size chosen for the water activity during the equilibration in desiccators (interval versus integral sorption, see Subsection 3.1.6). For very precise measurements a small step size should be preferred.

For keeping a constant temperature during equilibration the desiccators were stored in a cooled Gallenkamp incubator (temperature constancy: ± 0.4 degrees centigrade) for temperatures below 290 K and in ventilated Marius stoves (± 0.15 degrees centigrade). For the resorption measurements generally samples of about one gram in glass weighing jars were pre-dried over fresh phosphorous pentoxide at 303 K for about three days in an evacuated stove. This resulted in mass fractions of water below 0.0035 kg w./kg d.s. Simultaneously three samples were used for moisture determination (1.5 h at 403 K) and corrected for the observed small deviation with phosphorous pentoxide (Subsection 3.1.3). Subsequently the samples were equilibrated. Each sample was used two to four times at increasing water activities and at the end the mass fraction of water was determined for all samples. Each data point is the average of at least two independent measurements. At temperatures below 315 K glass desiccators with Apiezon L or T vacuum grease were used. At higher temperatures stainless steel desiccators sealed with a rubber O-ring with little Apiezon T grease were found more suitable. Equilibration times of this method are well comparable with those found with the sorption balance, provided that no pressure rise (leakage) occurs. The criterion applied for equilibrium was the same as that with the sorption balance. The desiccator method should be handled carefully paying special attention to (i) proper checks of deaeration of the salt slushes to avoid boiling, (ii) slow vacuum pumping, (iii) even distribution of vacuum fat at the seals, (iv) correct vacuum pressure and (v) temperature, (vi) clean sample containers, (vii) proper ratio of liquid and solid in the salt slushes (neither a dry layer on top, nor a thick layer of solution), when possible the slush should be stirred some times per day, (viii) instant closing of sample containers together with (ix) correct temperature equilibration (e.g. avoiding of condensation) before weighing, and (x) the use of accurate tables relating type of salt solution, temperature and possibly composition to the value of water activity. When all these details are observed the accuracy of this method is not much less than that claimed for a sorption balance.

5.2 SAMPLES DESCRIPTION

Although native starches are called *native* these isolated and purified plant components are in a state differing somewhat from that in the mature plant cell. However, since the conditions of isolation during the wet recovery of starch are very mild, it may be presumed that the recovered starch is still much like the original natural deposit. The native starches used in this study were all obtained in air-dry form from the supplier. Air-dry native starches are generally known to be stable materials that can be stored for many years without detectable differences. Microscopic control showed that the three native starch samples, on which is reported here, were visually representative samples of their species.

Native potato starch samples were obtained from two suppliers. The first sample which has been used for isotherm analysis and further sample treatment, was obtained from BDH (London). Specifications: analytical grade, mass fraction of water about 0.23 kg w./kg d.s., sulphated ash 0.3%, damaged starch 0.1% (Method 76-30A of the American Association of Cereal Chemists, St Paul, Minnesota, 1969). Two other native samples with differing esterified phosphate contents (lot numbers 27953 and 27983 with 0.08 and 0.22% P_2O_5 respectively, the highest and the lowest figure observed in the starch-recovery campaign of 1974) were obtained from the Potato Processing Research Institute TNO (Proefstation voor Aardappelverwerking TNO, Groningen). Their water sorption isotherms were measured within six months after harvesting and recovery (one isotherm determination takes up to four months). This was necessary because during still more prolonged storage the esterified phosphate has the tendency to split off.

Native wheat starch was obtained from BDH (London). Specifications: analytical grade, mass fraction of water about 0.16 kg w./kg d.s., sulphated ash 0.3%, damaged starch 0.7%.

Parts of both BDH native starch samples were *gelatinized* and subsequently freeze dried. This procedure was chosen because it ruptures the native starch structure completely and its effect may be compared with that of typical processing steps for starch-containing foodstuffs. For gelatinization about 0.1 kg of 5% starch suspension in aq. dest. was heated in a water bath at 373 K with continuous stirring. After visual setting, the gel was left for another ten minutes in the water bath, after which it was poured into a Petri dish (layer thickness 6 mm), cooled, frozen at 258 K and freeze dried overnight (during about 18 h at an absolute pressure of 1.3 N/m^2 and a radiation heating plate temperature of 320 K). After this treatment the sample still had the dimensions of the gel. An electron microscopical investigation of samples prepared this way revealed that their physical microstructure is

sponge-like. Photographs of structures of comparable samples were published by Berghofer & Klaushofer (1976). Samples gelatinized and freeze dried in this way were found to be devoid of crystallinity.

Native manioc starch was obtained via Dr Multon (I.N.R.A., France) from Compagnie du Benin (Chalon/Saône, France). Specifications: of high purity, mass fraction of water about 0.14 kg w./kg d.s., total ash 0.07%, cellulosic impurities 0.02%, amylose content 21.2% of dry matter, X-ray crystallinity 30%.

Amylose and *amylopectine* were obtained from AVEBE (Veendam). These samples were produced by means of the commercial fractionation process with magnesium sulphate mentioned earlier (Subsection 2.5.3). Since some degradation occurs during this process both samples were selected with respect to their high viscosity value in 1 N potassium hydroxide. A high viscosity correlates with a high average molecular weight. Some specifications are: Amylose-V, reference nr. 52010, amylose content 90% of dry matter, intrinsic viscosity: 1.47 [$\cdot 10$ m^3/kg]; Amylopectin-S, reference nr. 52009, amylose content 12.8% of dry matter, standard dynamic viscosity 0.95 [$\cdot 10$ m^3/kg]. These samples contain about 1% magnesium sulphate. Before isotherm measurement, the amylose sample was suspended four times in excess aq. dest. and washed until the draining water was sulphate-free. The amylopectin sample could not be washed as it is soluble in cold water. However, since magnesium sulphate does dissolve only at water activities somewhere above 0.9, no significant influence of this minor impurity at moisture sorption equilibria below this value may be expected.

Isotherms were also measured of the native BDH potato starch sample mentioned before, which was hydrolysed during 90 days according to Nägeli. This hydrolysis procedure which yields a higher crystallinity is as follows: 0.06 kg of starch (dry basis) was suspended in 0.002 m^3 of 16% sulphyric acid, kept at 298 K and resuspended daily by shaking by hand. After 30 and 60 days the sulphuric acid was decanted and renewed. Finally the acid-resistant residue was collected by filtration and washed with aq. dest. until acid-free. The dry matter left was about 0.036 kg so that roughly 40% was dissolved. This solubilized fraction of native potato starch is higher than the 25% found by Kainuma & French (1971).

5.3 CALCULATION PROCEDURES

All isotherm equations belonging to localized sorption models as given in Chapter 4 were fitted to the measured isotherms using the sum of least-squares method for minimizing the absolute differences between measured and calculated mass fractions of water. This was efficiently done with a general

data-fitting computer programme, named FITABS, developed for this specific problem* at the DEC 10 computer of the Agricultural University. The FITABS programme enabled the choice between five subroutines for curve fitting, the Newton-Taylor subroutine and four subroutines of the Philips OPTPAC 3 subroutine package (Kilsdonk, 1977). It was found that the Newton-Taylor subroutine and the Powell subroutine of the OPTPAC 3 package were best suited for the present problem. Both subroutines gave about comparable results. However, in some cases of four parameter equations, instabilities in the minimization process were encountered which could be overcome by invoking either one of the two subroutines. As the main criterion for good fit the average deviation between experimental and calculated mass fractions of water was set to be about two times the accuracy of determination, i.e. ± 0.002 kg w./kg d.s. However, this value was always considered in conjunction with the values for the correlation coefficients, the variances and the numbers of measuring points. A minor problem here was that the measuring points generally were not evenly distributed over the entire isotherm. The used definitions of correlation coefficient and variance are as follows:

$$\text{correlation coefficient} = 1 - \frac{\Sigma(W_{ca} - W_{me})^2}{\Sigma(W_{me} - \bar{W}_{me})^2}$$

$$\text{variance} = \frac{\Sigma(W_{ca} - W_{me})^2}{M - PAR}$$

Here W_{ca} and W_{me} denote calculated and measured mass fractions of water respectively, M is the number of measuring points and PAR denotes the number of parameters.
Isotherm curve simulation for comparison with the observed data was carried out with an adapted version of the computer programme KOMPLOT (RC publication 7, computer centre of the University of Groningen).

Polymer-solvent interaction theories were tested by direct parameter calculation from observed data and figurative methods. These and other more simple calculations were made using electronic desk calculators (Hewlett Packard, types HP-55 and HP-97).

* more detailed information on the programme can be obtained from the author.

6 RESULTS AND DISCUSSION

6.1 EQUILIBRIA FOR WATER VAPOUR SORPTION OF VARIOUS STARCH SAMPLES

This chapter compares experimental results with the theory presented before. In this first section some water on starch isotherms are reported and qualitatively discussed. A more quantitative approach is taken in the following sections.

Figure 6.1 show isotherms for three native starches, namely wheat starch, potato starch and manioc starch belonging to the crystallinity types A, B and C respectively. Also plotted in this figure is the isotherm of the same potato starch sample hydrolysed during three months according to Nägeli, which results in an improved crystallinity. For all four isotherms it is indicated by an R where, close to $a_w = 1$, the direction of the sorption process was reversed from resorption to desorption. A vertical arrow indicates when condensation was observed at this point. Comparison of the isotherms of the native starches confirms that potato starch has the highest water sorption capacity, the difference with the two other starches becoming insignificant at low water acitivities, $a_w < 0.25$ for desorption. Isotherms of native wheat starch and native manioc starch are almost indistinguishable. The measuring temperature for manioc starch was 5 centigrades higher, but a correction for this effect is barely significant. Thus, at low degrees of coverage up to nearly the monolayer value, all three native starches have about equal water sorption capacities. We found that this applies also to native starches of maize and rice. This indicates that all these native starches have a comparable sorption surface for water and that deviations in sorption capacity at higher degrees of coverage are mainly due to differences with respect to the starch structure. For instance, they could be of a steric nature.

Immediately beyond this low moisture range minor irregularities are observed in the smoothness of the isotherms. At mass fractions of water approximately corresponding to these irregularities the polymer reaches its glass transition range where its amorphous parts start to plasticize. These two matters might well be related.

An interesting result is also that, compared with its original, the hydrolysed potato starch sample has a significantly lower sorption capacity over the entire range of water activities except for desorption at values of $a_w > 0.9$ and near $a_w = 0.2$. The hydrolysed sample also exhibits a somewhat stronger hysteresis. At $a_w = 0.5$ the differences in mass fraction of water between desorption and resorption amount to approximately 0.05, 0.045 and

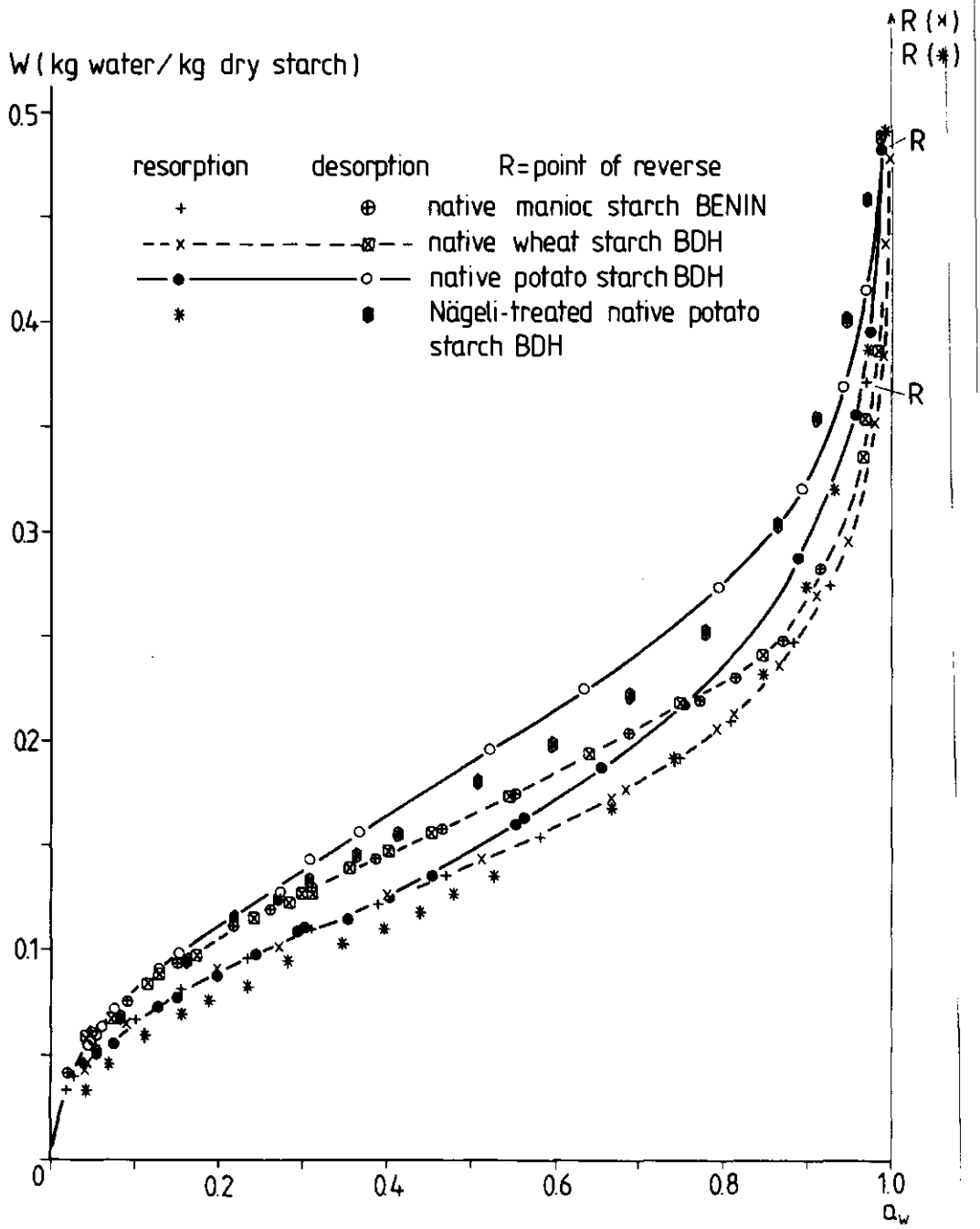

Figure 6.1. Resorption and desorption isotherms of four different starch samples. These are native starches of potato (BDH), wheat (BDH) and manioc (Benin), and native potato starch (BDH) partially hydrolysed according to Nägeli. Isotherm temperature 293.2 K, except for manioc starch at 298.2 K.

0.025 kg w./kg d.s. for the hydrolysed potato, native potato and native wheat (or manioc) starches, respectively. The hysteresis effects of all samples extend over the whole moisture range but are most pronounced in the middle area ($0.3 < a_w < 0.85$), which is the area of the glass-rubber transition. It is smaller for wheat and manioc starches, especially beyond $a_w = 0.88$, but it is remarkably large for hydrolysed native potato starch in that range. Native wheat and manioc structures are internally more strongly associated than those of native potato starch. Qualitatively this is probably the basis for the difference in water sorption capacities as well as in hysteresis effect. Reasoning this way, the increase of hysteresis due to hydrolysis may be explained by a weakening of the internal association, especially of the amorphous parts by the partial hydrolysis. The nature of the starch-water system leaves no space for any 'classic' explanation of hysteresis by capillary forces in hard-walled capillaries. Here, hysteresis is caused by structural weakness of the sample. The general reduction of the sorption capacity due to hydrolysis of the same sample can be explained by the increased crystallinity, since starch crystals have a limited sorption capacity (Section 3.2).

The native potato starch isotherm in Figure 6.1 is the one published before (van den Berg et al., 1975), apart from a few minor corrections which resulted from a close reinspection of the original measurements. The manioc isotherm results were measured as a part of the original ring test organized by Multon (1972-1974; Section 5.1). Isotherm data used for further analysis later on in this chapter are given in Appendix 2.*

Figure 6.2 shows resorption and desorption isotherms of the two major components of starch, namely of a sample consisting almost entirely of amylose and one of amylopectin. Both samples are fully amorphous. The amylopectin isotherm exhibits a larger hysteresis and below a water activity of 0.7 both isotherm branches resemble those observed for hydrolysed potato starch. Due to the much easier coagulation of amylose during the separation process of amylose and amylopectin, amylose will be more strongly internally associated than amylopectin with its branched structure. Although beyond $a_w = 0.9$ only one data point is available for either resorption or desorption for both samples, the locations of the points indicate that hysteresis is virtually absent at these high water activities. The absence of hysteresis in this high moisture range is also found with starch samples where the grain structure is destroyed by processes such as gelatinization and freeze drying.

Also shown in Figure 6.2 are desorption isotherms of two native potato

* The other numerical values plotted in this and following figures can be obtained from the author.

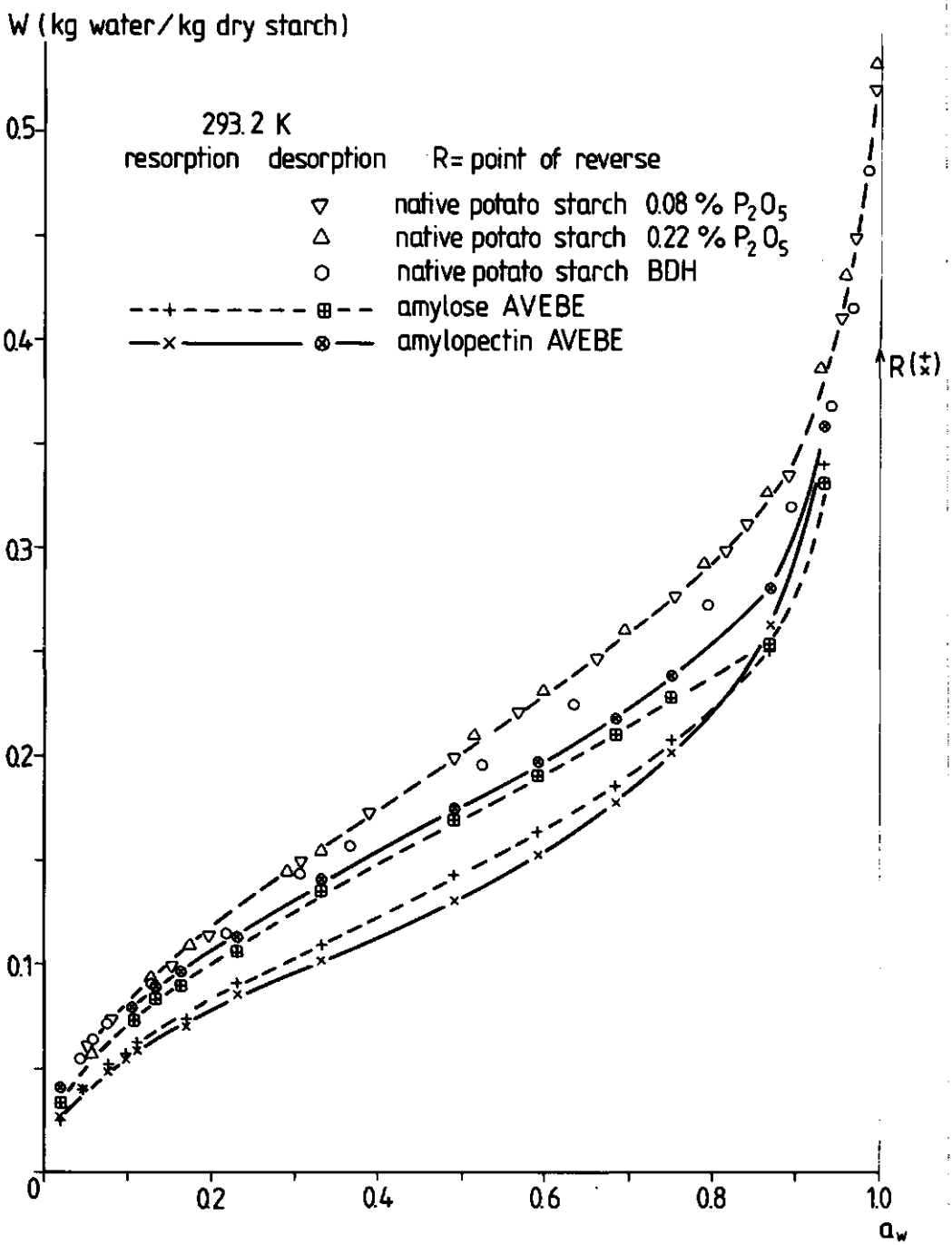

Figure 6.2. Water vapour sorption isotherms of five starch samples at 293.2 K. These are the desorption and resorption isotherms of amylose and amylopectin, and the first desorption isotherms of two native potato starch samples with different phosphate contents, and the desorption isotherm of BDH native potato starch for comparison. See text.

starch samples with somewhat differing natural phosphate contents. The comparison is interesting since these differences are responsible for a very significantly different viscosity behaviour in solution, especially during and after gelatinization. In esterified form phosphate acts as a natural cross-link between different starch chains. The isotherms for these two samples are almost identical over the entire range of water activities. At very high a_w where a gel system occurs, the high phosphate sample has the tendency to hold more sorbed water, but due to the steepness of the isotherm in this range more measurements are needed for definite conclusions. If there is an effect in water binding it is apparently confined to the solution area.

For reference purposes, the desorption isotherm values of Figure 6.1 for BDH native potato starch are also plotted in Figure 6.2. Beyond $a_w \sim 0.3$ they are lower in water content as compared with the phosphate-containing samples. Apart form a sometimes observed slight 'natural' variation (at most about 0.003 kg w./kg d.s.) for samples of the same nature but having a different origin, this difference is due to a different pretreatment before the isotherm determination. The phosphate samples were measured without prior drying (Section 5.1.2) because of the investigated relation with the viscosity behaviour. This type of 'maiden' isotherm runs for native starch samples results usually in somewhat higher sorbed water capacities as compared with the reproducible desorption isotherms obtained in the standard way. It shows the instability of starch material when it is subjected to this type of measurements.

Figure 6.3 contains isotherms which were obtained with samples of wheat and potato starch which were gelatinized and freeze dried. The data for potato starch have been reported before (van den Berg et al., 1975) and are plotted here only for the sake of reference; they are not complete. Also shown are the data for native wheat starch from Figure 6.1 in order to see the influence of the applied treatment. Gelatinization completely destroys crystallinity, whereas freeze drying 'fixes' the structure. Except for very high activities, the effect of the treatment is relatively small. In any case, the contrast with cellulose is great. Destruction of the crystalline structure of native cellulose about doubles its water sorption capacity (Urquhart & Eckersall, 1932).

As observed earlier with potato starch, the first resorption run of gelatinized wheat starch (GF1-resorption) gave data which show a slightly lower mass fraction of water and are not fully reproducible below $a_w \sim 0.9$. This is in contrast with the second resorption run (GF2-resorption) which is reproducible. The physical starch structure as derived from freeze drying apparently resets itself after having taken up water again.

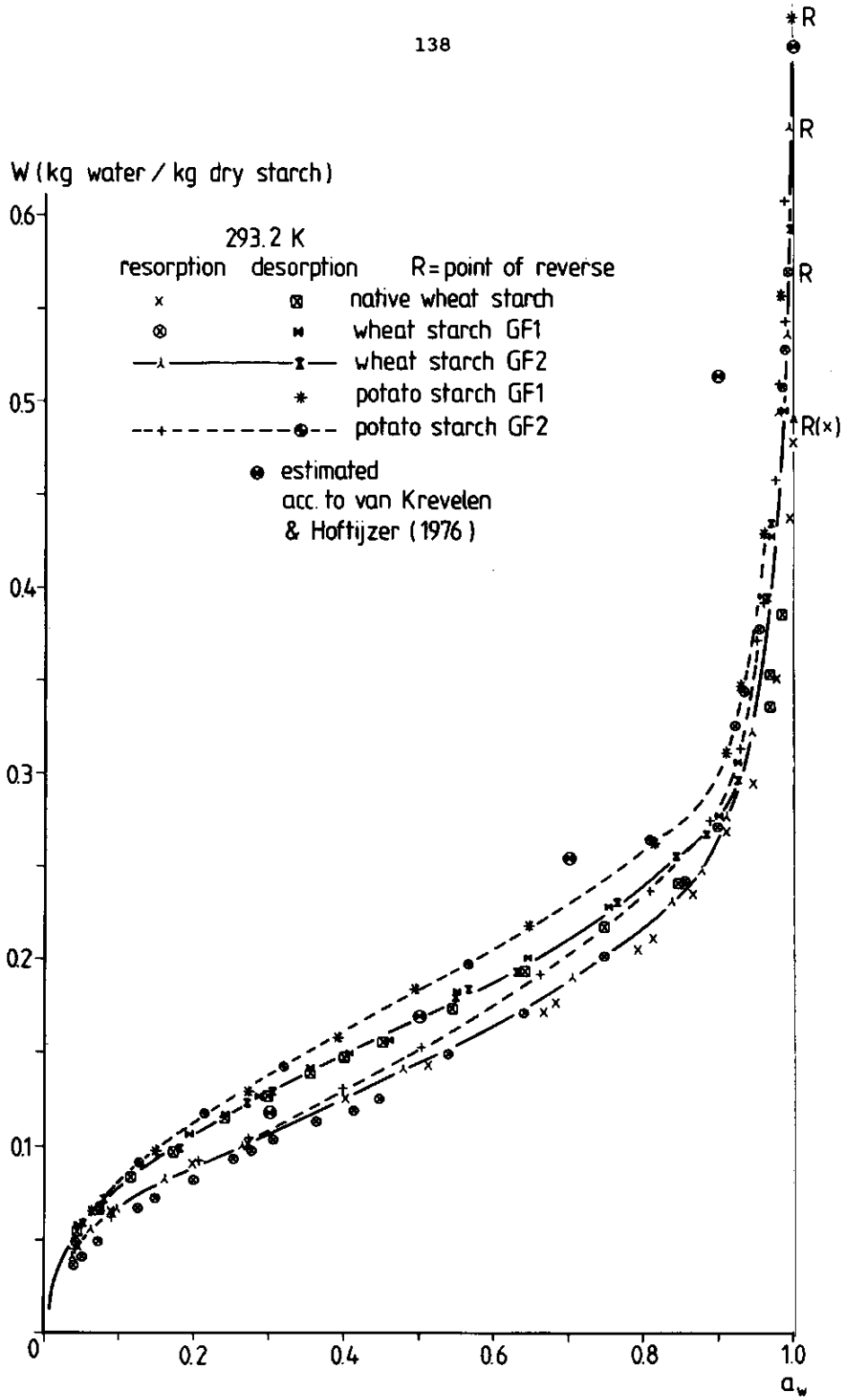

Figure 6.3. Resorption and desorption isotherms of gelatinized starch samples of wheat and potato at 293.2 K. Resorption and desorption isotherm of native wheat starch shown for comparison. See text.

This occurs also visibly in the freeze dried gel which deforms somewhat at $a_w \sim 0.9$, which is at the end of the glass-rubber transition range. Also for wheat starch after gelatinization the hysteresis above $a_w \sim 0.9$ becomes insignificant and the maximum water sorption capacity is no longer limited by the maximum swelling capacity of the starch grain. In agreement with the analysed volume relations of the water-starch system (Section 3.3) the steep rise of the isotherm starts at approximately 0.3 kg w./kg d.s. This agreement is more striking for the gelatinized starches than for the native ones due to the generally steeper rise of the isotherms with increasing water activity. It is also noteworthy that again at low degree of coverage the sorption equilibria are identical for native and gelatinized samples. The hysteresis of native potato starch above the monolayer coverage is significantly decreased by gelatinization (compare Figure 6.1). For wheat starch this is a smaller effect than for potato starch. Also the differences in water sorption capacity between the two native starches have become smaller by gelatinization, but have not disappeared completely. The remaining deviation must find its cause in differences in the amorphous structure of both starches.

In order to investigate the sorption behaviour inside the *hysteresis loop*, various *scanning experiments* were made. Generally, for activities beyond the monolayer value it was found that when a sorption run in either direction is reversed the equilibrium value traverses the hysteresis loop with an almost equal mass fraction of water, but it does not reach the other side. Instead, the equilibrium value follows a parallel curve close to the loop boundary. This general behaviour was briefly described earlier (van den Berg & Leniger, 1976, Figure 1). From this is follows that what is reported here as the *resorption* isotherm pertains to a condition of starch that in food processing practice is seldom attained, because a food material is usually not fully dried out. Thus, during rewetting, it will follow some scanning curve. At low degrees of coverage, roughly below the monolayer value, the scanning results are different since the loop is not traversed with an almost constant mass fraction of water. Figure 6.4 gives scanning data for native wheat starch on an enlarged scale. The numbers indicate the successive observations and altogether constitute two resorption-desorption cycles. Measuring point 117 resulted from a large desorption step. All other observed equilibria lay about at the same curve which is located close to the 'ordinary' desorption isotherm. The reversible sorption isotherm in Figure 6.4 must belong to a metastable condition of the sorbent. This condition was obtained (frozen in) close to the attainment of point 117. This result is a direct support of the view that the sorbent at these low water contents acts as a rigid physical adsorbent. What remains unsolved in this view is why, already at these low degrees of coverage, the removal of the very last traces of water suddenly changes the water sorption capacity of the sub-

stance so much. It is likely that the last traces of water are bound very specifically in the starch structure. It was found that the first two per cent of water are bound with a considerably higher binding energy and are very difficult to remove. When this water is removed parts of the structure change their conformation (collapse), with a concomitant reduction of part of the sorption surface. The initial situation can be restored only after the structure has become weak and flexible again. This could well explain the difference between the monolayer values observed for desorption and resorption.

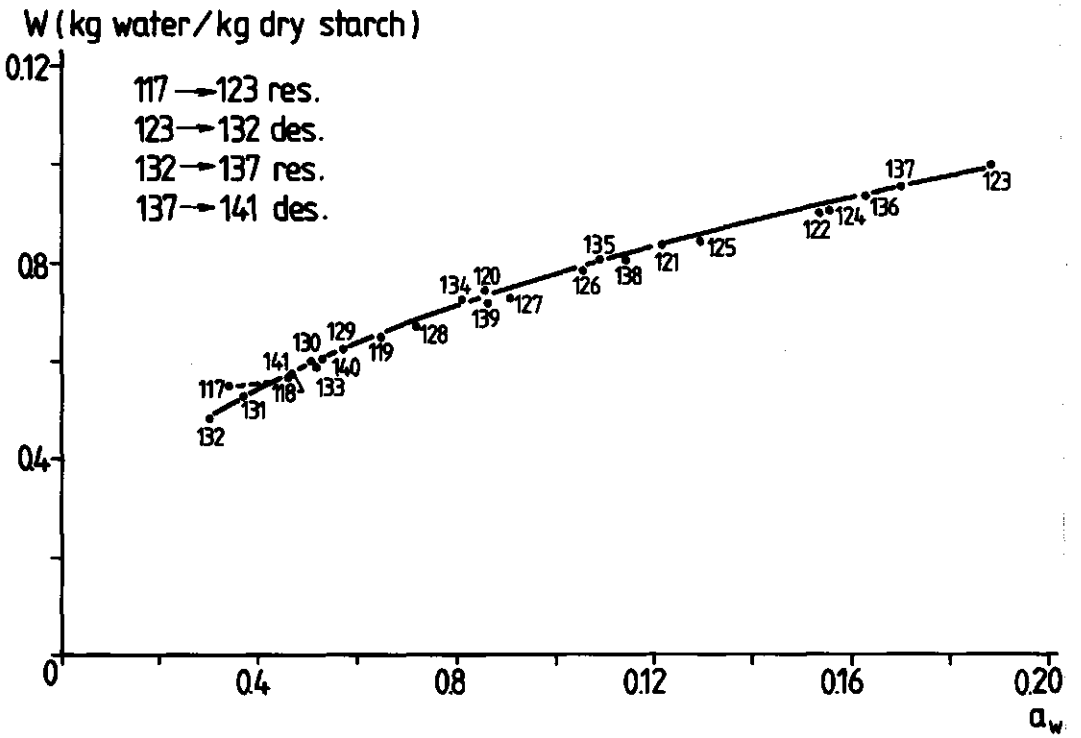

Figure 6.4. Two resorption and desorption scanning isotherm cycles for native wheat starch (BDH) in the low moisture range at 293.2 K. See text.

6.2 EFFECT OF TEMPERATURE

This section reports sorption equilibria at different temperatures and their analysis in terms of the B.E.T. and G.A.B. sorption models. The purpose is to see the sorption enthalpy and entropy effects separately.

Figure 6.5 shows resorption isotherms for native potato starch at four temperatures. These isotherms were fitted to the isotherm equations of the B.E.T., G.A.B. and entropic G.A.B. sorption models. The best values of the

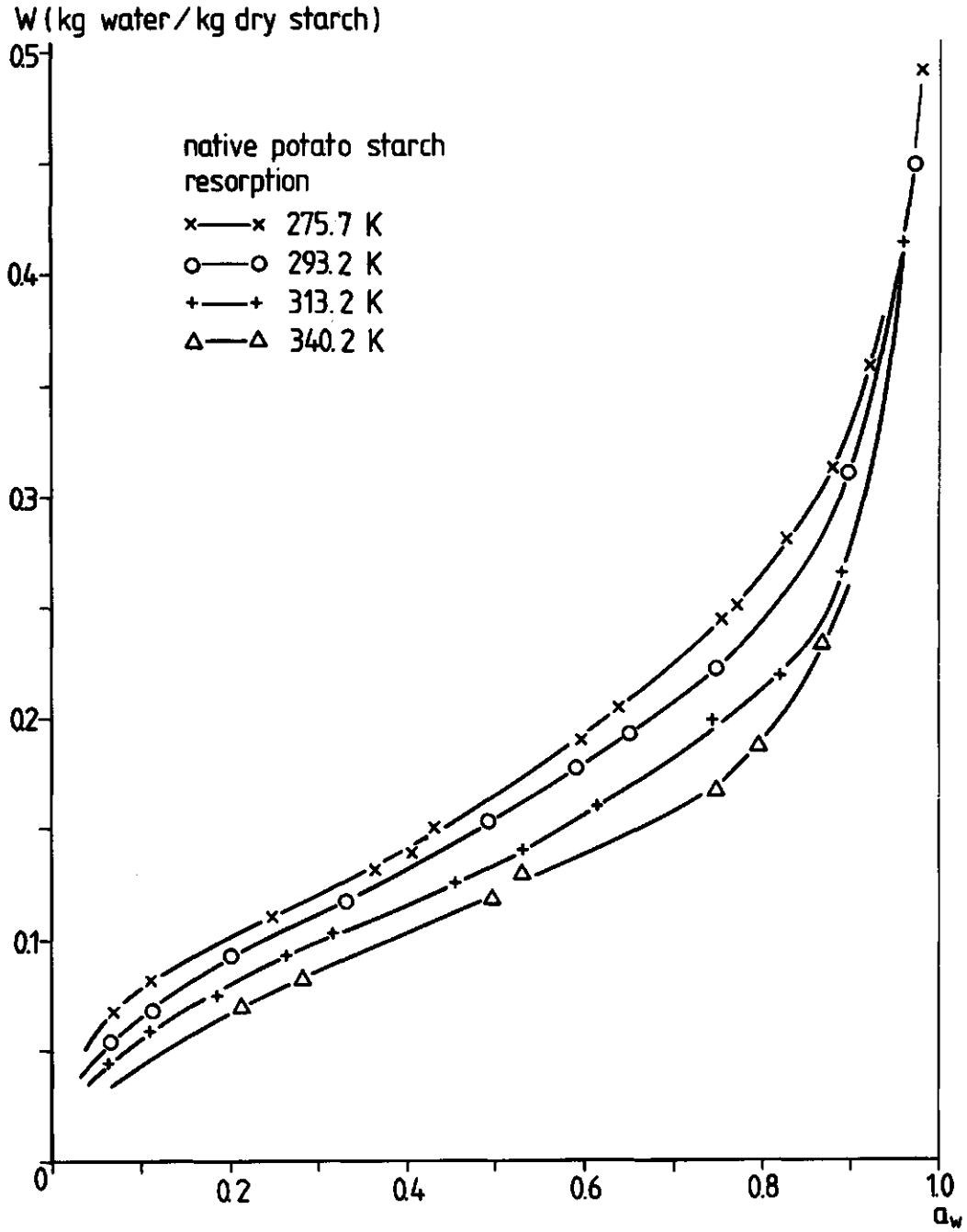

Figure 6.5. Resorption isotherms of native potato starch (BDH) at four temperatures.

parameters of the B.E.T. and the G.A.B. models are given in Tables 9 and 10. Unfortunately, for the viable a_w region of the B.E.T. equation at 340 K only a small number of data points were available, but from the agreement between the observed and calculated curve it was concluded that the observed tendency would not be influenced very much if more data points would have been available. The entropic G.A.B. equation did not supply additional information because its fit was not better than that of the G.A.B. equation. The genera results of the four parameter models of sorption are further discussed in Section 6.3.

Table 9. Results of resorption isotherm analysis for native potato starch in terms of the B.E.T. equation 4.4. Correlation coefficient and variance better than 0.997 and $0.26 \cdot 10^{-5}$, respectively.

Temperature K	Applicable a_w region up to	W_1 kg w./kg d.s.	C_B	Average deviation kg w./kg d.s.
275.66	0.30	0.0919	28.9	0.000192
293.16	0.35	0.0881	18.2	0.00103
313.16	0.35	0.0793	15.3	0.00097
340.16	0.40	0.0717	11.5	$\sim$ 0

Table 10. Results of resorption isotherm analysis for native potato starch in terms of the G.A.B. equation (4.23). Correlation coefficient and variance better than 0.996 and $0.16 \cdot 10^{-4}$, respectively.

Temperature K	Applicable a_w region up to	W_1 kg w./kg d.s.	C_G	K	Average deviation kg w./kg d.s.
275.7	0.9	0.1089	23.4	0.749	0.00262
293.2	0.91	0.1055	17.0	0.742	0.00189
313.2	0.90	0.0941	15.6	0.730	0.00210
340.2	0.81	0.1033	9.0	0.622	0.00215

The parameter values obtained in this way show the generally expected trend towards a decreasing binding energy for the first sorbed layer with increasing T, as judged from the C-parameters. This decreasing binding energy indicates an increasingly shorter residence time for the sorbed molecules in the first layer. In other words: at increasing temperature the character of the sorption process becomes less strongly localized. There is some mutual

compensation of the parameters, especially for the three parameter G.A.B. isotherm. In the B.E.T. and G.A.B. models the temperature dependence is contained only in the binding energy parameters C_B, C_G and K. Therefore the isotherms were fitted again with both equations now containing a fixed average value for W_1. The general result of this was that the observed trends were confirmed. They became more pronounced and more evenly distributed over the different temperature levels.

The parameters C_B, C_G and K from Tables 9 and 10 were further analysed, expliciting their temperature dependence through equations (4.8), (4.24) and (4.25). These equations can be written as follows:

$$\ln C_B = \ln \frac{j_1}{j_\ell} + \frac{H_1 - H_\ell}{RT}$$

$$\ln C_G = \ln \frac{j_1}{j_m} + \frac{H_1 - H_m}{RT} \qquad (6.1)$$

$$\ln K = \ln \frac{j_\ell}{j_m} + \frac{H_\ell - H_m}{RT}$$

These three functions are shown in Figure 6.6. The straight lines have been calculated using linear regression. From them values for the ratio of accommodation coefficients and the corresponding enthalpies are immediately obtained. These values are collected in Table 11.

Table 11. Entropy and enthalpy effects for sorption of water at native potato starch at ambient temperatures. Results from isotherm analysis at four temperature levels between 275 K and 340 K with the B.E.T. and G.A.B. models of sorption.

Parameter	Ratio of accommodation factors	Enthalpies of sorption (kJ/mole at 293 K)
C_B	$\frac{j_1}{j_\ell} = 0.25$	$H_1 - H_\ell = 3.14$
C_G	$\frac{j_1}{j_m} = 0.21$	$H_1 - H_m = 3.19$
K	$\frac{j_\ell}{j_m} = 0.30$	$H_\ell - H_m = 0.63$

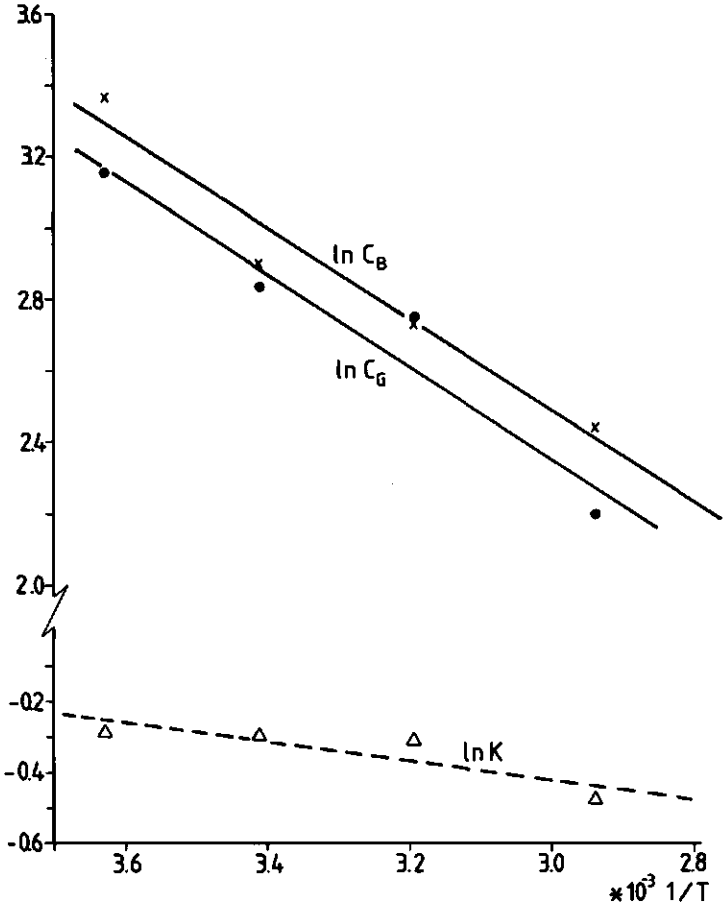

Figure 6.6. Relations of energy interaction parameters of the B.E.T. and G.A.B. models of sorption and the absolute temperature for native potato starch (BDH). Plotted according to equations (6.1).

Before further discussion of the obtained results it should be mentioned that the analysis of the enthalpy and entropy is not very sensitive this way, especially not for K. This can be illustrated by restricting the application of the analysis only to the lower three temperatures instead of to all four of them. This would shift the observed accommodation coefficient ratio to about its double value and decrease the entropy to a quarter. Therefore the values of Table 11 are only semi-quantitative. They show clearly that parameter K contains a considerable entropical part, relatively much more than the C parameters. It is also noteworthy that the ratios of accommodation coefficients as observed in this case deviate much more from unity than is usually assumed. The corresponding ratios derived from C_B and C_G indicate that, apart from energetic considerations, a sorbing molecule prefers accommodation in the multilayer over a place in the first layer by a

factor of four to five. Although this factor is semi-quantitative the trend agrees with a considerable increase in entropy for molecules sorbed in the second and further layers as compared with those in the first layer. This trend corroborates with the entropy results of the thermodynamic analysis presented in Section 3.4 (Figure 3.12).
The sorption enthalpy of the first layer as obtained by this analysis is only about one third of the net enthalpy of sorption obtained with immersion calorimetry. A further comparison between obtained values for sorption enthalpy will be given in Section 6.3.

6.3 COMPARISON WITH SORPTION THEORIES FOR HOMOGENEOUS SURFACES

6.3.1 General

This section reports results on the comparison of twelve B.E.T.-like isotherm equations for resorption and desorption of five starch samples. These samples are native and gelatinized starches (GF1) of potato and wheat, and Nägeli-treated native potato starch. The data are given in Appendix 2. The isotherm equations are (between brackets the equation number and identification code are given): the B.E.T. equation (4.4 - BET) with two adjustable parameters, the G.A.B. equation (4.23 - GAB) and the modified B.E.T. equations (4.30 - NBET), (4.42 - TLBET), (4.31 - PIR) and (4.63, with K = 1 - NSVBET), all with three adjustable parameters and six isotherm equations with four adjustable parameters, namely (4.32 - NGAB), (4.33 - PIRGAB), (4.47 - TLNBET), (4.45 - TLGAB), (4.51 - LBGAB) and (4.63 - NSVGAB). The condensed results of this comparison are reported in this chapter.

First some general remarks have to be made. While fitting sets of data points over different ranges of a_w to the isotherm equations, important mutual compensations of the adjustable parameters were observed, the more so with greater numbers of parameters. However, even for the B.E.T. equation, with only two parameters, one observes beyond $a_w \sim 0.4$ that a decrease of V_1 values is compensated by a strong increase in C_B, rising even to physically very unrealistic values. Evidently this complicates the evaluation and comparison of the different equations. Generally, the quality of different equations was judged on the basis of their ability to describe isotherms and on the quality of the parameters, especially their expected physical realism.

The results with a majority of the investigated isotherm equations were somewhat disappointing. Most new equations did not give an improvement in experimental isotherm description sufficient to justify the use of an additional adjustable parameter. Especially it was difficult to rival the results obtained with the G.A.B. equation, both in isotherm-predictive power

and physical significance of its three parameters. Below, only results with the more successful sorption models are reported in detail and further analysed.

6.3.2 Results with the B.E.T. equation

Table 12 gives the results of isotherm analysis with the B.E.T. equation. As usual this equation correctly describes the low moisture region of the experimental isotherms up to a_w values near 0.35 - 0.40, but overestimates the sorption capacity beyond this a_w value. A single case with a low monolayer value and a slightly stronger increasing sorption capacity (gelatinized potato starch, GF1 resorption) fits even up to $a_w \sim 0.46$. At these low coverages hysteresis is reflected only in the monolayer values W_1 which for desorption are about 25% higher than for resorption. The W_1 values for desorption are close to that corresponding with one water molecule per anhydroglucose monomer (0.1104 kg w./kg d.s.). For wheat starch they are a little lower than for potato starch.

Table 12. Results of isotherm analysis in terms of the B.E.T. equation for five different starch samples, resorption and desorption.

Sample	Applicable a_w region up to	W_1 kg w./kg d.s.	C_B	Average deviation kg w./kg d.s.
NPR	0.34 (8)	0.0847	21.5	0.00136
NPD	0.38 (10)	0.1075	19.4	0.00133
GPR	0.46 (11)	0.0791	16.8	0.00109
GPD	0.40 (11)	0.1036	22.6	0.00114
HPR	0.40 (9)	0.0738	19.1	0.00141
HPD	0.34 (8)	0.1076	15.1	0.00127
NWR	0.41 (5)	0.0799	30.3	0.00121
NWD	0.36 (11)	0.0968	24.1	0.00092
GWR	0.37 (10)	0.0799	18.6	0.00107
GWD	0.36 (6)	0.0988	23.7	0.00128

Sample identification:
G = gelatinized; N = native; P = potato starch; W = wheat starch; H = hydrolysed; R = resorption; D = desorption
( ) number of data points incorporated in applicable a_w region
Correlation coefficient > 0.9938
Variance < $0.4449 \cdot 10^{-5}$

The values for C_B are higher for native wheat starch than for native potato starch, but the significance of this effect is not great because C_B is a somewhat less sensitive parameter for location of the curve. Figure 6.1 shows that the differences in data points location are small, for resorption even not much beyond the accuracy of measurements in this a_w range. A systematically higher binding energy between water and native wheat starch when compared with native potato starch can be explained by the stronger internal association of wheat starch. When water molecules fit suitably into the starch structure a stronger internal association will result in relatively more water-starch contacts for the same number of water molecules present in the starch. The energy parameter values suggest this to be the case for native wheat starch.

6.3.3 Results with the G.A.B. equation

Isotherm analysis with the G.A.B. equation resulted in Table 13. These data show that except for two isotherms a satisfactory agreement is observed up to $a_w \sim 0.9$. In some cases the valid a_w region also had a lower boundary because the lowest data point caused a significant rise in the average deviation and was therefore disregarded. The desorption isotherms for the two potato starch samples (NPD, GPD) which gave a less satisfactory average deviation were found to show this behaviour with a decreasing number of data points down to nearly the applicable a_w region of the B.E.T. equation, where the value of K approaches unity. This result indicates that the adopted standard for delimitation of the applicable a_w range in this study is more sensitive than the one used before (van den Berg et al., 1975).

Comparison of the results obtained with the B.E.T. and the G.A.B. isotherm equation shows that the trends in the parameter values W_1 and C are comparable in both cases so that these trends may be taken as physically realistic. However, the monolayer values for the G.A.B. equation are considerably higher. For resorption and desorption they are located on either side of the value for one water molecule per anhydroglucose monomer. Except for one case, the values for C_G are somewhat lower than for C_B, a difference, however, which is not very significant. The accuracy of the thus obtained values for the three parameters W_1, C_G and K is estimated to be $\pm$ 0.005, $\pm$ 1.0 and $\pm$ 0.02 respectively.

Another interesting result is that the values for K in Table 13 are systematically higher for resorption than for desorption. Because the other interaction-energy parameter, C_G, which is mainly of an enthalpic nature, does not exhibit this trend, it is concluded that this effect reveals an entropy difference between the states of the multilayer during resorption and desorption. This could well be caused by differences between the distributions of water molecules over the polymer matrix during its swelling and shrinking.

Table 13. Results of isotherm analysis in terms of the G.A.B. equation for five different starch samples, resorption and desorption.

Sample	Applicable a_w region	W_1 kg w./kg d.s.	C_G	K	Average deviation kg w./kg d.s.
NPR	0.05 - 0.90 (15)	0.1012	17.6	0.740	0.00166
NPD	0.05 - 0.90 (13)	0.1399	17.4	0.651	(0.00337)
GPR	0.045 - 0.88 (17)	0.1058	12.0	0.712	0.00206
GPD	0 - 0.90 (16)	0.1353	20.0	0.639	(0.00341)
HPR	0 - 0.90 (16)	0.0871	17.9	0.760	0.00155
HPD	0 - 0.88 (15)	0.1281	17.0	0.677	0.00215
NWR	0 - 0.88 (11)	0.0982	27.3	0.681	0.0015
NWD	0.045 - 0.89 (16)	0.1288	21.1	0.584	0.00209
GWR	0 - 0.91 (17)	0.0960	17.4	0.728	0.00169
GWD	0 - 0.81 (11)	0.1228	22.8	0.648	0.00182

Sample identification:
G = gelatinized; N = native; P = potato starch; W = wheat starch; H = hydrolysed; R = resorption; D = desorption
( ) number of data points incorporated in applicable a_w region
Correlation coefficient > 0.9986
Variance < $0.104 \cdot 10^{-4}$

Furthermore it can be generally concluded that the analysis of this type of experimental isotherms with the G.A.B. equation must be preferred to that with the B.E.T. isotherm equation. Analysis with the G.A.B. equation combines a description of the experimental isotherm which is far superior to that of the B.E.T. equation with more, and probably better, physico-chemical information on the sorptive interaction.

6.3.4 Results with other three-parameter isotherm equations

Table 14 collects results obtained with isotherm equations (4.30) and (4.31), both of which are based on models of sorption with a limitation of the number of sorbed molecules per site. Both equations have an equally good ability to describe the major part of the experimental isotherms, almost as good as the G.A.B. equation.

The observed values for the parameters W_1 and C_B in Table 14 are about the same as those from the B.E.T. equation. The value of n for the number of layers is an additional parameter. The values for n are systematically high-

Table 14. Results of isotherm analysis in terms of the equations of B.E.T. for a limited number of molecules per site (4.30-NBET) and that of Pickett (4.31-PIR).

Sample	Applicable a_w region up to	W_1 kg w./kg d.s.	C_B	n	Average deviation kg w./kg d.s.
NPR NB	0.70(14)	0.0828	22.4	5.5	0.00178
PI	0.80(15)	0.0833	23.1	3.7	0.00156
NPD NB	0.80(13)	0.1085	19.5	5.0	0.00167
PI	0.80(13)	0.11212	17.8	3.1	0.00191
GPR NB	0.88(18)	0.0778	18.0	6.9	0.00216
PI	0.88(18)	0.0812	15.6	4.0	0.00161
GPD NB	0.84(15)	0.1061	21.1	4.8	0.00119
PI	0.84(15)	0.1105	18.8	2.9	0.00171
HPR NB	0.79(14)	0.0733	19.6	5.7	0.00151
PI	0.86(15)	0.0737	19.5	3.9	0.00159
HPD NB	0.80(14)	0.1054	16.2	4.6	0.00213
PI	0.80(14)	0.1010	14.6	2.9	0.00147
NWR NB	0.80(9)	0.0801	30.6	5.0	0.00219
PI	0.80(9)	0.0829	27.2	3.1	0.00117
NWD NB	0.89(17)	0.0977	23.7	4.4	0.00142
PI	0.79(16)	0.1019	20.8	2.7	0.00108
GWR NB	0.79(15)	0.0781	19.5	5.7	0.00176
PI	0.87(16)	0.0791	19.5	3.7	0.00161
GWD NB	0.87(12)	0.0987	24.2	4.6	0.00167
PI	0.80(11)	0.1023	21.6	2.9	0.00129

Sample identification:
N = native; G = gelatinized; P = potato starch; W = wheat starch; H = hydrolysed; R = resorption; D = desorption
NB and PI denote results for the NBET and PIR equations, respectively
( ) number of data points incorporated in applicable a_w region
Correlation coefficient > 0.9975
Variance < $0.104 \cdot 10^{-4}$

er for the NBET equation (4.30). Since the cause of the limitation of the number of sorbed molecules at a site remains a matter of speculation the further physical interpretation of this parameter remains vague. It is therefore doubtful whether the value of this modification for practice is more than just a tool to describe experimental isotherms more successfully than is possible with the simple B.E.T. equation. Theoretically the Pickett equation (4.31) is even less founded. It is certainly not true that (4.31) should be preferred over (4.30) as was suggested by Rounsly (1961). The observed values for W_1 and C_B in both equations show small systematic differences which for the isotherm description compensate each other together with the influence of the third parameter.

Comparison of the experimental isotherms with the B.E.T. equation modified for the first two sorbed molecules (4.42) shows that this equation is a slight improvement of the simple B.E.T. equation. However, it extends the range of applicability only to $a_w \sim 0.6$. Table 15 gives results of this comparison. (4.42) tends to predict isotherms with a high degree of coverage

Table 15. Some results of isotherm analysis by the equation of B.E.T. modified for the first two sorbed molecules at a site being different from further sorbed molecules (4.42-TLBET).

Sample	Applicable a_w region up to	W_1 kg w./kg d.s.	C_B	C_T	Average deviation kg w./kg d.s.
NPR	0.60(13)	0.0550	37.8	5.3	0.00151
NPD	0.57(11)	0.0736	31.7	4.2	0.00198
GPR	0.59(12)	0.0607	23.1	2.6	0.00116
GPD	0.59(13)	0.0693	34.5	5.3	0.00147
HPR	0.59(12)	0.0487	24.4	5.8	0.00081
HPD	0.55(11)	0.0663	20.9	6.5	0.00125
NWR	0.55(6)	0.0515	43.8	7.8	0.00101
NWD	0.50(13)	0.0641	38.7	5.5	0.00132
GWR	0.64(14)	0.0496	24.7	7.5	0.00168
GWD	0.59(9)	0.0601	28.1	10.2	0.00190

Sample identification:
N = native; G = gelatinized; P = potato starch; W = wheat starch; H = hydrolysed; R = resorption; D = desorption
( ) number of data points incorporated in applicable a_w region
Correlation coefficient > 0.9970
Variance < $0.85 \cdot 10^{-5}$

just beyond the monolayer value due to the preferential formation of the second layer in the sorption model. This effect results in our case in drastically decreased values for W_1 and increased values for C_B when compared with the results of the simple B.E.T. equation. The binding energy parameter C_T for the second molecule at a site shows values spread between 2.5 and 8. The physical meaning of this spread for samples which are chemically so well comparable is not clear. The ratio between C_B and C_T lies between 4 and 7 which is also difficult to reconcile with the observed energy effects of the first and second layer of molecules (Section 3.4). In spite of this somewhat doubtful physical meaning the parameter values for native potato starch will be considered later in comparison with the other observed energy parameters (Subsection 6.3.7).

The finally observed three-parameter isotherm equation is not explicitly mentioned in Chapter 4. However, this equation is an obvious boundary case of equation (4.63) for $K \rightarrow 1$. This modified B.E.T. equation, assuming a varying number of sites in the sorption model, was found to be a poor fitting equation with an applicable a_w range up to about 0.55. The equation gave values for W_1 of roughly 0.20 and for C_B of about 5, together with values for S' of near 0.3. These results point to mutual compensation of parameters in the mathematical model rather than to physically realistic information.

A comparison of isotherm description ability of the B.E.T. equation (4.4) and the five mentioned three-parameter equations is shown in Figure 6.7 for the resorption isotherm of native potato starch.

6.3.5 Results with four-parameter isotherm equations

Of the six isotherm equations with four parameters one (4.47-TLNBET) is directly derived from the B.E.T. model. The others are all modifications of the G.A.B. model of sorption. Obviously, an equation that already describes the isotherm data over 90% of the scale cannot be very much further improved by introducing another parameter. A visual impression of the ranges of isotherm description of the six equations is given in Figure 6.8, again for the resorption isotherm of native potato starch. In this case the results of the three equations LBGAB, NGAB and NSVGAB were found to be identical to that of the unmodified G.A.B. equation.

The TLNBET equation (4.47) is a slight improvement of the NBET equation (4.30) extending the boundary of the applicable a_w range from about 0.75 to 0.80 - 0.85. Values for W_1 range between 0.5 and 0.8; C_B takes values from 20 to 43; C_T from 5 to 8 and n from about 5 to 12. In all cases the range of applicability of this four-parameter equation is not yet as good as that of the G.A.B. equation with three parameters.

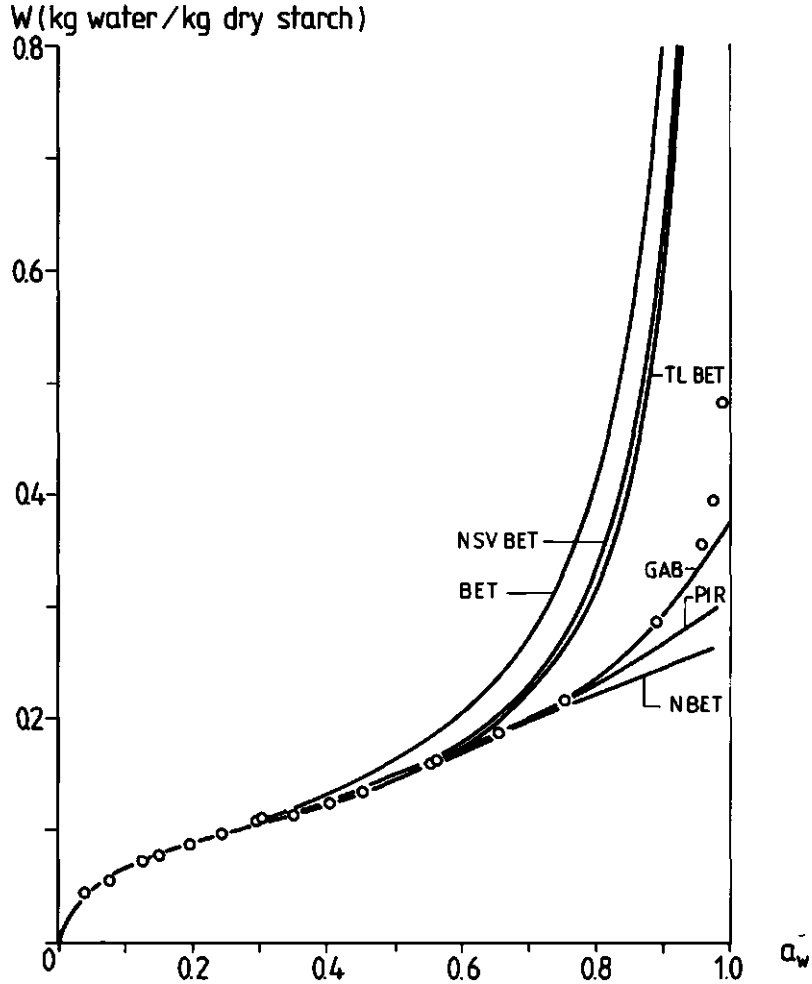

Figure 6.7. Description of the resorption isotherm for native potato starch (293.2 K) with six isotherm equations. Parameters: BET: W_1 = 0.0847, C_B = 21.5; NSVBET: W_1 = 0.2120, C_B = 5.23, S' = 0.2964; TLBET: W_1 = 0.0550, C_B = 37.8, C_T = 5.3; GAB: W_1 = 0.1012, C_G = 17.6, K = 0.74; PIR: W_1 = 0.0833, C_B = 23.1, n = 3.7; NBET: W_1 = 0.0828, C_B = 22.4, n = 5.5.

With respect to their isotherm description ability only the TLGAB equation (4.45), out of the other equations, may be considered as an improvement of the G.A.B. model (4.23). (4.45) fits most isotherms up to $a_w \sim 0.95$ within the average deviation limit, but fails (also) to describe the very high moisture points in the typical solution area. This discrepancy is of course stronger with isotherms of the gelatinized samples that increase very steeply beyond $a_w \sim 0.91$. Table 16 compares typical results obtained with the TLGAB equation and the G.A.B. equation for some identical data sets. Besides a slight improvement in the average deviation the TL-modification shifts the values for W_1 significantly downward, and those for C_B and K upward. Again it is difficult to conclude whether we look here at an effect with physical

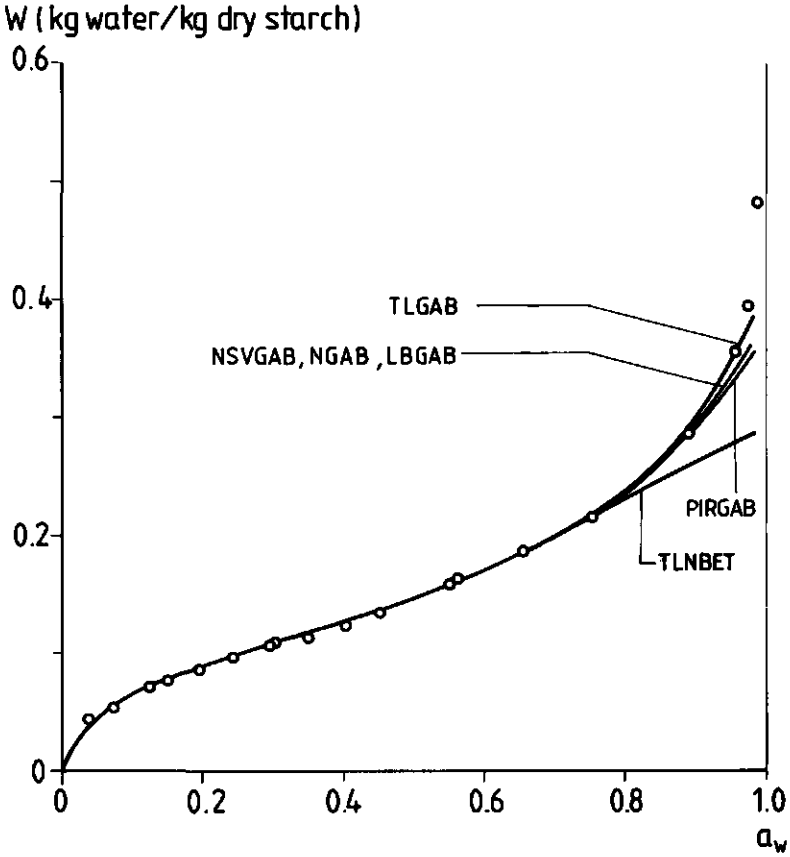

Figure 6.8. Description of the resorption isotherm for native potato starch (293.2 K) with six four-parameters isotherm equations. Parameters: TLGAB: W_1 = 0.0697, C_G = 27.4, C_T = 3.2, K = 0.812; LBGAB: W_1 = 0.1012, C_G = 19.52, K = 0.664, E = 1.115; NGAB: W_1 = 0.09935, C_G = 19.66, K = 0.746, n = 10^{10}; NSVGAB: W_1 = 0.1012, C_G = 17.6, K = 0.74, S' = 1.0; PIRGAB: W_1 = 0.09975, C_G = 18.1, K = 0.751, n = 9.98; TLNBET: W_1 = 0.0578, C_B = 38.78, C_T = 8.37, n = 4.1.

meaning or purely at the result of mutual compensation in the original equations. The TLGAB model is modified only with respect to its assumed properties of the second layer. This is difficult to reconcile with an improved isotherm description at the a_w level where the third layer of sorbate molecules already approaches full coverage.

The other modifications of the G.A.B. model yield in nearly all cases an applicable a_w range comparable to that for the original G.A.B. equation. The obtained parameter values approach those observed for the unmodified G.A.B. equation or internally compensate for the new parameter. Evidently these

Table 16. Comparison of the results of isotherm analysis in terms of the G.A.B. equation (4.23) and the TLGAB equation (4.45).

Sample		Applicable a_w region	W_1 kg w./kg d.s.	C_G	C_T	K	Average deviation kg w./kg d.s.
NPR	g	0.05 - 0.97	0.0974	19.4		0.762	0.00230
	t		0.0697	27.4	3.2	0.812	0.00195
GPD	g	0 - 0.90	0.1353	20.0		0.639	0.00341
	t		0.1023	28.9	2.5	0.677	0.00265
HPR	g	0 - 0.90	0.0870	17.9		0.761	0.00155
	t		0.0604	25.3	3.4	0.824	0.00135
HPD	g	0 - 0.88	0.1281	17.0		0.677	0.00215
	t		0.0800	23.6	4.8	0.777	0.00167
NWD	g	0 - 0.89	0.1264	22.6		0.594	0.00253
	t		0.0954	33.7	2.6	0.621	0.00179
GWR	g	0 - 0.91	0.0960	17.4		0.728	0.00169
	t		0.0786	23.1	1.8	0.756	0.00168

Sample identification:
N = native; G = gelatinized; P = potato starch; W = wheat starch; H = hydrolysed; R = resorption; D = desorption
g = results with (4.23); t = results with (4.45)

modifications are not effective for this type of experimental isotherms. Reviewing the results with the four-parameter isotherm equations, it can be generally concluded that in comparison with the three-parameter G.A.B. equation none of the four-parameter modifications presented in Chapter 4 is an improvement sufficient to justify the use of a fourth parameter. For the phenomenological description of the isotherm over the widest a_w range possible, the TLGAB equation with four parameters can be used, but for general use and interpretation of the sorptive interaction the unmodified, three-parameter G.A.B. equation is preferred.

6.3.6 Note on the parameter W_1

In Subsections 6.3.2 and 6.3.3 it was found that the values of the parameter W_1 are close to the value of one water molecule per anhydroglucose monomer (0.1104 kg w./kg d.s.). In order to see whether this monolayer value also geometrically agrees, the expected sorption surface may be compared with the surface of the sorbed molecule. For the water molecule a cross section of

0.105 nm² (derived from the liquid density) was assumed. The sorption surface of starch may be modelled as the sum of the sorption surfaces of the glucose monomers, available at one side only, due to the prevalent conformation in helices with a predominantly apolar interior. Taking the glucose monomer simply as a circle with a diameter equal to the length of the monomer from oxygen to oxygen (0.425 nm; Arnott & Scott, 1972) a cross section of 0.142 nm² is obtained. This simplified geometry model of a water molecule on a circle is not entirely satisfactory since we know that the first water molecules establish more than two hydrogen bonds in four possible tetraedric directions, but the similarity of the two cross sections does suggest that monolayer coverage indeed corresponds to about one water molecule per glucose monomer.

6.3.7 Comparison of sorption enthalpies from various models

With the results reported so far the net sorption enthalpy at different degrees of coverage can be derived from various sorption models. For native potato starch (resorption) also results from the temperature effect analysis (Section 6.2) as well as from direct measurements are available. The parameter values from isotherm analysis vary for the different starch samples but as a whole the values of the energy parameters obtained for native potato starch are not far from the average values observed for the different samples. It is striking that the C parameters (C_B, C_G, C_T) are relatively high for native wheat starch which is internally strongest associated.

Figure 6.9 collects for native potato starch as a function of the degree of coverage, the molar net enthalpies of (re)sorption of water as seen by four sorption models. Also shown are the results of the temperature effect analysis and those obtained earlier from immersion calorimetry. In the case of the enthalpy calculation from the parameters of the four sorption models (1, 3, 5 and 6 in Figure 6.9) it was assumed that the accommodation coefficient ratios are unity. It will be clear that in case these ratios are smaller the calculated enthalpy differences are greater, which shift the net enthalpies of sorption more towards the directly determined value. For example, assuming a ratio of unity the experimentally observed value of -11.7 kJ/mol yields a C_B of 121.6, while a ratio j_1/j_ℓ of 0.25 (see Table 11) would yield 30.4, a value in the order of those experimentally observed. The levels of the net sorption enthalpies for the first sorbed molecules in the four models are well comparable, only the valid regions of water content vary according to the observed monolayer values.

The 'pure' net enthalpy values (2 and 4 in Figure 6.9) for the first sorbed molecules as obtained from the temperature effect analysis with the B.E.T. and G.A.B. models of sorption (Section 6.2), show a larger deviation from

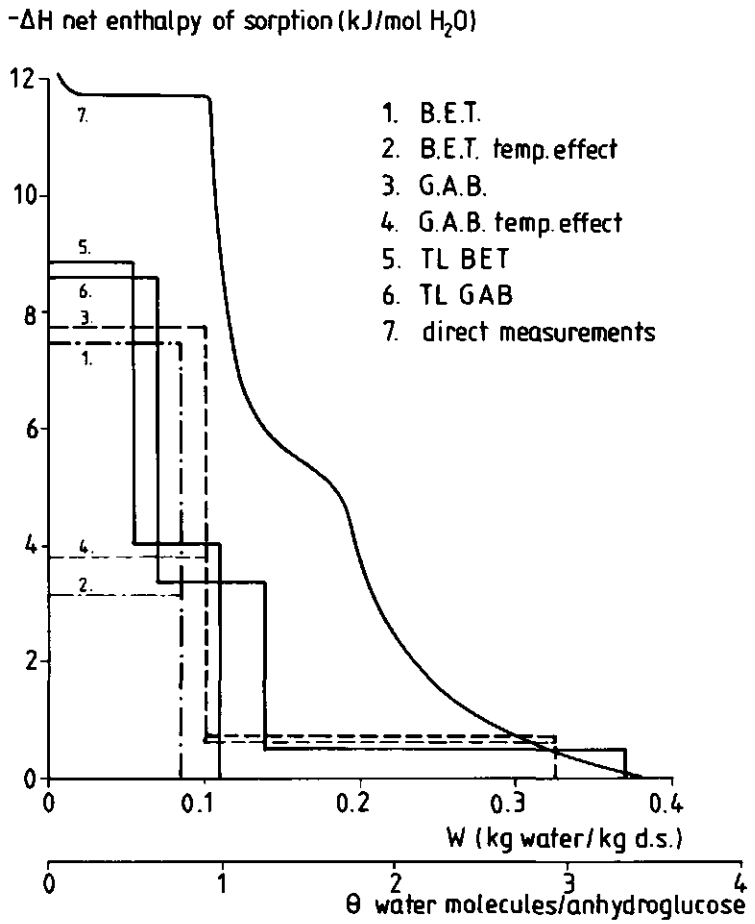

Figure 6.9. Comparison of molar net enthalpies of water (re)sorption as a function of water content for native potato starch, as derived from isotherm analysis using different sorption models, with directly determined results. The vertical boundaries for the first layer correlate with the various observed monolayer values of the sorption models. The end of the applicable a_w region for the G.A.B. and TLGAB equations determined the extent of the multilayer. Zero enthalpy corresponds to pure liquid water. See text.

the directly determined value than the direct parameter results of the same models of sorption. It is interesting to see that, parallel to the best isotherm descriptive ability, the G.A.B. model and its somewhat improved version TLGAB yield also for the interaction energy the best agreement with direct measurements.

6.4 COMPARISON WITH POLYMER-SOLVENT INTERACTION THEORY

6.4.1 Results obtained with the Flory-Huggins equation

The classical way, already proposed by Flory (1953, page 515) for testing equation (4.34), is to plot the observed values of the parameter χ for polymer-solvent interaction against ϕ, the volume fraction of polymer. Such plots for the relevant parts of the ten isotherms analysed before (Section 6.3) are shown in Figure 6.10. In order to relate mass and volume fractions of the polymer for potato and wheat starches we used the volumic mass values of 1 650 and 1 635 kg/m^3, respectively. This figure includes also the demixing limit (at $a_w = 1$) as predicted by (4.34) and the three upper values for χ that were calculated for polyanhydroglucose by the method of van Krevelen & Hoftyzer (1976). The latter values deviate strongly from ours. The curve which fits the observed values for native wheat starch (upper part) is identical to the one found earlier for the same starch by Taylor et al. (1961). The accuracy of the values thus calculated for χ is estimated at ± 0.010 - 0.015 beyond $\chi = 0.6$. Below this value, where χ is decreasing steeply with ϕ, the accuracy is somewhat lower. The decrease of χ with decreasing water contents (for starch even to about -2 at the lowest moisture levels) is commonly observed for water and polar polymers (Molyneux, 1975; Cohen Stuart, 1980, page 45). It demonstrates the strong interaction between water and the polymer, which evidently is not accounted for by the one-parameter equation of Flory and Huggins (4.34).

Figure 6.10 reveals interesting differences between the different starch samples. At these high water contents the observed χ values for wheat starch are higher than those for potato starch, although for the gelatinized samples in the constant upper part these differences are almost insignificant. In this moisture range, especially for native starches, water is a slightly better solvent for potato starch than it is for wheat starch. We may recall that in the low moisture range this affinity, as judged from the C values (Section 6.3), is the other way round. The first water molecules are somewhat more tightly bound by the more associated wheat starch, while the same association prevents the wheat starch granule to swell to the same extent as the potato starch granule.

The differences between native and gelatinized samples caused by destruction of the structure of the granule were mentioned earlier (Section 6.1). Rupturing of the granule by gelatinization and freeze drying produces a constant χ of about 0.76 without a visible hysteresis, between volume fractions for starch of 0.5 and 0.69. These values relate to water activities beyond $a_w = 0.9$. Thus in this range (4.34) describes the water sorption isotherm of the gelatinized samples accurately. Although more measuring points for the native starches in this moisture range would have been beneficial, it is

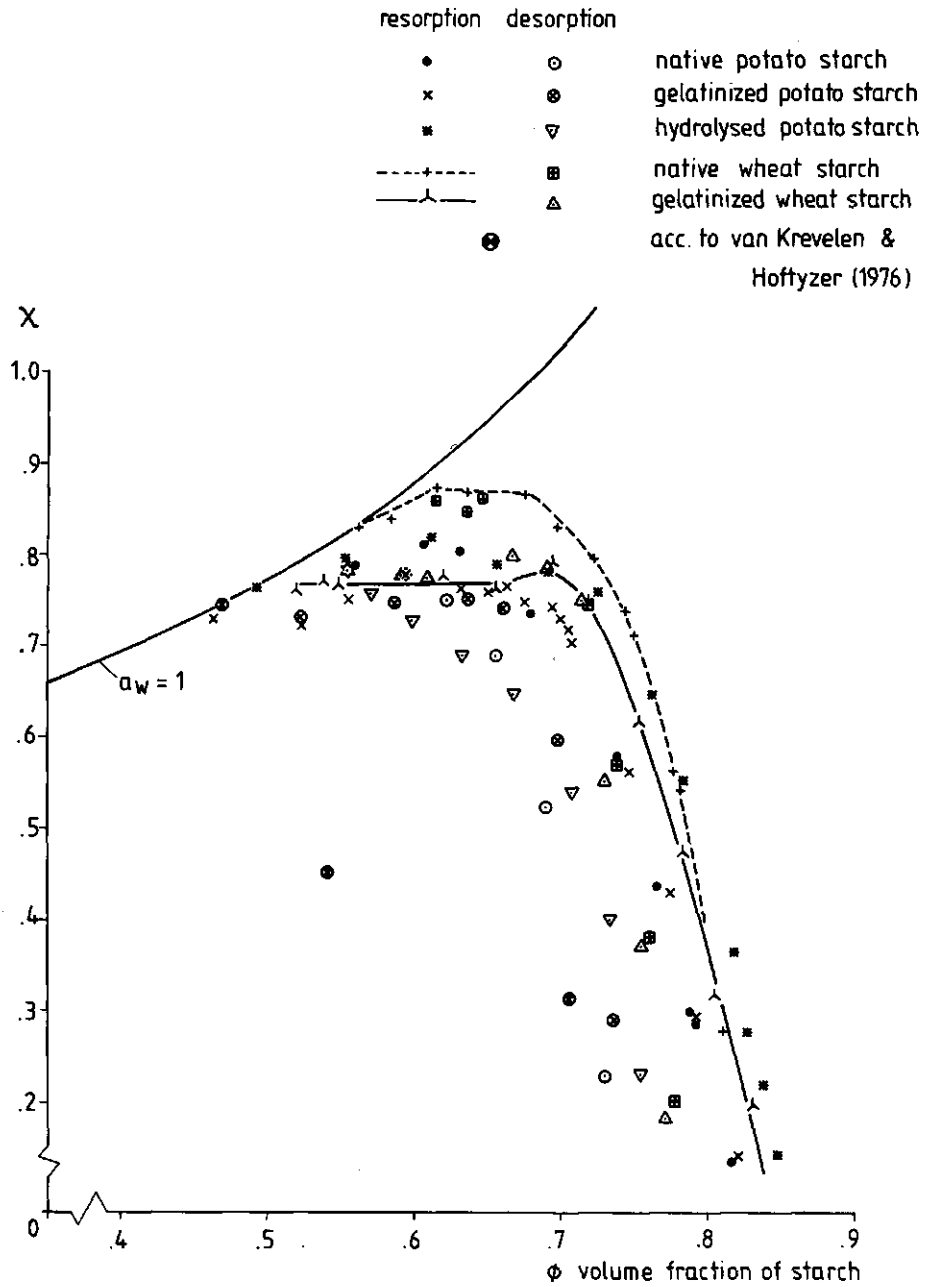

Figure 6.10. Experimental values of the polymer-solvent interaction parameter χ as a function of volume fraction of starch for five different starch samples, resorption and desorption.

clear that there are distinct differences with the gelatinized samples. The observed χ values for the native (and hydrolysed) samples are less constant and even display a slight maximum. Also the hysteresis effect, less so for native wheat starch, pertains to high water fractions. The observed maximum is most probably due to the uneven swelling properties of the granule. After the structure is sufficiently adapted, further water is taken up more easily. The maximum χ values relate to mass fractions of water of 0.32 for native wheat starch and 0.37 kg w./kg d.s. for both hydrolysed and native potato starch. At these moisture levels unrestricted (free) water is already amply available in the starch.

6.4.2 Interpretation in terms of some modified Flory-Huggins equations

In order to extend the range of isotherm description three extensions of the Flory-Huggins equation were compared with our data, two of them without success. One of the latter was derived recently by Kleintjens (1979) for branched polymers (amylopectin!). He derived the following concentration dependence for the interaction parameter χ:

$$\chi = \frac{(1 - \psi)\phi}{1 - \psi\phi} \cdot \chi_1 \qquad (6.1)$$

Here χ_1 denotes the theoretical ε/kT and ψ is a complicated semi-empirical parameter related to surface ratio, chain branching and other properties of interacting pairs of polymer segments and solvent molecules. This relation, however, was found to be unable to fit the observed values for water and starch any better than (3.34).

The second modification was proposed in Section 4.5 and is simple and obvious. It assumes the monolayer water to be part of the polymer. This makes χ a measure of the interaction between water and starch which is covered with one water molecule per sorption site. This correction affects both the volumic mass of the polymer and the mass fraction of water. In this extension the polymer volume fraction ϕ in (4.34) reads:

$$\phi = \frac{1 + W_1}{1 + W_1 + \rho(W - W_1)} \qquad (6.2)$$

where W is the mass fraction of water, W_1 is that of the monolayer and ρ is the volumic mass of starch (kg/10^{-3} m^3) containing W_1 kg w./kg d.s. Values for W_1 were taken from the former results of the B.E.T. and G.A.B. equations. Unfortunately, comparison of this new equation with the experimental data did not yield a constant level for χ values at relevant moisture ratios, not even for the gelatinized samples.

The third correction was the further reaching modification for a swelling gel with a Gaussian distribution of chain lengths between the network junctions and is given by (4.35). For the isotherms of the gelatinized samples equation (4.35) could not extend the applicable a_w range ($\sim 0.90 < a_w < 1$) which was observed for (4.34). For the native samples, however, (4.35) generally could describe the isotherms satisfactorily beyond $a_w \sim 0.83 - 0.88$. Apparently, for these samples Z corrects the non-constant χ in this range. For a thorough testing of this general conclusion the availability of more data points at these high moisture ratios would have been desirable. Only for native wheat starch more than five points were at our disposal in the relevant moisture range.

Table 17 gives the optimized results for five isotherms. Particularly noteworthy is the hysteresis effect displayed by the observed parameter values. Such hysteresis is hard to reconcile with a swelling gel containing fully flexible polymer chains and casts some doubt on the applicability of the model in case of a swelling starch granule. A jump in χ values between 0.7 and 0.4 would mean a significant difference in hydration between resorption and desorption. The effective chain length (Z) shows at the same time an improbable jump from 14 at resorption to 4.6 at desorption. An increase in the value of Z would be more likely for a gel containing more water during desorption when compared with resorption. Apparently starch granules are not cross-linked gels with a Gaussian chain distribution. For this case equation (4.35) can be seen as a phenomenological extension of (4.34) able to describe the isotherm at high moisture levels, but further with limited value.

Table 17. Results of isotherm analysis in terms of the Flory-Huggins equation corrected for swelling (4.35).

Sample	Applicable a_w region down to	χ	Z	Average deviation in a_w
NPR	0.88(4)	0.635	9.5	0.0101
NPD	0.88(4)	0.44	4.8	0.0057
HPR	0.85(5)	0.70	14.6	0.0048
HPD	0.85(5)	0.40	4.67	0.0015
NWR	0.82(8)	0.685	8.8	0.0132

Sample identification:
N = native; H = hydrolysed; P = potato starch; W = wheat starch; R = resorption; D = desorption
( ) number of data points incorporated in applicable a_w region

Another obvious extension connected with the results for the native samples is to account for the crystalline parts of the starch which do not sorb water beyond 0.3 kg w./kg d.s. A correction of this type shifts the results for the native samples somewhat towards those of the gelatinized products but it is not nearly able to bridge the entire difference. From this it might be concluded that dry native starch cannot be regarded simply as 30 wt% loose crystallites embedded in an otherwise amorphous mass.

6.5 A COMBINED MODEL FOR DESCRIPTION OF SORPTION ISOTHERMS OF WATER ON STARCH

Based on the foregoing results, this section briefly describes a combined model of sorption which is proposed for the description of entire water on starch isotherms. The proposed model combines the G.A.B. sorption theory in the low a_w range with that of Flory-Huggins, if necessary corrected for swelling, for the high a_w range. The transition between these two theories lies near $a_w \sim 0.9$. Close to this point also the mechanism of localized sorption in the water-starch system is succeeded by that of polymer-solvent interaction upon increasing hydration. The direct influence of the starch surface becomes negligible after about three molecules/monomer have been sorbed. By way of example, Figure 6.11 shows the isotherm description for native potato starch with equations (4.23) and (4.35).

A mathematical problem in combining the G.A.B. equation (4.23) with one of the Flory-Huggins type (4.34 or 4.35) is that the latter cannot be written explicitly in terms of volume fraction (or moisture ratio). Therefore, one single analytical equation cannot be given. Also, the transition between the two equations should have a continuous character. The two criteria for this transition are:

$$\begin{aligned} \theta(4.23) &= \theta(4.35) \\ \frac{\partial\theta(4.23)}{\partial a_w} &= \frac{\partial\theta(4.35)}{\partial a_w} \end{aligned} \qquad (6.3)$$

In view of the different curvatures of equations (4.23) and (4.35) at the point where they equalize, the second criterion is not guaranteed. In practice a mathematical procedure should help to smooth the transition. An example of this is incorporated in the next combined isotherm equation set:

$$\begin{aligned} \theta &= f \cdot (4.23) + (1 - f) \cdot (4.35) \\ & f = 1 \text{ at } a_w < 0.88 \\ & 1 > f > 0 \text{ at } 0.88 < a_w < 0.92 \\ & f = 0 \text{ at } a_w > 0.92 \end{aligned} \qquad (6.4)$$

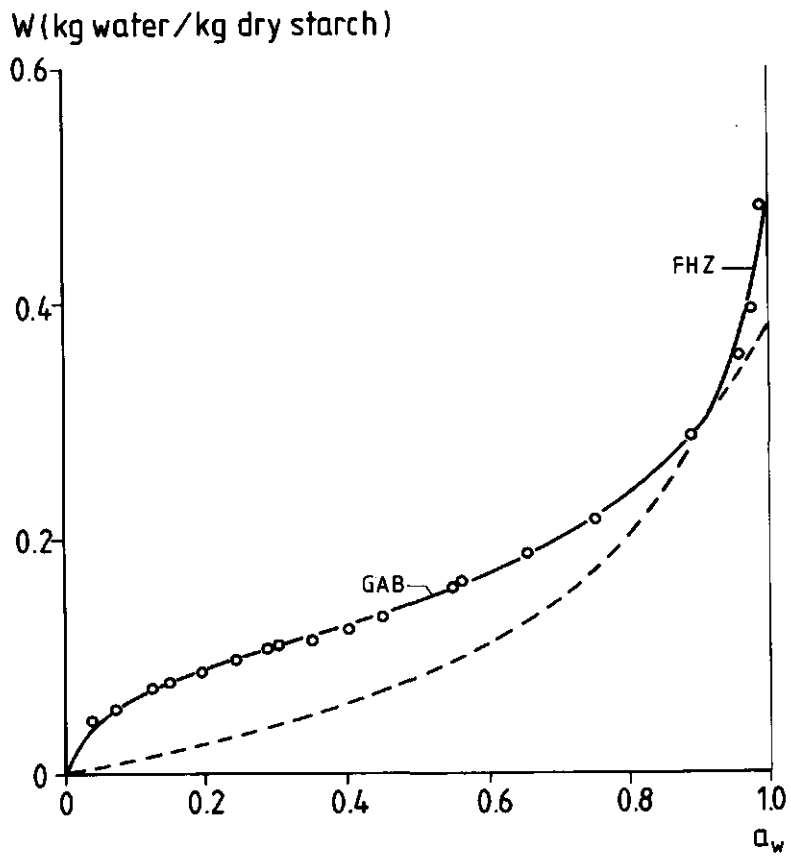

Figure 6.11. Description of the resorption isotherm of water vapour on native potato starch at 293.2 K by means of equations (4.23) and (4.35). Parameter values are: W_1 = 0.1012, C_G = 17.6, K = 0.74; χ = 0.635, Z = 9.5.

where f is an empirical factor weighing the mutual contributions of (4.23) and (4.35) in the combined model. The range $0.88 < a_w < 0.92$ was arbitrarily chosen and may be any range near $a_w = 0.9$ where the different equations should take over. For starches of which the granule structure is ruptured, instead of (4.35) equation (4.34) can be used yielding a set of equations which predict the isotherm with four parameters. These four or five parameters all have a physical meaning which is directly related to the sorption process.

Physically it would have been somewhat more elegant to base the combined model of sorption more strictly on added contributions from the different

starch parts to the sorption process. Theoretically, in case of partially crystalline starch a Langmuir term should be added to two multilayer sorption terms, one for the crystalline part (limited water uptake) and one for amorphous starch. To this end, a Flory-Huggins term must be added for the amorphous part. However, the boundaries between the different contributions cannot be judged on the basis of our results. At least sorption data of more crystalline starch would have to be available. Moreover, it remains difficult to say exactly where solution formation as a sorption mechanism becomes predominant over multilayer sorption. In this connection we just recall (Chapter 4) that with regard to their mathematical formulation the two mechanisms do not differ that much.

7 CONCLUSIONS

From the experimental results the model for sorption of water on starch as outlined in Section 3.6 was generally confirmed. The combined sorption mechanisms of localized (ad)sorption on homogeneous surfaces and polymer-solvent interaction are well illustrated by the adequate description of the entire sorption isotherm with two combined isotherm equations representing both mechanisms. These are the equation from the theories of Guggenheim, Anderson and de Boer (G.A.B.) up to $a_w \sim 0.9$, and that of Flory and Huggins beyond that value. The direct influence of the starch surface, with the anhydroglucose monomers as the sorption sites, becomes negligible after about three water molecules have been sorbed per site. This first sorbed water profoundly alters the starch characteristics due to its influence on the glass transition temperature.

Native starches from potato (B-type) and wheat (A-type) exhibit minor but distinct differences in sorption capacity, related to their differences in physical structure. Different treatments that change the native grain structure and its extent amounts of crystallinity influenced the sorption characteristics to a minor extent. Only complete destruction of the granule structure increased the amount of sorbed water significantly beyond $a_w \sim 0.91$. In that case sorption equilibria in this high moisture range were described by the simple Flory-Huggins equation with $\chi \sim 0.76$.

All starches show a significant hysteresis between resorption and desorption, granular starches do so even over the entire range of water activities. The cause of hysteresis is most probably uneven swelling. Destruction of the granular structure causes hysteresis to disappear beyond $a_w \sim 0.9$, while more crystalline, i.e. more rigid, samples (after partial hydrolysis) exhibit more pronounced hysteresis.

In the crystalline parts of native starches, water plays a specific role as the component of the crystalline structure. For B-starch these crystals are made up of a hexagonal arrangement in which starch helices are combined with structured water. Single helices are more likely to occur in this structure than double helices.

SUMMARY

The objective of this study was to obtain more insight in the interactions between water and starch in its solid state, especially the mechanism of water sorption and the specific role of water in the starch structure.
The structure and major water relations of native potato starch were reviewed and investigated and the results compared with those of some other starches such as native wheat starch. Later the study focuses at sorption isotherms for water vapour and their interpretation.
This thesis can be divided roughly into four main parts: (i) the broad introductory chapter 2, (ii) a discussion on water relations of starch in Chapter 3 (iii) the fourth Chapter on general sorption theories, and (iv) the experimental Chapters 5 and 6.

After introduction of the substances water and starch, their nature, and some properties of general importance, the physical structure of native starch is critically reviewed. Native starch is a unique natural deposit with crystalline and amorphous parts. Based on literature and some own results, an adapted model for the fine architecture of native potato starch is proposed. (Figure 2.9)

Subsequently, the major static aspects of water-starch interactions are reviewed, analysed, and in several cases amplified with own research results. Sorption isotherms, temperature influence, hysteresis, sorption mechanisms, state of aggregation and phase transitions, density relations, heat effect of interaction, diffusion, non-freezable water, and some results from NMR-spectroscopy for the starch-water system receive attention. Especially new in this discussion is the analysis of the glass-rubber transition temperature of starch and the action of water on it. Because water is a plasticizer of the amorphous parts of the starch structure it profoundly influences many physical properties of the starch-water system. Amorphous starch weakens when taking up water over the range between 0.11 and 0.25 kg water per kg dry starch and becomes gel-like beyond 0.30 kg w./kg d.s. The proposed structure of the mixed water-starch crystals (B-type) prevailing in native potato starch are briefly described. Dry B-starch crystals were found to extend their volume by approximately 5% when taking up about 25% water. The results from the analysis of the water relations are condensed into a detailed model (Section 3.6) proposed for water sorption on dry starch. Sorption is governed mainly by two mechanisms. These are localized sorption at homogeneous surfaces with the anhydroglucose monomers acting as sorption sites, and polymer-solvens interaction. The first water molecules are sorbed at sites with a binding energy exceeding that of two hydrogen bonds. The relaxation times of these first molecules are estimated in the same order as those of molecules in ice.

For the mathematical modelling of the sorption, theories belonging to both mechanisms are then reviewed and in some cases extended. In the case of localized sorption models based on the Langmuir and Brunauer, Emett & Teller theories, special attention is given to corrections for the deviating properties of molecules sorbed beyond the first one at a site, and to restriction of their number. Especially the correction for the average multilayer properties, proposed earlier by Guggenheim (1966), Anderson (1946), and de Boer (1953), denoted here with the acronym G.A.B., was founded to result in a powerful isotherm equation with three physically significant parameters. Also modifications accounting for differing properties between first and the second sorbed molecule and variation in the number of sorption sites with the adsorbed amount are described. Mutual relations between sorption models were analysed. As one of the results it was found that homogeneous sorption in multilayers is mathematically identical to depression of vapour pressure according to Raoult's law. In addition, the isotherm equation proposed by Hailwood & Horrobin (1946) for water sorption by polymers is identical to the G.A.B. equation. Further the Flory-Huggins polymer-solvent interaction theory and two modifications of it are briefly reviewed. The findings of this part are general and not restricted to starch.

The final part describes and discusses experimental isotherm results. Variation with respect to temperature of different origins and treatments (gelatinization and freeze drying, separation in components and partial hydrolysis) lead to somewhat deviating sorption characteristics. Only when the granule structure is destroyed, the sorption capacity beyond $a_w \sim 0.91$ increases significantly.
All starches exhibit significant sorption hysteresis and insignificant equilibrium instabilities, reflecting the strong influence of water on the structure of starch. The hysteresis is especially strong in the glass-rubber transition range. The effect is explained by uneven swelling.
With respect to water dry starches behave like physical sorbents, rigid until they are plasticized. The monomer sites remain predominant in the sorption process until they are covered with approximately three water molecules. This first part of the isotherm is well described by the G.A.B. equation (up to $a_w \sim 0.9$). Beyond this level the isotherm of gelatinized starch can be described with the simple Flory-Huggins equation with $\chi \sim 0.76$. For native starches this isotherm part can be predicted with the same equation corrected for swelling. An isotherm equation combining the G.A.B. model with three parameters and the Flory-Huggins equation with one or two parameters, all with physical significance, is able to predict the sorption isotherm of water vapour on starch accurately.

SAMENVATTING

Het onderwerp van deze studie zijn de *wisselwerkingen* tussen *water* en vast *zetmeel*. Zetmeel is de voornaamste energiedrager in onze voeding. Het is de hoofdcomponent van eetbare knollen en granen waarin het tijdens de groei wordt afgezet in de vorm van korrels. De vraag naar de binding van water aan zetmeel is niet alleen interessant voor voedingsmiddelentechnologen die zetmeelhoudende landbouwprodukten verwerken tot houdbare voedingsmiddelen. Ook voor technologen en chemici die zetmeel winnen in zuivere vorm en vervolgens verwerken tot vele produkten met zeer uiteenlopende eigenschappen, is dit van belang want droog zetmeel is sterk *hygroscopisch*, d.w.z. trekt krachtig water aan. De vraag naar de binding van water in bijv. een custardvla (zetmeelgel met een smaakje), zal bij ieder die dit leest wel eens opgekomen zijn. Dit onderzoek richtte zich echter niet zo zeer op gelen en oplossingen van zetmeel (zetmeel in overmaat water) maar op het drogere gebied (water in overmaat zetmeel). Deze laatste zetmeel-water systemen, waarvan veel minder bekend is, hebben een niet meer verzadigde dampspanning. Bij kamertemperatuur, zonder toepassing van conserveermiddelen, is een produkt pas houdbaar bij dampspanningen beneden 70% van de verzadigingswaarde (*wateractiviteit* of *relatieve dampdruk* < 0.7).

Qua aard valt dit onderzoek zowel onder de *grensvlak fysische chemie* als wel onder de *polymeer fysica*. Dit komt doordat als water met droog zetmeel in aanraking komt, het kleine, polaire watermolecule een sterke binding aangaat met de iets grotere, eveneens polaire bouwstenen (*anhydroglucose-monomeren*) van de gigantische zetmeelmoleculen. Deze binding wordt voornamelijk bepaald door waterstofbruggen die een aanzienlijke bindingsenergie hebben (20-25 kJ/mol). De eerste ongeveer 10 gew. % water in zetmeel heeft een bindingsenergie groter dan die van twee waterstofbruggen. Zowel water als zetmeel veranderen sterk onder elkaars invloed. Een watermolecule in aanraking met een droog zetmeeloppervlak gaat veel meer lijken op een molecule in ijs dan op één in water, terwijl het zetmeel dat in droge vorm hard en bros is, voorbij ca. 10 gew. % water langzamerhand week wordt doordat delen van het zetmeelmolecule beweeglijk worden. Bijna alle eigenschappen van zetmeel worden hierdoor beïnvloed. De monomeren van zetmeel kan men zien als het *oppervlak* waarop water *adsorbeert* (ongeveer één watermolecule per monomeer). Omdat echter dit oppervlak zo bijzonder groot is en direct de homogeen verdeelde moleculaire bouwstenen van het zetmeel betreft, is het niet mogelijk hier goed onderscheid te maken tussen waterbinding als *grensvlak*- of *bulk*-verschijnsel, d.w.z. tussen *ad*sorptie (aan oppervlakken) of *ab*sorptie (moleculair verdeeld in de andere stof). Het liefst gebruiken we hiervoor dan ook de algemene term *sorptie*. Dit te meer daar de sterke invloed van zetmeel op het gesorbeerde

water is weggeëbd zodra ongeveer 3 watermoleculen per monomeer aanwezig zijn en het sorptiemechanisme van aard verandert. Voorbij dat punt hebben watermoleculen hun eigenschappen die vrijwel identiek zijn aan die in vrij water en is het grootste (amorfe) deel van het zetmeel geheel week en flexibel (gelachtig) geworden. De waterdampspanning van het mengsel nadert dan al tot de verzadigingswaarde.

Dit proefschrift bevat globaal vier delen: (i) een algemeen inleidend hoofdstuk 2, (ii) een discussie over de belangrijkste water relaties van zetmelen vanuit een voornamelijk fysisch chemische optiek in hoofdstuk 3, (iii) hoofdstuk 4 beschrijft relevante sorptietheorieën en (iv) het eigenlijke onderzoek is beschreven in de hoofdstukken 5 en 6.

Na introductie van de stoffen water en zetmeel wordt in hoofdstuk 2, naast enige algemene eigenschappen vooral de fysische structuur van natief zetmeel behandeld. Vooral over aardappelzetmeel is veel bekend. Dit type zetmeel werd gekozen als onderzoeksobject dat waar mogelijk werd vergeleken met tarwezetmeel. Natieve zetmelen hebben amorfe en kristallijne delen die per zetmeelsoort verschillende kristaltypen kunnen vertonen. Zo bevat tarwezetmeel een z.g. A-type kristal en aardappelzetmeel een B-type. Met behulp van literatuurgegevens en enkele eigen onderzoeksresultaten kon een aangepast model worden opgesteld voor de ultrastructuur van natief aardappelzetmeel dat ongeveer 30% kristallijne delen bevat.

Hoofdstuk 3 geeft een overzicht van de stand van kennis over sorptie- (of dampdruk) isothermen voor waterdamp (de relatie tussen watergehalte en wateractiviteit), de invloed van de temperatuur hierop, iets over hysterese, d.i. het verschil dat wordt gevonden tussen bevochtigen en drogen en vervolgt met een analyse van enkele belangrijke water relaties van zetmelen. Behandeld worden de aggregatietoestand en faseovergangen in zetmeel, dichtheid, warmteeffect bij menging van water en zetmeel, diffusie, niet-bevriesbaar water en enkele resultaten van NMR spectroscopie. Zowel literatuurgegevens als eigen onderzoeksresultaten worden gebruikt. Uit deze analyse komt globaal het beeld van wisselwerkingen naar voren dat hiervoor is beschreven.

Vervolgens werden sorptietheorieën onderzocht en deels aangepast om de gemeten dampdrukisothermen wiskundig te kunnen beschrijven met behulp van de twee sorptiemechanismen die, blijkens het geschetste sorptieproces, de interacties tussen water en zetmeel voornamelijk beheersen. Dit zijn gelocaliseerde sorptie op een homogeen oppervlak èn polymeer-oplosmiddel interactie volgens de theorie van Flory en Huggins (Flory, 1953). Aan gelocaliseerde sorptie die het grootste deel van de isotherm bepaalt, is het meeste aandacht gegeven. Als uitgangspunt dienden de theorieën van Langmuir (1918) en Brunauer, Emmett & Teller (B.E.T., 1938). De belangrijkste aanpassingen die

werden onderzocht zijn correcties voor de eigenschappen van de moleculen die sorberen voorbij de zgn. monomoleculaire laag. In de B.E.T. theorie worden deze moleculen verondersteld simpelweg vloeistofeigenschappen te bezitten. Het bleek dat een correctie hiervoor, eerder onafhankelijk van elkaar voorgesteld door Guggenheim (1966), Anderson (1946) en de Boer (1953), een krachtige isothermvergelijking (hier G.A.B. genoemd) opleverde welke de experimentele isotherm over 90% van zijn traject kan beschrijven met maar drie parameters, alle met belangrijke informatie over het sorptieproces. Ook enkele andere mogelijke correcties en onderlinge relaties tussen sorptietheorieën werden geanalyseerd. De resultaten hiervan zijn van algemene aard en niet beperkt tot zetmelen.

Het laatste deel beschrijft en interpreteert meetresultaten van dampdrukisothermen. De invloeden worden beschreven van isothermtemperatuur op vier niveaus, van oorsprong (aardappel, tarwe en manioc) en van verschillende behandelingen (geleren en vriesdrogen, scheiding in componenten en gedeeltelijke hydrolyse). De in het algemeen geringe verschillen welke hiervan het gevolg zijn worden verklaard op grond van verschillen in physische structuur tussen de monsters. Alleen geleren en vriesdrogen (vernietiging van de korrelstructuur) leidt tot een aanzienlijk hogere sorptiecapaciteit boven een wateractiviteit van 0.91. In dat gebied kan de isotherm goed worden beschreven met de polymeer-oplosmiddel wisselwerking theorie van Flory en Huggins. Voor gegeleerde monsters kan dit met slechts één parameter ($\chi \sim 0.76$), andere monsters behoeven een tweede parameter om de zwelling te verdisconteren. De gehele isotherm kan dus worden beschreven met in totaal vier of vijf parameters in de gecombineerde isothermvergelijking van beide sorptietheorieën.
Waarin de theorie niet goed voorziet is het hysterese effect en de kleine instabiliteiten in gemeten isothermen die vooral werden veroorzaakt doordat zetmeel zo grondig verandert onder invloed van water. Hysterese is het grootst in het gebied waar zetmeel week wordt; het verdwijnt in het hoogste vochtgebied (wateractiviteit >0.9) bij geleerde monsters en wordt daar juist groter na gedeeltelijke afbraak van de amorfe korreldelen. Ongelijke zwelling tijdens drogen en bevochtigen van het polymeer zetmeel is vrijwel zeker hiervan de belangrijkste oorzaak. Dit verschijnsel illustreert ook fraai de gecompliceerde wisselwerking tussen beide stoffen waarvan de grote lijn uit het bovengeschetste beeld duidelijk wordt, doch waarin vele interessante details nadere opheldering behoeven.

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APPENDIX 1

LITERATURE VALUES FOR VOLUMIC MASS OF STARCH WITH INFORMATION ON METHOD OF MEASUREMENT AS FAR AS AVAILABLE FROM THE REFERENCE

reference	sample of starch	mass fraction of water (kg w./kg d.s.)	volumic mass (kg/m^3)	temperature K	method of determination
1.	native potato	air-dry	1500 - 1503	290 - 291	
		dry	1633.3	"	
	native marantha	air-dry	1504	"	
		dry	1565	"	
2.	native wheat	conc. H_2SO_4	1625.8	293	py water
		54 days, partial vacuum	1429.2	"	py petr. aether
		conc. H_2SO_4	1624.4	"	py water
		13 days, partial vacuum	1453.1	"	py chloroform
		dried at 373 K	1490.3	"	py chloroform
		with dry H_2 stream	1617.3	"	py water
3.	native potato	dry	1650	290.5	py water (starch table average)
4.	native potato	dry	1648	290.5	(probably: py water)
	native maize	dry	1620	"	
	native wheat	dry	1629	"	
5.	native potato	air-dry ($\sim$ 0.25)	1442	293	dg benzene-carbon tetrachloride

reference	sample of starch	mass fraction of water (kg w./kg d.s.)	volumic mass (kg/m^3)	temperature K	method of determination
6.	native maize	dry	1635 - 1640	288.7	py water (starch table average)
7.	native wheat	air-dry	1500.4	293	py palatin oil
8.	native wheat	dry	1633.5	293	py water (starch table average)
9.*	native potato	~ 0	1512	293	dg chloroform-carbon tetrachloride
	gelatinized potato	~ 0	1508	"	"
		0.029	1515	"	"
		0.216	1425	"	"
		1.45	1175	"	"
10.*	native potato	dry	1511	303	py xyleen
	native wheat	dry	1542	"	"
	native maize	dry	1517	"	"
	native manioc	dry	1521	"	"
	native rice	dry	1510	"	"
	native sorghum	dry	1500	"	"
11.	native potato	vacuum dry	1650		
	native rice	vacuum dry	1646		

reference	sample of starch	mass fraction of water (kg w./kg d.s.)	volumic mass (kg/m³)	temperature K	method of determination
12.*	native potato	0.1095	1499.3	298	py paraffin oil
		0.2082	1461.0	"	"
		0.2953	1426.7	"	"
		0.3951	1388.8	"	"
13.	dissolved potato	dry	1666.7		py water
14.	native wheat	dry	1600 (± 20)	293	dye dilution method
		0.45	1330 - 1370	"	"
15.	native wheat	dry	1583 - 1596	293	py water (starch table average)
16.	dissolved soluble starch (Merck)	(probably 0.11)	1533	313	oscillation method, water Paar densimeter
17.*	native potato	~ 0	1486		
		0.177	1426		
		0.399	1383		
		0.917	1259		
18.	native starch (average value)	dry	1625 (for potato starch somewhat higher)		

py = pycnometer; dg = density gradient column

* more data are given in original reference

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13. Lamm (1934)
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16. El-Saied (1979)
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APPENDIX 2

ISOTHERM DATA FOR WATER VAPOUR SORPTION OF DIFFERENT STARCH SAMPLES.
Pairs of W (kg w./kg d.s.) and a_w. Temperature 293.16 K.

resorption		desorption	
W	a_w	W	a_w
Native wheat starch			
0.0460	0.04045	0.6084	1.0000
0.06515	0.08775	0.3853	0.9863
0.09015	0.1981	0.3527	0.9694
0.1017	0.2705	0.3352	0.9679
0.12535	0.4013	0.2402	0.8485
0.14345	0.5131	0.2179	0.7483
0.1718	0.6665	0.1938	0.6405
0.1767	0.6836	0.1739	0.5458
0.2057	0.7929	0.1556	0.4540
0.2119	0.8129	0.1472	0.4021
0.2351	0.8663	0.1393	0.3556
0.2658	0.9109	0.1278	0.3101
0.2947	0.9485	0.1267	0.2997
0.3516	0.9787	0.1217	0.2846
0.3835	0.9911	0.1151	0.2419
0.4373	0.9938	0.0965	0.1729
0.4780	0.9993	0.0877	0.1305
0.6084	1.0000	0.0836	0.1158
		0.0670	0.0747
		0.0567	0.0494
		0.0536	0.0429
Wheat starch, gelatinized and freeze dried			
0.0365	0.0387	0.5685	0.9923
0.0410	0.0500	0.4946	0.9876
0.0490	0.0713	0.4271	0.9711
0.0676	0.1249	0.3951	0.9591
0.0714	0.1494	0.3058	0.9265
0.0818	0.1999	0.2769	0.9009
0.0939	0.2506	0.2461	0.8566
0.0975	0.2755	0.2283	0.7550
0.1029	0.3058	0.2009	0.6479

resorption		desorption	
w	a_w	w	a_w
0.1124	0.3629	0.1824	0.5540
0.1186	0.4133	0.1565	0.4612
0.1251	0.4469	0.1493	0.4077
0.1494	0.5389	0.1409	0.3572
0.1713	0.6385	0.1260	0.2866
0.2019	0.7463	0.1165	0.2442
0.2418	0.8539	0.1060	0.1929
0.2708	0.8981	0.0685	0.0750
0.3241	0.9224	0.0583	0.0500
0.3776	0.9530		
0.5069	0.9847		
0.5274	0.9891		
0.5685	0.9923		

Native potato starch

0.0451	0.0399	0.4819	0.9875
0.0552	0.0746	0.4156	0.9679
0.0729	0.1258	0.3685	0.9417
0.0777	0.1504	0.3200	0.8932
0.0877	0.1962	0.2732	0.7940
0.0976	0.2434	0.2247	0.6342
0.1086	0.2934	0.1958	0.5225
0.1106	0.3012	0.1564	0.3655
0.1140	0.3504	0.1432	0.3062
0.1244	0.4027	0.1278	0.2720
0.1348	0.4526	0.1146	0.2191
0.1600	0.5523	0.0985	0.1515
0.1632	0.5614	0.0905	0.1258
0.1873	0.6542	0.0713	0.0751
0.2164	0.7532	0.0631	0.0595
0.2869	0.8887	0.0590	0.0501
0.3552	0.9560	0.0541	0.0426
0.3945	0.9740		
0.4819	0.9875		

Potato starch, gelatinized and freeze dried

0.0354	0.0394	0.7055	0.9980
0.0393	0.0494	0.5561	0.9831
0.0481	0.0747	0.4288	0.9620

resorption		desorption	
w	a_w	w	a_w
0.0631	0.1250	0.3460	0.9309
0.0682	0.1504	0.3117	0.9079
0.0782	0.1929	0.2635	0.8130
0.0875	0.2348	0.2184	0.6467
0.0983	0.3025	0.1951	0.5430
0.1108	0.3504	0.1839	0.4943
0.1216	0.3960	0.1585	0.3939
0.1328	0.4495	0.1448	0.3474
0.1605	0.5548	0.1380	0.3019
0.1780	0.6384	0.1282	0.2737
0.2070	0.7328	0.1129	0.2052
0.2528	0.8459	0.0966	0.1491
0.2556	0.8553	0.0896	0.1256
0.2614	0.8662	0.0720	0.0758
0.2687	0.8772	0.0654	0.0612
0.2927	0.8981	0.0597	0.0500
0.3100	0.9165	0.0545	0.0422
0.3284	0.9250		
0.3551	0.9397		
0.4160	0.9686		
0.4862	0.9766		
0.5548	0.9814		
0.7055	0.9980		

Potato starch, hydrolysed native

0.0332	0.0416	0.6276	1.0000
0.0452	0.0679	0.4885	0.9875
0.0593	0.1121	0.4580	0.9733
0.0691	0.1554	0.4077	0.9486
0.0757	0.1893	0.3541	0.9123
0.0825	0.2342	0.3025	0.8656
0.0943	0.2838	0.2513	0.7789
0.1035	0.3497	0.2212	0.6894
0.1098	0.3974	0.1980	0.5976
0.1179	0.4399	0.1806	0.5097
0.1272	0.4797	0.1552	0.4127
0.1354	0.5286	0.1453	0.3638
0.1689	0.6681	0.1325	0.3075
0.1908	0.7448	0.1250	0.2700
0.2306	0.8473	0.1150	0.2177

resorption		desorption	
w	a_w	w	a_w
0.2726	0.8981	0.0951	0.1624
0.3198	0.9330	0.0879	0.1340
0.3863	0.9733	0.0668	0.0830
0.4913	0.9921	0.0511	0.0530
0.6276	1.0000	0.0431	0.0396

Native potato starch at four different temperatures

275.7 K

0.0675	0.0700
0.0816	0.1124
0.1107	0.2490
0.1315	0.3640
0.1392	0.4050
0.1513	0.4306
0.1898	0.5970
0.2047	0.6400
0.2440	0.7554
0.2505	0.7730
0.2803	0.8300
0.3125	0.8820
0.3591	0.9250
0.4917	0.9865

293.2 K

0.0536	0.0661
0.0680	0.1131
0.09215	0.20115
0.1179	0.3307
0.1535	0.4910
0.1773	0.5914
0.19225	0.65155
0.2222	0.7500
0.3100	0.9000
0.4491	0.9759

313.2 K

0.0440	0.0626
0.0585	0.1121
0.0742	0.1870

0.0925	0.2650
0.1025	0.3160
0.1039	0.3288
0.1250	0.4550
0.1400	0.5317
0.1598	0.6155
0.1985	0.7468
0.2183	0.8232
0.2648	0.8920
0.4146	0.9641

340.2 K

0.0690	0.2138
0.0819	0.2833
0.1179	0.4958
0.1290	0.5300
0.1668	0.7485
0.1868	0.7970
0.2334	0.8700

PERSOONLIJKE GEGEVENS

Op 19 juli 1943 werd ik geboren te Baambrugge (gemeente Abcoude). Wat meer bewust groeide ik op in Tiel, waar ik na het lager onderwijs de HBS-B opleiding volgde. In 1960 volgde mijn studie aan de Landbouwhogeschool, richting levensmiddelentechnologie, welke in september 1968 werd afgerond. Tijdens mijn studie deed ik praktijkervaring op bij enkele fruitverwerkende bedrijven in Israel en Frankrijk en bij de Gist- en Spiritusfabrieken in Delft. Van september 1968 tot februari 1969 was ik als tijdelijk docent technologie verbonden aan de Hogere Agrarische Scholengemeenschap te 's Hertogenbosch. Vanaf maart 1969 ben ik als wetenschappelijk medewerker aan de Landbouwhogeschool werkzaam in onderwijs en onderzoek. In het kader van de ontwikkelingssamenwerking verbleef ik in 1973 bijna drie maanden aan de Universiteit van Ife, Nigeria, voor een samenwerkingsproject met de jonge afdeling Food Science and Technology, aldaar.
Mijn vakgerichte belangstelling gaat vooral uit naar waterrelaties van voedingsmiddelen, met name voorspelling van wateractiviteit, naar simultane processen voor de winning van plantaardige olie en eiwit en aspecten van aangepaste technologie bij de verwerking van agrarische produkten.

Druk: Verweij Wageningen b.v.