

CLAY-ORGANIC INTERACTIONS

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by

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Based on research carried out in the department of chemistry
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N.I.H.E. Dublin

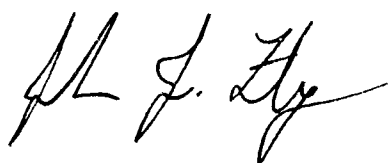
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DECLARATION

I declare that the work described within this thesis is all my own work.

A handwritten signature in cursive script, appearing to read 'J. J. Flynn', written in black ink.

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ABSTRACT

The aim of this present work was to study the interaction of various organic compounds with a range of cation exchanged montmorillonites. The first part of the study involved investigating the rate of sorption of methanol, Propan-2-ol (1-propanol), 2-methyl-propan-2-ol (t-butanol), tetrahydropyran (THP), tetrahydrofuran (THF), and 1,4-dioxan, onto a Wyoming montmorillonite saturated with Al^{3+} , Cr^{3+} , or Fe^{3+} -cations using isothermal gravimetry in the temperature range 18° - 105°C , using samples of differing weights and grain size distributions. The sorption rates for all the compounds increased with decreasing sample and grain size demonstrating that inter- rather than intraparticle mass transfer was the rate limiting process. The optimum sample parameters (2mg sample of $<45\mu\text{m}$ grain size, pretreated at 120°C with a vapour flow of $>200\text{cm}^3\text{min}^{-1}$) yielded integral diffusion coefficients at 18°C of $1.1 \times 10^{-14}\text{m}^2\text{s}^{-1}$ for t-butanol for the Cr^{3+} -form, and $2.0 \times 10^{-14}\text{m}^2\text{s}^{-1}$ for methanol and 1-propanol for the Al^{3+} -form, $0.5 \times 10^{-14}\text{m}^2\text{s}^{-1}$ for 1,4-dioxan for the Cr^{3+} -clay, and $3.5 \times 10^{-14}\text{m}^2\text{s}^{-1}$ for THF and $2.4 \times 10^{-14}\text{m}^2\text{s}^{-1}$ for THP both on Al^{3+} -clay. In general the sorption rate decreased as $\text{THF} \gg \text{THP} > \text{methanol} \gg 1\text{-propanol} > \text{t-butanol} > 1,4\text{-dioxan}$. For the alcohols sorption rate no temperature dependence was found, but the rate was found to be dependent on the cations present with $\text{Fe}^{3+} < \text{Cr}^{3+} < \text{Al}^{3+}$. In general the cyclic ether sorption rate of THF and THP was dependent on concentration or the 1,4-dioxan sorption rate was retarded by bidentate coordination to Al^{3+} -ions at the edges of the clay platlets.

The second part of the investigation involved the examination of the interactions of the alcohols and cyclic ethers with various cation exchanged montmorillonite. Variable temperature (20° , 50° , 100° , 150° , and 200°C) infra-red and temperature programmed desorption profiles (20° - 800°C) were recorded for Na^{+} , Ca^{2+} , Al^{3+} , Fe^{3+} , and Cr^{3+} -exchanged montmorillonite, presaturated with methanol, propan-1-ol (n-propanol),

1-propanol, t-butanol, THF, IHF, and 1,4-dioxan. The alcohol saturated trivalent cation-exchanged samples exhibit desorption maxima at 20° and 110°C (methanol), 30° and 160°C (n-propanol), 20° and 110°C (1-propanol), and 30°, 50°, and 70°C (t-butanol). The alcohol saturated Na⁺ and Ca²⁺-montmorillonite exhibit desorption maxima at higher temperatures than in the 1-propanol (20° and 140°C) and t-butanol (30°, 90° and 110°C) desorption profiles, but at the same temperature for methanol and n-propanol. This behaviour is interpreted in terms of acid-catalysed dehydration of 1-propanol and t-butanol to alkenes, and n-propanol to di-prop-1-yl ether over M³⁺-exchanged montmorillonite. The cyclic ether saturated montmorillonite exhibit little uniformity in the positions of the desorption maxima from the different cation exchanged forms, (listed in Table 6.111.), but some trends are discernable and these results are interpreted as acid-catalysed ring opening of the THF and IHF to form alkenes which would undergo oligomerisation in the M³⁺-montmorillonites. 1,4-Dioxan was found to desorb without modification, indicating that in both a dynamic and an equilibrium sense, 1,4-dioxan is relatively stable towards acid attack in these systems.

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CHAPTER 1

1.1 Clay Minerals an Introduction

In the following thesis some of the properties of Wyoming Montmorillonite clay will be investigated and later discussed. The term 'clay' may be considered from two perspectives, firstly the mineralogical term clay

This refers to a group of mineral compounds, the products of weathering, formed by hydrothermal action and deposited as sediment. Grim¹ defines clay as a natural, earthy, fine-grained material, which develops 'plasticity' if mixed with a limited amount of water. Plasticity means the ability of the clay to be deformed under applied pressure, with retention of the deformed shape upon removal of the applied pressure.

The second perspective is the particle size definition of a clay. The Wentworth² scale defines a clay as any material whose particle size is $4\mu\text{m}$ or less in any soil or naturally occurring earthy material. This scale is primarily used to define a clay mineral in geological and mineralogical investigations

throughout this thesis a slightly different particle size definition of a clay mineral will be used. The technique of slaking a clay in water is commonly used to separate clay minerals from non-clay mineral components in a soil or naturally occurring earthy material. When the soil is slaked the larger particles sink to the bottom, leaving the fine-grained clay minerals in suspension, and the larger clay mineral particles break down to a particle size of $2\mu\text{m}$ or less. The suspended clay particles may be collected and sedimented to give a reasonably pure clay mineral fraction. (this process of separating clay from non-clay minerals is covered in greater detail in section 2),

of a particle size not greater than 2 μ m.

The investigation of the structure and properties of clay minerals has become a precise science. However the use of, and experimentation with clays, dates from antiquity, when the earliest earthenware vessels and ceramics were made. The first serious scientific investigations of montmorillonite clay began much more recently, when in 1847 Damour and Salvett⁴² gave the name montmorillonite to a clay from the Montmorillon region of France. At this time some of the properties of clays were being studied and the results documented, (eg. in 1852 Way³ investigated the ability of clays to adsorb organic compounds (manures))

The chemical analysis of the clays, whose physical properties were being examined, yielded little information. It was found that all clay minerals had very similar chemical compositions, consisting of mainly silica, alumina, magnesia and water in varying amounts. However these clays of similar chemical composition exhibited very different physical properties. The difficulty in obtaining a reasonably pure clay mineral, and the fine-grained nature of the clay, caused this situation to persist until the middle of this century. The development of separation and preparation techniques for purifying clays, combined with the electron microscope, infra-red, X-ray and differential thermal analysis techniques have led to a rapid increase in the knowledge and understanding of the relationship between the chemical composition or structure of the clay and the physical properties of that clay mineral.

Clay minerals are today described as hydrous aluminium (or magnesium) silicates. All clays have these fundamental components with appreciable amounts of iron, alkalies, alkaline

earths and water. The great diversity of properties and similarity of composition is explained by the differences in the structural arrangements of these chemical components, which gives rise to the diverse physical properties.

Simply clays may be described as layer silicates, that is, comprised of layers or sheets where each sheet is a two dimensional polymer of one of two basic unit cells. A very brief mention of the structure of the 2:1 type layer silicate, montmorillonite will serve to illustrate the basic structure of a clay, (see Fig 1.1.)

The silicate layers are made up of three sheets, formed from two basic structural units. The basic structural unit of the tetrahedral sheet is a silicon cation with four oxygen ions or hydroxyl groups, tetrahedrally coordinated about the cation. In a 2:1 type clay, two of these sheets are separated by an octahedral sheet, which is a two dimensional polymer of an aluminium cation octahedrally coordinated by six oxygen ions or hydroxyl groups. (this structure is outlined in much greater detail in the following chapter).

These layers of silica and alumina sheets carry a net negative charge, (when isomorphous substitution has occurred). It is this charge on the layers that gives rise to many of the properties of a montmorillonite clay. Substitution of cations of a different charge, than aluminium or silicon into the sheet structure causes this accumulation of negative charge on the clay layers. This excess charge on the clay layers is balanced by the sorption of additional exchangeable cations between the layers, (ie interlayer cations)

The charge on the layers also helps to maintain

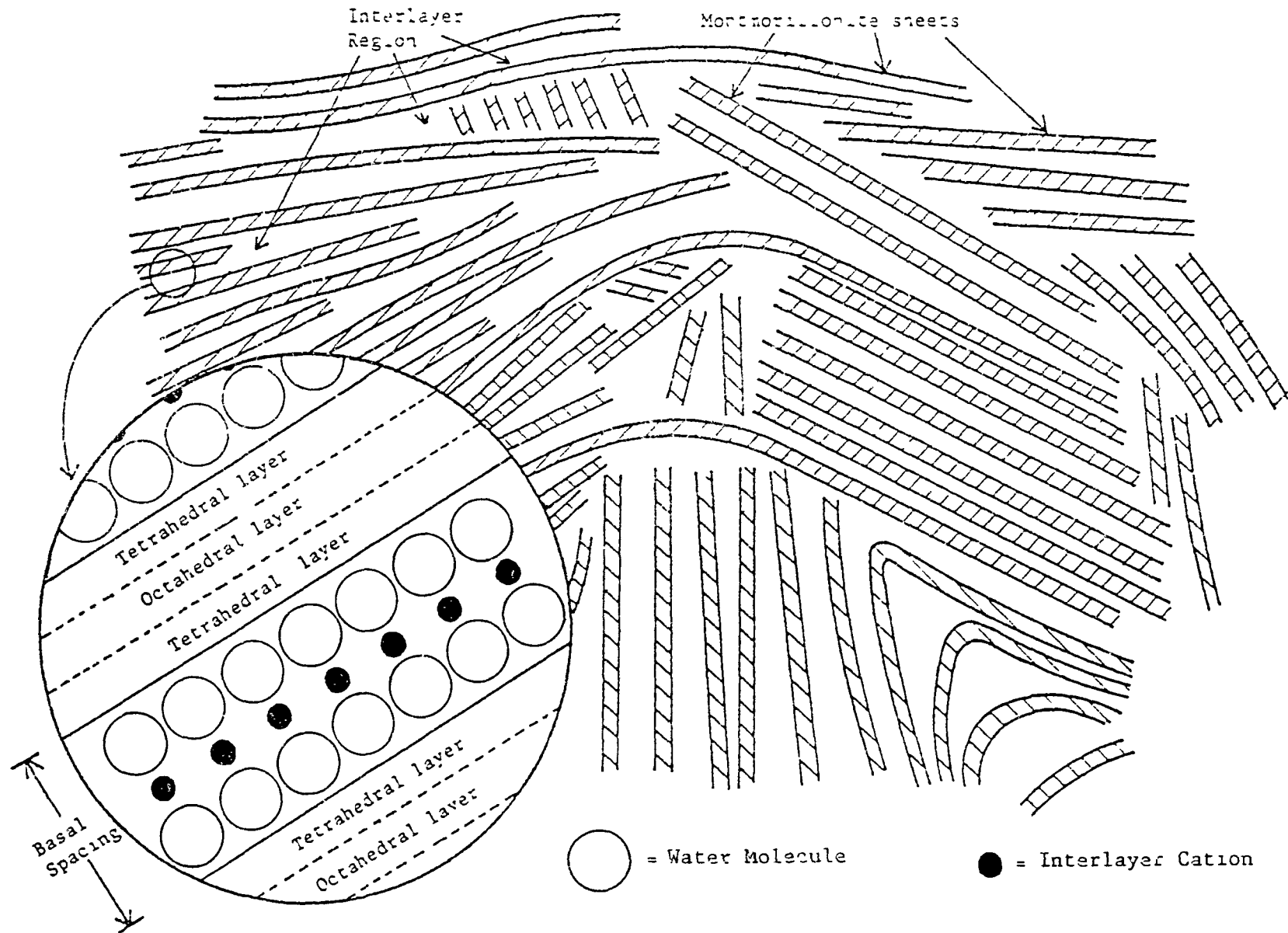


Figure 4

Fig 1.1. Schematic diagram of a clay grain, showing interlayer region in the insert. (adapted from Cebula et al⁸⁶)

the clay in a stable structural state. The electrostatic interactions between the negatively charged layers and the interlayer cations, combined with Van Der Waals forces and hydrogen bonding between the water molecules of the hydration sphere of the interlayer cations and the oxygen molecules and the hydroxyl groups of the tetrahedral sheets, bind the layers together.

The diversity of physical properties in clays with a similar structure is due to the possible substitution of cations in any of the three types of sites, ie. tetrahedral, octahedral or interlayer. An example of this is the swelling property of montmorillonite, that is the ability of the clay to absorb water into the interlayer space and so expand or swell. Although common in many clay types, it is the feature of montmorillonite that gives rise to one of its newer applications as a solid acid catalyst.

Ion exchanged montmorillonites may be used to successfully catalyse a great variety of chemical reactions. Table 1.i. gives a brief outline of the types of reactions for which this type of solid acid catalysts have been used. This is a short synopsis from a long list of reactions for which cation-exchanged montmorillonites may be used. If the formation of ethers is examined more closely, using reaction type 2 (from table 1.i.), the formation of Methyl-t-Butyl Ether (MTBE) from Methanol and Isobutene occurs, as an example. Then under certain conditions the acid catalyst will give a high yield of MTBE with very little production of impurities due to side reactions as shown by Adams et al⁶. The interest in the production of MTBE is due to its application as an alternative, non-lead based compound added to gasoline (or petrol), to increase

TABLE 1.i.

<u>No.</u>	<u>Reaction Type.</u>	<u>Reference.</u>
1.	Alkene + Water = Alcohol eg. $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} = \text{C}_2\text{H}_5\text{OH}$	5,6
2.	Alkene + Alcohol = Ether. eg. $\text{CH}_3\text{OH} + \text{CH}_2=\text{C}(\text{CH}_3)_2 = \text{CH}_3-\text{O}-\text{C}(\text{CH}_3)_3$	7,8
3.	Alkene + Carboxylic Acid = Ester. eg. $\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{COOH} = \text{CH}_3\text{COOC}_2\text{H}_5$	9,10
4.	Diels Alder Cycloaddition Reaction. eg. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CHR} = \text{C}_6\text{H}_9\text{R}$	11
5.	Dehydration of Alcohols to Ethers. eg. $\text{RCH}_2\text{CH}_2-\text{OH} + \text{R}-\text{OH} = \text{RCH}_2\text{CH}_2-\text{O}-\text{R} + \text{H}_2$	12
6.	Elimination of Ammonia from Primary Amines. eg. $\text{RCH}_2-\text{NH}_2 + \text{RCH}_2-\text{NH}_2 = \text{RCH}_2-\text{NH}-\text{CH}_2\text{R} + \text{NH}_3$	13,14
7.	Elimination of Hydrogen Sulphide from Thiols. eg. $\text{RCH}_2-\text{SH} + \text{RCH}_2-\text{SH} = \text{RCH}_2-\text{S}-\text{CH}_2\text{R} + \text{H}_2\text{S}$	15

its octane rating. With increasing awareness of the environmental damage caused by alkyl lead compounds, there is a parallel interest in any process that provides cheap, alternative compounds, such as the use of clay catalysts to synthesise MTBE.

The ability of smectite clays to catalyse such reactions, to intercalate inorganic cations, and to absorb water and organic molecules into the interlayer are all properties of clays that have been exploited. In this thesis, the rate of uptake and the relationship between the rate of uptake and the structure and polarity of the molecules being absorbed, will be investigated. Also the type of site on the clay to which these adsorbed molecules bond, and the strength of that interaction will be investigated for a variety of compounds, in an attempt to understand the interlayer processes of a cation-exchanged montmorillonite clay in greater detail.

CHAPTER 2

The Structure of Clay Minerals, Their Cation-Exchange Capacity and Swelling Properties.

2.1. The Basic Sheet Silicates

All clay minerals are formed from two basic sheet-forming units, the silicon tetrahedral unit and the aluminum or magnesium octahedral unit. These units combine to form two-dimensional sheet structures, which are stacked one on top of the other to form the clay layers in a clay particle.

2.1.1 The Tetrahedral Sheet

The silicon tetrahedral unit (Fig 2.1.a) is polymerised into a two-dimensional array or sheet, by linkage of three oxygen atoms at the base of each tetrahedron, with three adjacent tetrahedra, to form a flat tetrahedral sheet. The bases of the tetrahedra all lie in the same plane and the apices all point in the same direction (Fig 2.1.b). The chemical composition of the single tetrahedron is SiO_4 , and the chemical composition of the tetrahedral sheet is expressed as $Si_4O_6(OH)_4$, with open hexagonal rings of oxygen atoms infinitely repeated in two dimensions. (Fig 2.1.1)

2.1.1.1 The Octahedral Sheet.

The octahedral sheet is based on either an aluminum-oxygen octagon (Gibbsite) or a magnesium-oxygen octagon (Brucite). The aluminum or magnesium is coordinated with six oxygen atoms or hydroxyl groups. The octahedral units (Fig 2.1.1.1.a) are polymerised into a two-dimensional array or sheet, known as the octahedral sheet. Here the oxygen atoms and hydroxyl groups combine to form two parallel planes with the cation lying between these planes (Fig 2.1.1.1.b.) The hydroxyl species is

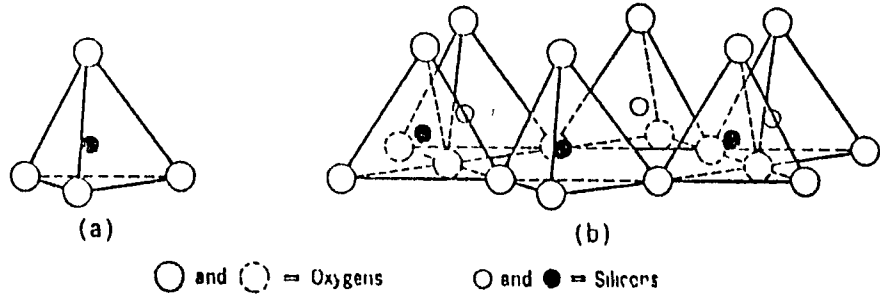


Fig. 2.1: Diagrammatic sketch showing.

(a) A single silica tetrahedron.

(b) the sheet structure of silica tetrahedrons.

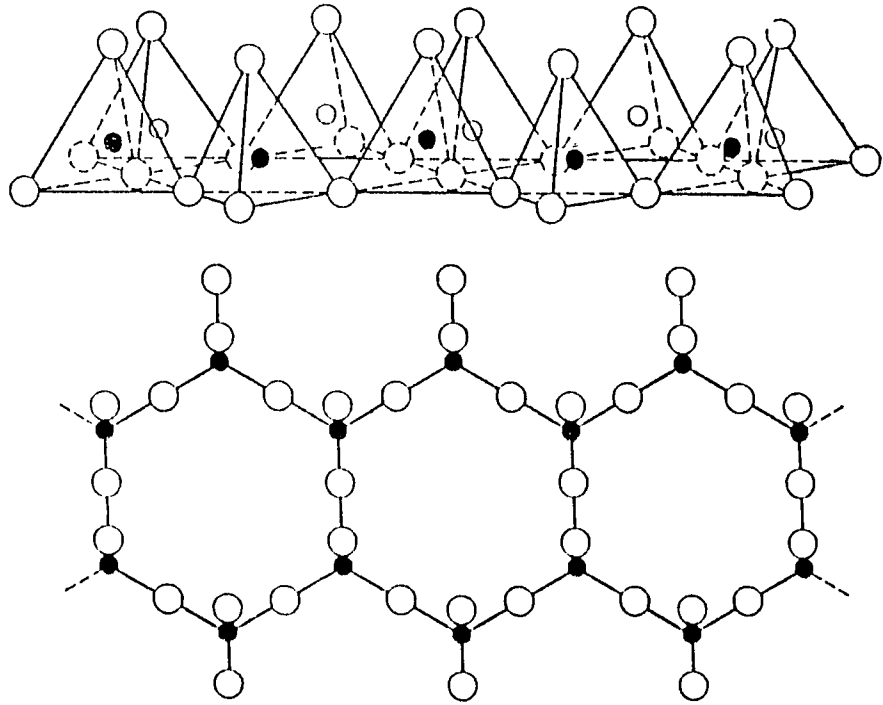


Fig. 2.11. A view of the silica tetrahedral sheet projected on the plane of the base of the tetrahedrons, showing the hexagonal network.

formed in the sheet when the oxygen atoms gain a negative charge, due to the bonding between the octahedrons in the sheet, and bind a proton (H^+) to satisfy their valency requirements.

2.2 The Layer Silicates

The differences between the various types of clays is the way in which the tetrahedral and octahedral sheets combine to form the clay layer. In fact the ratio of tetrahedral to octahedral sheets and the type of cation in the sheets, is the basis for a classification system used to assign clays to various groups (eg table 2.1)

The symmetry and almost identical dimensions of the tetrahedral and octahedral sheets, allows for sharing of the oxygen atoms between the two sheets (Fig 2.1v.). When one tetrahedral and one octahedral sheet combine to form a layer, this is said to be a 1:1 type clay such as a kaolinite. If two tetrahedral sheets sandwich one octahedral sheet between them, this is known as a 2:1 type clay, of which smectite clays are an example. This combining of the tetrahedral and octahedral sheets occurs when the oxygen atoms at the apices of the tetrahedral sheets are shared with the plane of oxygen atoms in the octahedral sheet (as shown in Fig 2.1v.)

2.3 The Structural Classification of Clays

Most clays fall into either the 1:1 or 2:1 type clay groups, and clays that are not members of these groups are usually structurally modified 1:1 or 2:1 clay types. Table 2.1. lists the major groups of clays and arranges them according to their structural classification. It also gives some examples of the clay minerals belonging to these groups. The differences between clays are often expressed in terms of the following three

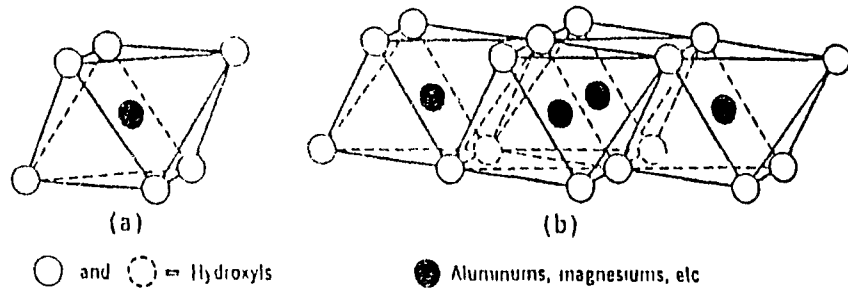
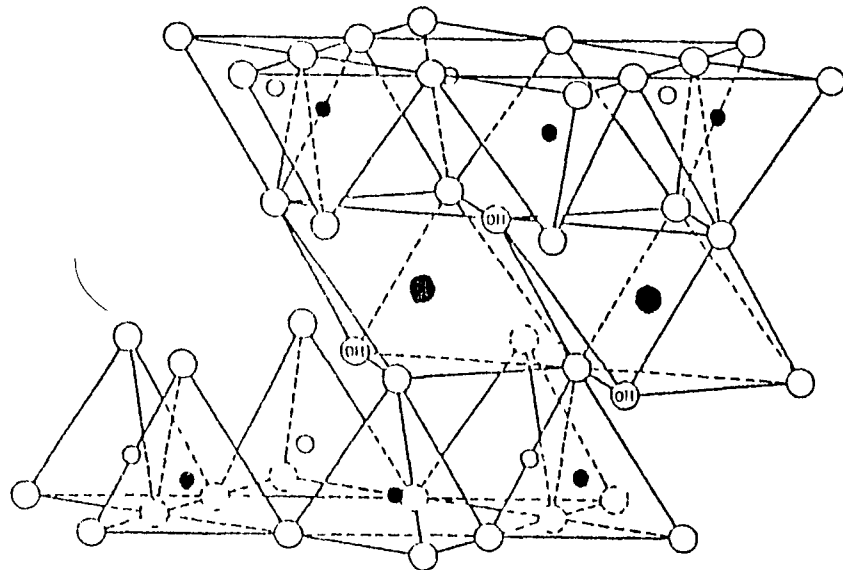


Fig. 2.111. Diagrammatic sketch showing.

(a) A single octahedral unit.

(b) The sheet structure of the octahedral units.



○ Oxygens (OH) Hydroxyls ● Aluminum, iron, magnesium
○ and ● Silicon, occasionally aluminum

Fig 2.1v: Diagrammatic sketch of the combined tetrahedral and octahedral sheets in a smectite clay.

parameters,

- (1) The layer charge.
- (11) Isomorphous substitution or interlayer cations.
- (111) Ability to intercalate water, organic molecules or cations.

This basis will now be used to examine some of the clay types shown in Table 2 1.

(a) the Kaolinite-Serpentine Group

examples: kaolinite $[Al_4Si_4O_{10}(OH)_8]$

Chrysotile $[Mg_6Si_4O_{10}(OH)_8]$

- (1) Overall the layers are amphoteric carrying a negative charge on one side of the layer and a positive charge on the opposite side
- (11) Interlayer cations do not occur as hydrogen bonding and strong electrostatic forces hold the layers tightly together
- (111) Intercalation is limited, but is possible with polar molecules.

(b) the Pyrophyllite-talc Group.

examples: Pyrophyllite $[Al_4Si_8O_{20}(OH)_4]$

Talc $[Mg_6Si_8O_{20}(OH)_4]$

- (1) Carry no layer charge
- (11) Isomorphous substitution does not occur
- (111) Intercalation is rare, although there have been some reports that water molecules and organic molecules have been detected between the layers.

(c) the Smectite Group.

examples: Montmorillonite $[(Na_{0.6})(Al_{3.4}Mg_{0.6})Si_8O_{20}(OH)_4]$

$[(Na_{0.6})(Mg_6)(Si_{7.4}Al_{0.6})O_{20}(OH)_4]$

- (1) Carries a layer charge of 0.5-1.0 units per unit cell.
- (11) Isomorphous substitution readily occurs, with the cations absorbed to balance the layer charge.

TABLE 2.1.

<u>Type</u>	<u>Clay Group.</u>	<u>Sub Group</u>	<u>Mineral.</u>
1:1 1:0	Kaolinite-Serpentine	Di-octahedral Kaolinites Tri-octahedral Kaolinites	Kaolinite Halloysite Chrysotile
2:1 1:0:1	Pyrophyllite-Talc	Di-octahedral Pyrophyllite Tri-octahedral Talc	Pyrophyllite Talc
	Smectite	Di-octahedral Montmorillonite Tri-octahedral Saponites	Montmorillonite Nontronite Saponite Hectorite Glauconite
	Vermiculite	Di-octahedral Vermiculite Tri-octahedral Vermiculite	Vermiculite
	Illite	Di-octahedral Illite Tri-octahedral Illite	Illite
	True Mica	Di-octahedral Mica Tri-octahedral Mica	Muscovite Paragonite Phlogopite Biotite
	Brittle Mica	Di-octahedral Brittle Mica Tri-octahedral Brittle mica	Margarite Clintonite
2:1:1 (1:0:1 modified)	Chlorite	Di-octahedral Chlorite Tri-octahedral Chlorite	Pennine Donbassite Clinochlore Prochlorite

(111) Intercalation of a wide range of compounds is well documented^(5 - 15)

(d) The Vermiculite Group

examples: Vermiculite $[(Mg_{0.6})(Al_4)(Si_{6.8}Al_{1.2})O_{20}(OH)_4]$

- (1) Carry a high layer charge of 1-2 units per unit cell.
- (11) Isomorphous substitution occurs only in the tetrahedral sheet.
- (111) Intercalation of water and organic molecules also occurs.

(e) The Illite Group

examples: Illite $[(K_{1.6})(Mg_6)(Si_{6.4}Al_{1.6})O_{20}(OH)_4]$

- (1) Carry a layer charge of about 1.6 units per unit cell.
- (11) Isomorphous substitution occurs, but exchange of the interlayer cations is difficult.
- (111) Strong interlayer bonding makes intercalation very rare.

(f) The True Mica Group

examples: Muscovite $[(K_2)(Al_4)(Si_6Al_2)O_{20}(OH)_4]$

- (1) Carry a layer charge of 2 units per unit cell, causing strong interlayer bonding.
- (11) Interlayer substitution of cations is rare.
- (111) Intercalation is also very rare.

(g) The Brittle Mica Group

examples: Margarite $[(Ca_2)(Al_4)(Si_4Al_4)O_{20}(OH)_4]$

- (1) Carry a layer charge of 4 units per unit cell, causing very strong interlayer bonding.
- (11) Isomorphous substitution in tetrahedral sites only.
- (111) Intercalation is consequently very rare.

(h) The Chlorite Group

examples: Douvassite $[Al_8Si_5O_{22}(H_2O)_7]$

Clinochlore $[Mg_{12}Si_8O_{20}(OH)_6]$

- (1) No layer charge occurs in this group.

- (ii) Interlayer cations are not replaceable.
- (iii) Intercalation of water occurs only when the hydrogen bonding between the layers is disrupted.

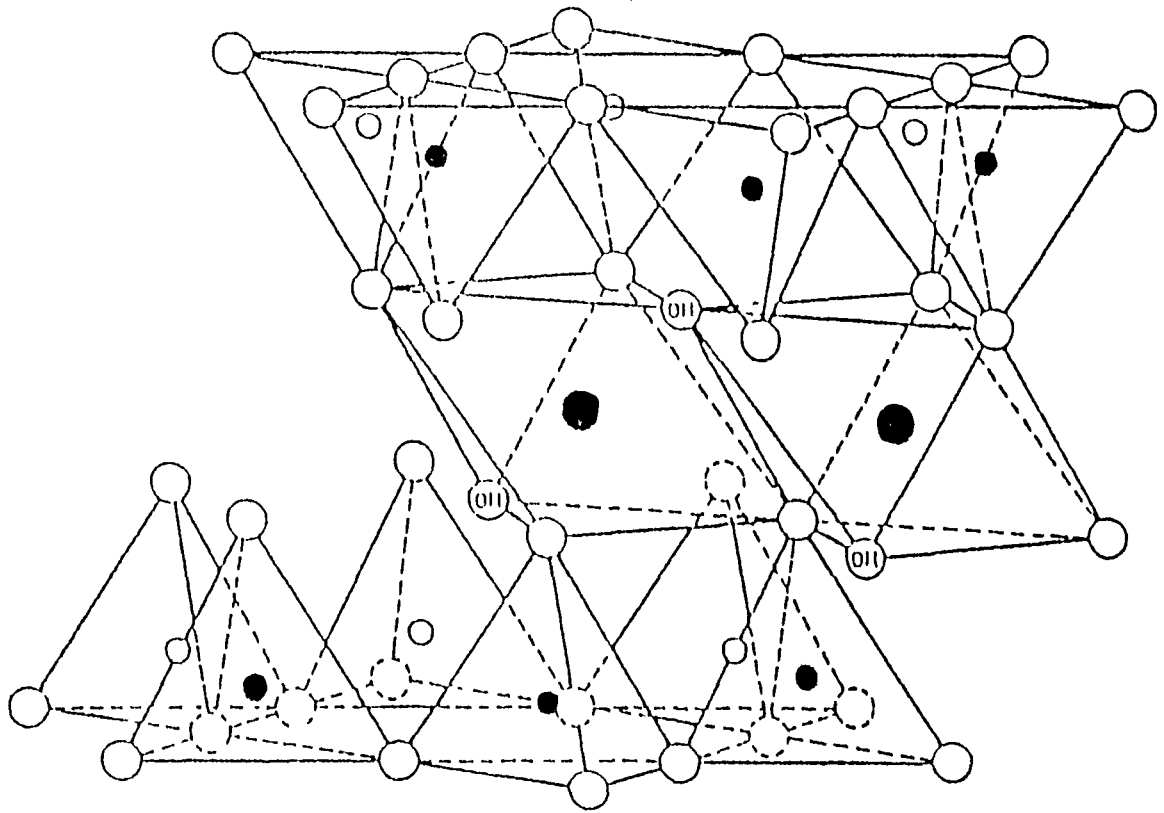
Following this brief overview of the different clay types, the mineral montmorillonite from the smectite group of 2:1 type clays will be considered in greater detail

2.4 The Structure and Properties of Montmorillonite

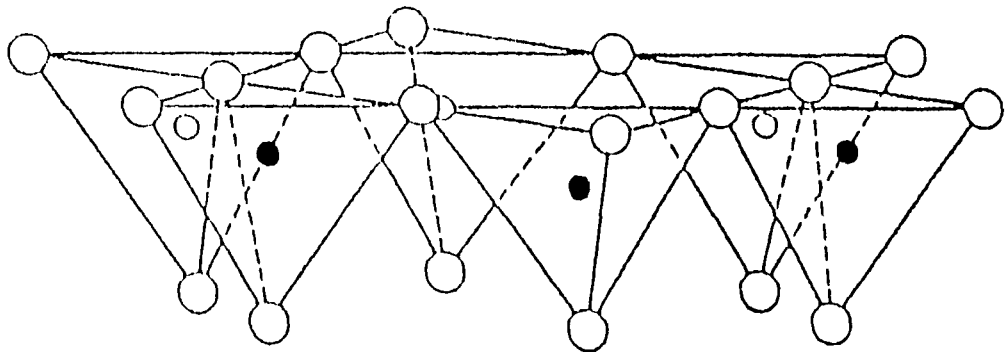
A two-dimensional representation of the three-dimensional structure of montmorillonite is shown (Fig 2 v.). This is the Hofmann-Endel-Wilm¹⁶ model of the structure of montmorillonite, as modified by Marshall²⁴, Madgefrau and Hofmann⁶⁰, and Hendricks¹⁸. This is generally accepted as the structure of montmorillonite and is the model that will be used throughout this thesis.

Montmorillonite layers differ from the other pyrophyllite clay layers, in that the montmorillonite is an aluminous smectite, i.e. Al^{3+} cations are isomorphously substituted by Mg^{2+} or Fe^{2+} cations in the octahedral sheet. This results in the accumulation of a negative charge on the layers. Isomorphous substitution of Si^{4+} cations by Al^{3+} cations in the tetrahedral sheet also occurs, but to a much lesser extent.

The modifications of the Hofmann-Endel-Wilm model suggested by Marshall and Hendricks, were to account for the large cation exchange capacity of montmorillonites. They postulated that the isomorphous substitution in the tetrahedral and octahedral sheets, results in a negative charge on the layers. This charge is balanced by the uptake of cations into the interlayer, the electrostatic or Van der Waals forces between these cations and the layers, not only maintains the clay in a stable structure, but also accounts for many of the properties of a montmorillonite,



Exchangeable cations
in H_2O



○ Oxygens ⊙ Hydroxyls ● Aluminum, iron, magnesium
○ and ● Silicon, occasionally aluminum

Fig. 2.v: Diagrammatic sketch of the Hofmann-Endel-Wilm and Marshall-Hendricks model of a smectite clay.

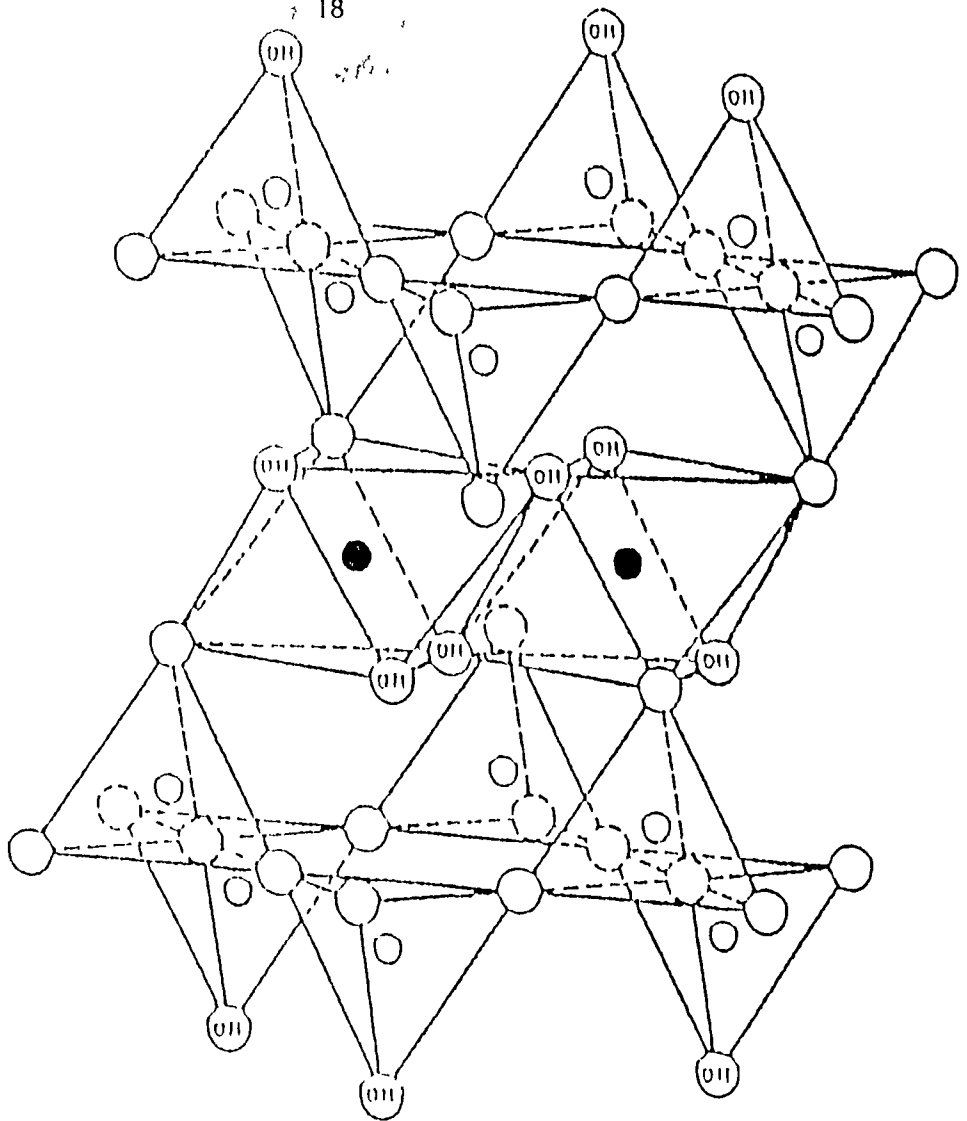
especially intercalation of organic molecules and water.

It should be noted that Edelmann and Favajee¹⁷ suggested an alternative structure for montmorillonite in the 1940's, as shown in Fig 2 vi. This shows every alternate silicon tetrahedron in the tetrahedral sheet is inverted, so that all the apical oxygen atoms in the tetrahedral sheet do not lie in the same plane. This was later modified from every alternate tetrahedron to 20% of the tetrahedrons in the tetrahedral sheet being inverted. This was to account for the observed cation exchange capacities of montmorillonite, which could not be explained by the previous suggestion. Any gaps that occur in the structure as a result of inverting the tetrahedrons, are filled by hydroxyl groups, which also replace apical oxygen atoms on the outer side of the tetrahedral sheet.

With this structure they suggest, no isomorphous substitution occurs in either the tetrahedral or octahedral sheets. Dissociation of the hydroxyl groups on the layer surface is said to account for the cation exchange capacity of montmorillonite. This structure is not widely accepted today, although it has been suggested that the Edelmann-Favajee model is representative of a Cheto montmorillonite clay, and the modified Hofmann et al model represents the Wyoming montmorillonite clay. In this thesis only the modified Hofmann et al model will be considered.

2.5 The Cation Exchange Capacity of Montmorillonite.

Naturally occurring clay minerals have the ability to absorb certain cations, (naturally occurring montmorillonite is usually a sodium cation exchanged clay, although some calcium cations are often present). If this clay is exposed to a solution of a different cation, it is possible to replace the previously



Exchangeable Cations
 nH_2O

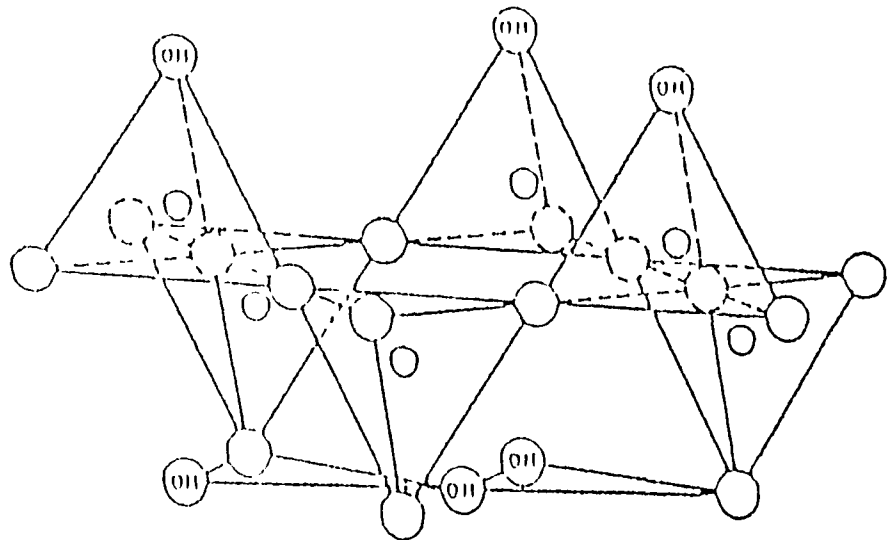


Fig. 2.vi: Diagrammatic sketch of the Edelman and Favejee model of a smectite clay.

sorbed cations with those in the solution. Attempts to determine the cation exchange capacity (cec) of a clay were among the earliest clay properties discussed in the scientific literature i.e. Way's⁴ paper in 1847. The cec of a clay is usually expressed in milliequivalents of exchangeable cations per 100 grams of clay, (meq/100g), for montmorillonite this is usually 80-150 meq/100g. The cec of a clay is influenced by several factors, and to a large extent depends on the structure of the clay.

(1) Broken Bonds at the Edges of the Silicate Layers

This is a significant factor in 1:1 type clays, such as halloysite as no isomorphous substitution occurs, so broken bonds become the major contributing factor to the cec of a 1:1 type clay. In the case of 2:1 type clays, such as the smectite minerals isomorphous substitution is extensive, hence broken bonds account for only 15-20% (or less) of the total cec of these clays.

(2) Isomorphous Substitution

For montmorillonite clays this is usually Mg^{2+} or Fe^{2+} cations for Al^{3+} cations in the octahedral sheet, and less commonly Al^{3+} for Si^{4+} in the tetrahedral sheet. The negative charge on the clay layers caused by isomorphous substitution, is balanced by the uptake of cations into the interlayer or interlamellar space. This process accounts for about 80% of the total cec of a montmorillonite clay.

(3) Replacement of the Hydrogen Atoms of Exposed Hydroxyl Groups

This is thought to account for any remaining cec of a montmorillonite, not already accounted for by the previous two processes. Consequently this represents a small amount of the total cec of montmorillonite clays. Kaolinite or 1:1 type clays have an exposed plane of hydroxyl groups on one side of the silicate layer, so replacement

of the hydrogen atoms of these groups, would make a significant contribution to the total cec of kaolinite clays. However, this is not thought to be the case as the hydrogen ions or protons are very tightly bound to the oxygen atoms, making it difficult to displace them with a sterically large di- or tri-valent cation. Indeed this is one of the arguments against the Edelman-Favajee model for the structure of montmorillonite, since the inversion of 20% of the silicon tetrahedron's in the tetrahedral sheet exposes a hydroxyl surface to the interlayer space, and displacement of the protons from these groups would have to account for about 80% of the cec of montmorillonite clays, and this is thought to be unlikely. Table 2.11 gives an indication of the magnitude of the cec's of different clay types

TABLE 2.11

<u>Mineral</u>	<u>Cation Exchange Capacity.</u>	
Kaolinite	3-15	meq/100g.
Halloysite $4H_2O$	40-50	meq/100g.
Montmorillonite	80-150	meq/100g.
Vermiculite	100-150	meq/100g.
Illite	10-40	meq/100g.
Chlorite	10-40	meq/100g.

2.6. The Exchangable Cations

The position of the exchangable cation in the clay structure is determined largely by the size and charge of the cation. Of the total cec of montmorillonite approximately 20% of the exchangable cations are associated with broken bonds at the edges of the silicate layers. Here the cation is held beside

the negatively charged site, or it may be bonded to an oxygen atom of a dissociated hydroxyl group. The remaining 80% of the cec is due to the exchangeable cations being held on or between the basal surfaces of the silicate layers. This occurs when a negative charge accumulates on the clay layers due to isomorphous substitution within the layer structure.

The positions of sites within the interlayer occupied by the cations depends greatly on the hydration state of the clay. For example, in an anhydrous montmorillonite the cation may occupy the hexagonal cavity in the tetrahedral sheet, (see Fig 2.iii.). If the cation is small enough. If the clay becomes partly hydrated and adsorbs one layer of water into the interlayer the cation will remain in the hexagonal cavity. However, when two or more layers of water are adsorbed by the clay, the cation is displaced and lies between the two layers of water, i.e. separated from the basal planes of the montmorillonite by a layer of water (Fig 2.vii.) on each side. The precise position of the cation in the interlayer not only depends on the hydration state of the clay, but also on the charge and size of the cation in question. However, the 20% of the cations bound at the clay layer edges are unaffected by the hydration state of the clay.

The term ion-exchanged clay refers to a clay whose available cation sites are saturated, usually with the naturally occurring cation, mostly sodium in the case of montmorillonite. These cations are then exchanged or replaced with a different cationic species using a cation exchange process. However not every cationic species is exchangeable, and the following rules govern whether a cation is exchangeable or not.

(1) Ions of higher valency replace those of lower valency, and

are bound more tightly to the interlayer exchange sites.

(ii) If the ions have the same valency. The larger the ion, the better it will be at displacing a smaller ion of the same valency. This rule holds until the exchanging ion's size and coordination properties do not allow it to fit the hexagonal cavity of the tetrahedral sheet optimally. It should be noted that hydrogen is an exception to these rules as it can behave as a di- or tri-valent cation.

2.7. Sorption by Clays.

2.7.1. Adsorption of Water by Layer Silicates.

Swelling or the adsorption or intercalation of water into the interlayer space causes the basal spacing of the clay (Fig 2.viii) to increase, or the clay to increase in volume, i.e. swell. This process is greatly influenced by the nature of the interlayer cations. The water in the interlayer is an integral number of water molecules thick. The number of layers of water formed was shown to depend upon the exchangeable cation and the partial pressure of the water. Norrish²⁰ showed that the layers of a sodium montmorillonite could be expanded, stepwise, (i.e. water layer on top of water layer), to a basal spacing of 40\AA (anhydrous sodium montmorillonite has a basal spacing of about 9.6\AA). When the basal spacing increases above 40\AA the layers are taken to be completely dissociated. However, it was also shown that calcium montmorillonite clay could not be significantly expanded beyond 15.4\AA , and this basal spacing corresponds to two layers of water in the interlayer. This type of limited expansion was also found for potassium and magnesium cation-exchanged montmorillonite clays. This agrees with Ballantine et al.⁴³ findings that the physical characteristics of

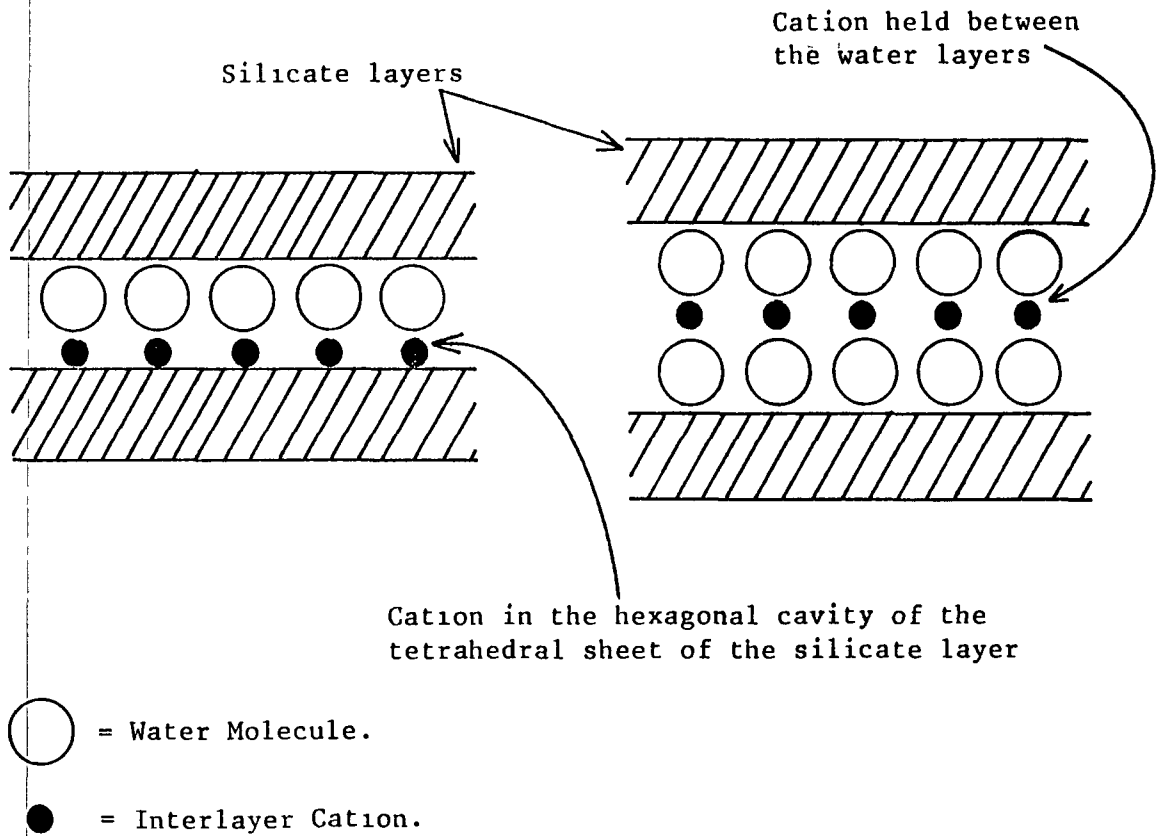


Fig 2.vii. The location of the cation in hydrated montmorillonite.
(note, this depends on the water content of the clay)

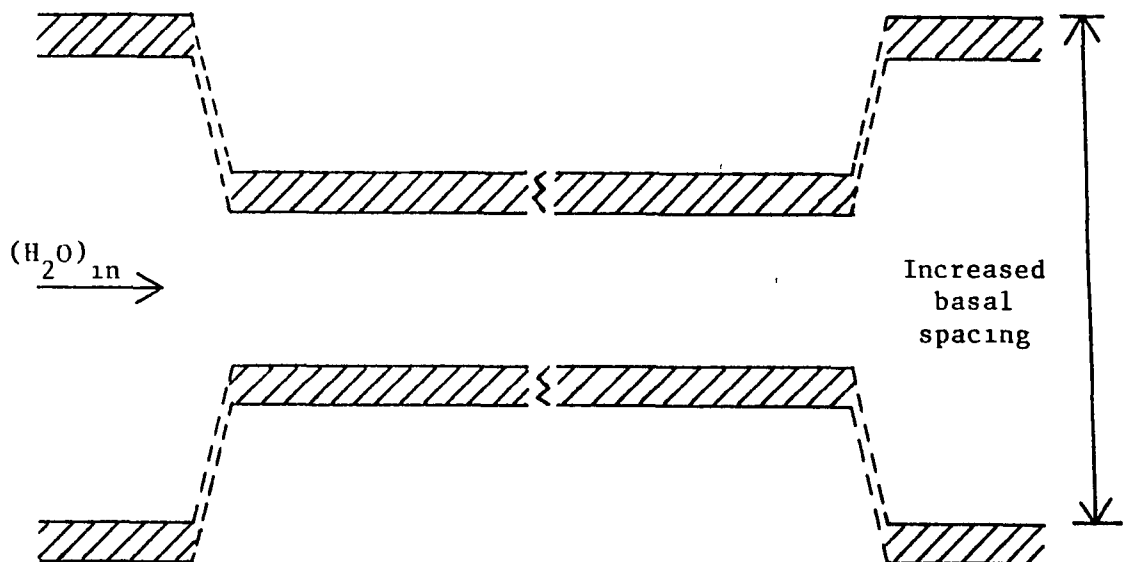


Fig 2.viii. The expansion of the clay layers upon intercalation.
(note, the clay layers expand from the edges inwards)

smectites are related to the interlayer sheets of water. Also the layer charge which is low for montmorillonites (see section 2.3.C), influences the tendency of the clay to intercalate water layers, and other organic molecules. The clay minerals with a high layer charge have a lower tendency to intercalate water or organic species by swelling, as the electrostatic interactions between the layers and the cations, make it more difficult, (ie more energy is required), for the intercalating molecules to force the layers apart.

Interlayer water molecules have been found to be very stable, and this is thought to be due to the fact that six water molecules fill the coordination or hydration sphere of the interlayer cations, forming hydrogen bonds with the oxygen atoms and hydroxyl groups of the silicate layers. Further uptake of water is thought to form hydrogen bonds with the existing oxygen atoms of the water in the cation hydration sphere, and the oxygen atoms and hydroxyl groups of the silicate layers. This continues with certain cations such as sodium until the interactions between the silicate layers and the cations in a water suspension are so remote that the layers may be considered to be completely dissociated.

2.7 (11). Adsorption of Polar Organic Molecules on Inorganic

Cation Exchanged Clays.

Polar organic molecules are readily intercalated by many clay minerals and especially by ion-exchanged montmorillonite clays. Fig 2.1x. represents Mac Ewans²² findings that a halloysite or 1:1 type clay intercalates a single layer of polar organic molecules, due to the amphoteric nature of the halloysite layers. Montmorillonite on the other hand can form

multilayers of interlayer polar molecules, due to the overall negative charge on the montmorillonite layers. Recent infra-red studies²³ have shown that polar organic molecules in the interlayer do not follow the pattern shown by the simple model in Fig 2.1x. But they actually compete with water molecules in the hydration sphere of the interlayer cation, occupying sites in the outer coordination sphere of the cations. In some cases such as a strongly polarising cation, the polar organic molecules can occupy sites in the inner coordination sphere of the cations, and Al³⁺ cation-exchanged montmorillonite clay gives an example of this effect.

2.8. Sedimentation of Montmorillonite as a Separation Technique.

This is based on Stokes' Law for particles of a radius, a , falling with terminal velocity, v , through a liquid medium viscosity, η

$$F = 6\pi a\eta v$$

F = the force on the particle

The international standard maximum limit is $\sim 2\mu\text{m}$ for the particle diameter of a montmorillonite clay. The solution of clay and water is mechanically stirred for one hour to ensure an even distribution of clay particles throughout the water. This solution is allowed to stand for a calculated time, and the top 10cm fraction of the solution is siphoned off. This is then centrifuged to sediment the clay particles. A reasonably pure clay is obtained, as most of the impurities such as micas, quartz, and iron-oxide bonded platelets have a greater density than the clay fraction, so they will sink further than 10cm during the sedimentation period.

So assuming spherical particles Stokes' Law becomes,

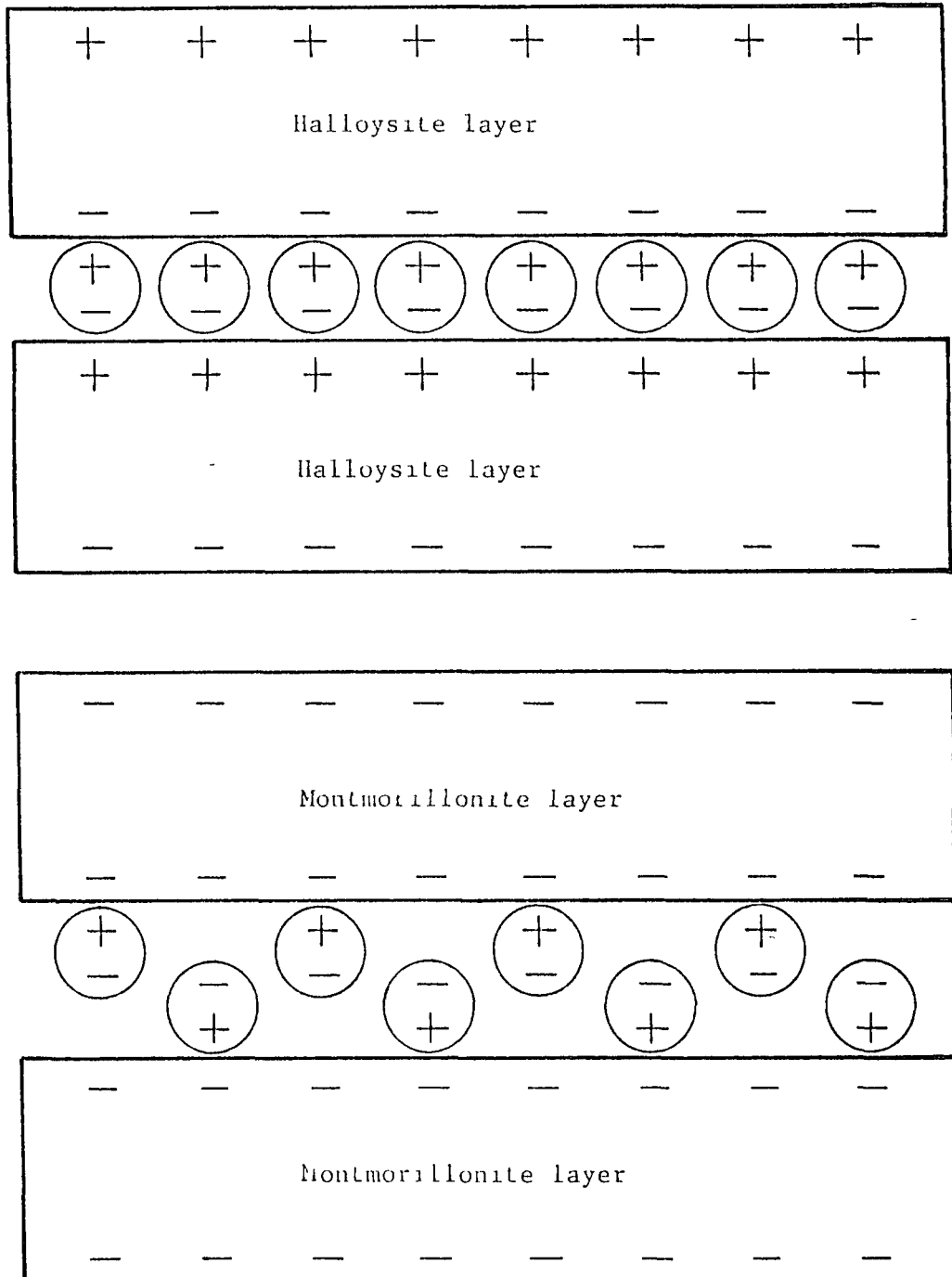


Fig 2.1x. Schematic diagram of the positions of polar molecules in the interlayer of a 1:1 type clay and a 2:1 type clay (note, the amphoteric nature of the 1:1 type clay)

$$F = mg = (4/3)\pi a^3 \gamma g$$

where γ = the particle density = $2.65 \times 10^3 \text{ Kgm}^{-3}$

$$a = 10^{-6} \text{ m}$$

$$\xi = 10^{-3} \text{ Kgm}^{-1} \text{ s}^{-2} \quad (\text{at } 20^\circ \text{C})$$

$$v = \text{distance/time} = d/t$$

$$g = 9.81 \text{ ms}^{-2}$$

therefore, the sedimentation period is :-

$$t = (9/2)\xi(d/\gamma a^2 g)$$

So if the clay solution is left to stand overnight (> 16 hours) the particle size obtained will be $< 1.4 \mu\text{m}$, hence conforming to the international standard particle size definition.

CHAPTER 3Experimental Procedures.3.1 Preparation of the Basic Montmorillonite Clay

A raw or unprocessed Wyoming montmorillonite clay was used, (supplied by Volclay Ltd., Wallasey, Cheshire). The raw clay is processed using a sedimentation technique to remove impurities such as flakes of mica, quartz and other non-clay minerals, leaving a sodium exchanged montmorillonite clay (this may be 80% sodium and 20% calcium depending on its origin).

Firstly a suspension of approximately 10g clay/1000 cm³ of distilled water is mechanically stirred for 1 hour. The container is then covered and left to stand overnight (ie >16 hours), the upper 10cm fraction of the suspension is then siphoned off and stored, (the explanation for these times and volumes is given in chapter 2 section 8) the volume of suspension removed from the container, is replaced with an equal volume of distilled water, stirred for 1 hour, and the whole process is repeated 3 or 4 times with the siphoned off fraction (this contains the clay of interest) being stored each time. The initial stock suspension may then be discarded as it contains mainly the impurities from the raw clay.

The stored fractions contain the sodium exchanged montmorillonite clay of a particle size <2 μ m. This clay is extracted from the suspension by centrifugation, with the water being discarded and the clay sludge being left to air dry on a clock glass for 1 or 2 days, in an atmosphere that is free from solvent vapours. When dry the clay is ground to a fine powder using an electric coffee mill or a pestle and mortar, and is stored for use at a later date.

3 2. Preparation of Cation Exchanged Montmorillonite Clays.

The sodium exchanged montmorillonite clay is the usual naturally occurring form of the clay, and as described in chapter 2, it is possible to prepare other cation-exchanged forms of montmorillonite. For these studies three ion-exchanged forms that are commonly used clay catalysts were chosen, i.e. aluminium-exchanged montmorillonite ($\text{Al}^{3+}\text{-M}$), chromium-exchanged montmorillonite ($\text{Cr}^{3+}\text{-M}$), and iron-exchanged montmorillonite ($\text{Fe}^{3+}\text{-M}$). The technique used to prepare these clays is identical in each case, except, that the appropriate salt is used to give the cation required, eg. aluminium sulphate for a $\text{Al}^{3+}\text{-M}$ clay.

A 0.3M solution of the sulphate salt of the appropriate cation is prepared. The air dry, previously prepared sodium-exchanged clay is added to this solution while continually stirring with a magnetic stirrer, in a ratio of 5mg clay/40cm³ of sulphate solution. The resulting suspension is stirred vigorously for 30 mins. and then centrifuged at 3000rpm for a further 30 mins. The supernatant is discarded and the clay resuspended in an equal volume of distilled water. This suspension is again stirred for 30 mins., and centrifuged for 30 mins. at 3000rpm and the supernatant discarded. This is regarded as one wash, and is repeated until the clay has been washed at least 6 times. This washing is to remove any of the unadsorbed cations that may get trapped between the clay particles during centrifugation. To check that the clay has been thoroughly washed the supernatant from the sixth or final wash may be given a U.V. scan to detect the presence of any remaining sulphate salts. Also if the appropriate sulphate salt is not available, a good second preference is the nitrate salt of the cation.

When the washing is complete the clay sludge is spread

on a clock glass, dried and ground to a fine powder as before. The efficiency of the exchange process may then be tested using a back exchange technique

A final important note about the exchange procedure is that the PH of the sulphate solution, the clay suspension and each successive suspension after washing is monitored. It is best to maintain the PH below PH 3 as a neutral or alkaline PH could lead to the formation of hydroxy-metal species on the clay surface. The coatings of hydroxyl groups on the surface can cause erroneous results in the interpretation of the results of diffusion and adsorption studies involving that clay. Should the PH rise above PH 3 it may be reduced using a few drops of Conc. H_2SO_4 , if a sulphate salt is being used, or Conc. HNO_3 , if the nitrate salt is in use.

3.3 Preparation of Infra-Red Films and X - Ray Diffraction Slides.

X-Ray diffraction slides are prepared using standard glass microscope slides cut in half to form two glass squares approximately $2 \times 2 \text{cm}^2$. These are then coated with a layer of the clay slurry (before the prepared clay has been allowed to dry) the thickness of the clay layer is not critical in XRD slides, however a film of 0.5-1.0mm thick is adequate. These slides are then labelled and air dried in an atmosphere free from solvent vapours, when dry they may be stored in a dessicator until required.

Infra-red films are also prepared from the clay slurry before it is dried, using a polyethylene sheet to prepare the clay films. A sheet of polyethylene approximately 2cm wide is taped across a glass plate (Fig 3.1.), a few drops of the clay slurry are placed on the end of the sheet, and are spread along the sheet using the glass rod shown in Fig 3.11. This rod acts like a rolling

pin to spread the clay along the polyethylene sheet. However the rod is raised from the surface of the sheet by 3 layers of 'Sellotape' which effectively governs the thickness of the clay film on the polyethylene sheet. The clay is then left to air dry as before, after which the clay film is removed from the polyethylene sheet by stretching it across a blade, causing the film and sheet to separate (Fig 3 111). The clay is then cut into flakes approximately $2 \times 2 \text{ cm}^2$, as this size is adequate to fill the sample holder in the I.R. cell.

Some important points to note about this technique, are that the thickness of the clay film is critical, i.e. if the clay film is too thick it will not transmit the I.R. radiation and is useless, yet if the film is too thin, it will fall to pieces when it is removed from the polyethylene sheet. Consequently the clay film must be thick enough to be self-supporting and thin enough to transmit the I R radiation. The viscosity or density of the clay slurry used to make the films influences these factors greatly. If the slurry is too thick or has a high clay water ratio the film will be too dense to transmit the IR radiation, and will be of little use. Conversely if the clay water ratio is low the film will be too weak to support itself when removed from the polyethylene backing and so will crumble to pieces. As a general rule, equal volumes of distilled water and clay slurry from the end of the centrifuge tube will give a suitable clay water ratio, to make a good I.R. film.

The optimal thickness of the film was found to be 3 layers of 'Sellotape', any less and the films crumbled, any more than 3 layers and the films were too dense to transmit I.R. radiation. Once prepared the I.R. films were placed in holders

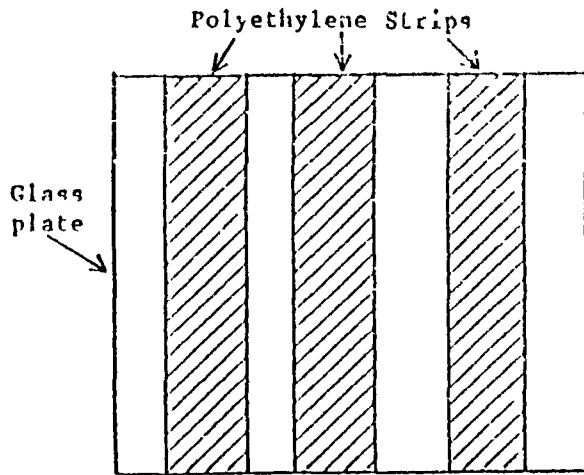


Fig 3.i. Schematic diagram of the glass plate used to make clay films.

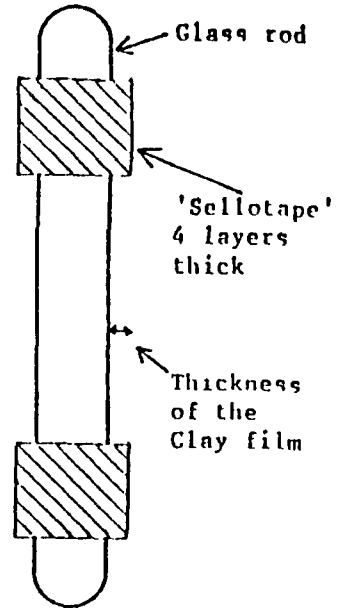


Fig 3.ii. Schematic diagram the roller used to make the clay films

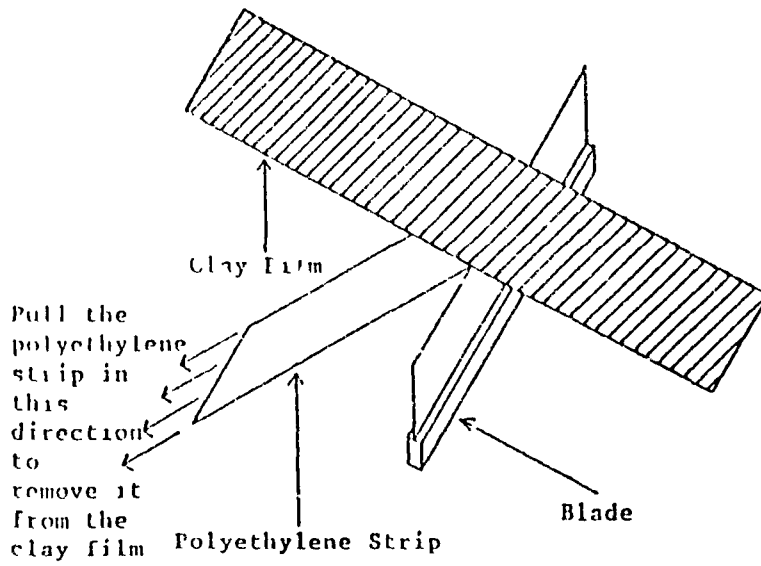


Fig 3.iii Schematic diagram of the method used to remove the clay film from the polyethylene strips

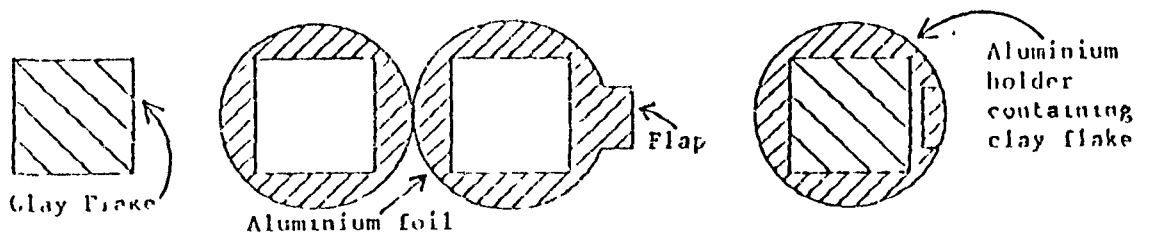


Fig 3 iv. Schematic diagram of the clay flake holder for the IR cell.

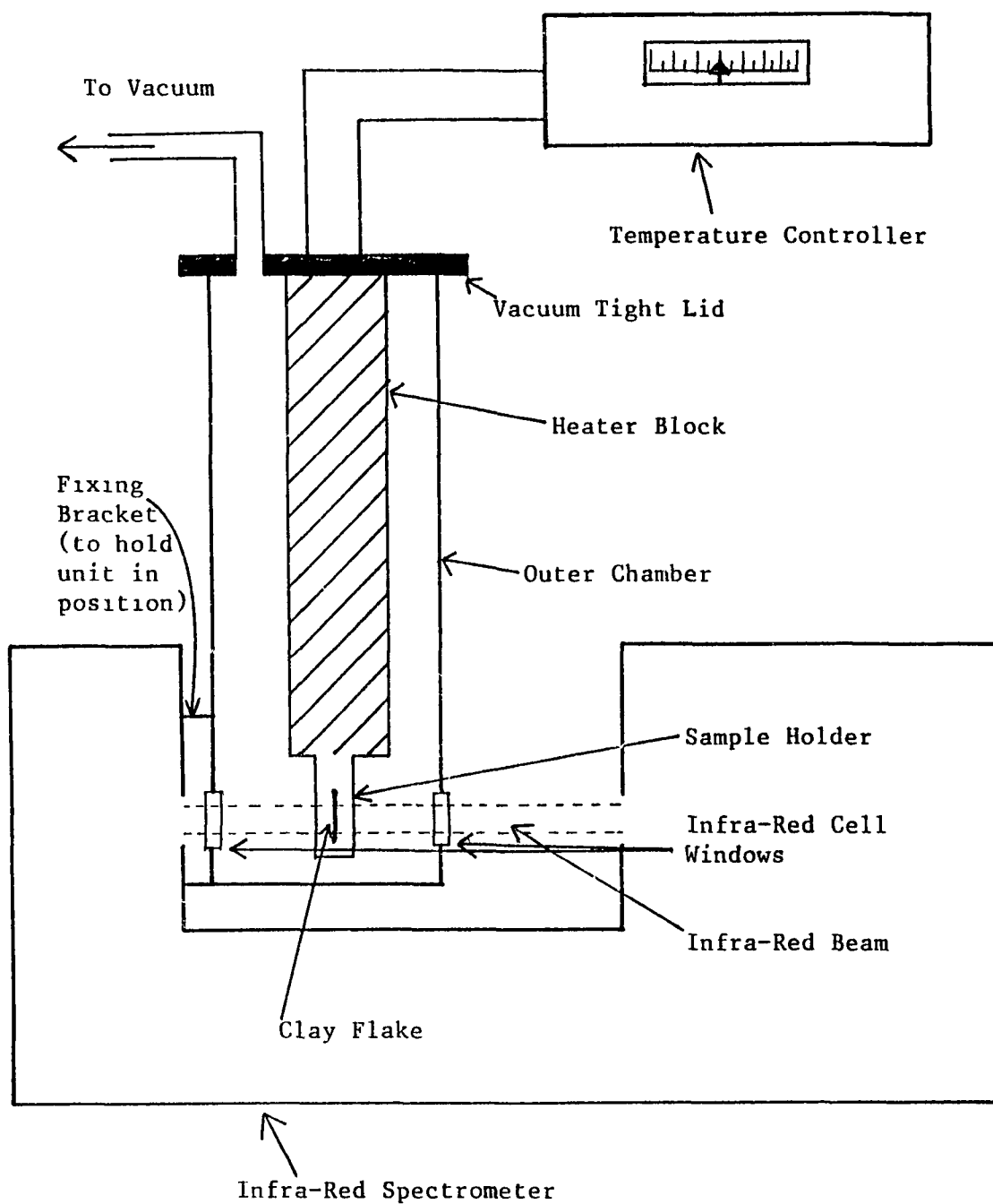


Fig 3.v. Schematic diagram of the infra-red variable temperature cell used to record the infra-red spectrum of the clay flakes at various temperatures under vacuum.

cut from heavy duty aluminum foil (Fig 3.iv.) labelled and stored in a dessicator with the XRD slides. This holder serves two purposes, firstly it provides protection for the fragile clay film while moving it about, and secondly it fits tightly into the circular sample holder of the variable temperature cell of the I R instrument, (Fig 3 v).

3.4. Grain-Size Preparation

The clay powder prepared and ground as described in 3.1. and 3.2. was graded according to its grain size for use throughout these investigations. The clay was ground to a fine powder in one of two ways, for clay samples of $>1g$ an electric coffee mill was used to circumvent laborious hand grinding. For clay samples $<1g$ a pestle and mortar was used, because the coffee mill did not work efficiently with small quantities of clay.

Once ground to a powder the clay was separated into the following grain size groups.

- (i) $>250\mu m$
- (ii) $250-125\mu m$
- (iii) $125-65\mu m$
- (iv) $65-45\mu m$
- (v) $<45\mu m$

This was done using sieves with the appropriate mesh size supplied and certified by Retsch, Haan, West Germany. After sieving, the different clay fractions were stored in glass vials in dry conditions where no solvent vapours were present.

3.5. Thermal Gravimetric Analysis (TGA)

The diffusion or uptake experiments were carried out using a Stanton Redcroft TG-750 Thermobalance in conjunction with a purpose built gas delivery system and a dual pen Linseis

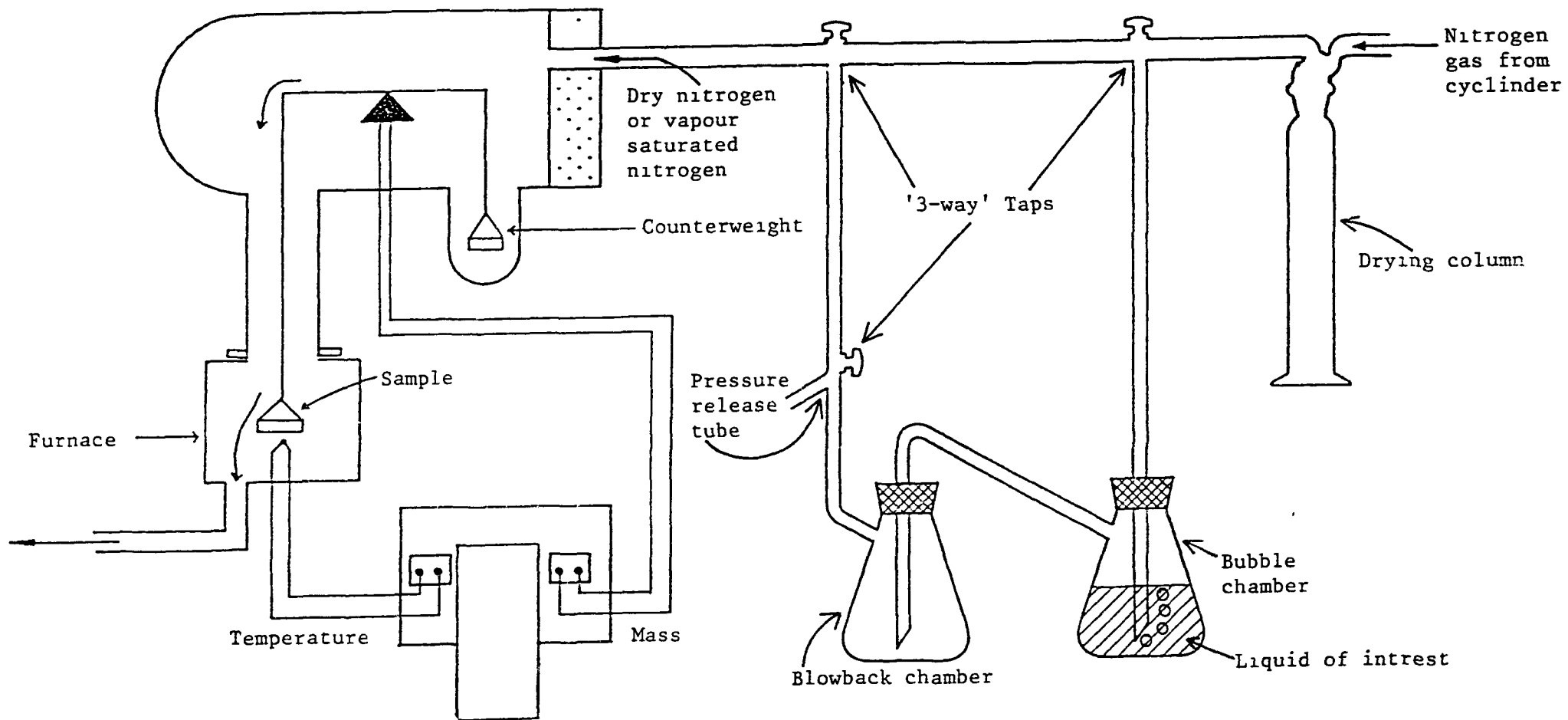


Fig 3.vi. Schematic diagram the thermobalance and the gas delivery system used throughout the experiments

chart recorder (Fig 3 vi) the same experimental set up with the addition of a derivitising unit on the balance output was used for the temperature programed desorption studies, using different operating conditions as detailed in section 3.6.

The furnace was calibrated in the range 18-305°C using the known melting points of the compounds listed in table 3.1.

Table 3 1

Melting Point Temperature (°C)	Compound.
42-44	Diphenyltin dichloride
70-73	2,2'-Bipyridyl
104-105	triphenyltin chloride
187-189	4-Aminobenzoic Acid
205-207	3,5-Dinitrobenzoic Acid
237-241	Dimethylglyoxime
302-305	2-Mercaptobenzimidazole

The dry nitrogen gas was passed through a drying column, consisting of a 4Å synthetic zeolite, followed by P₂O₅ with a visible moisture indicator (ie. it turned green on contact with water). The nitrogen flow was measured at the output from the thermobalance, using a bubble flow meter and a stopwatch. For the diffusion studies a flow of >250cm³min⁻¹ was found to be optimal (Fig 3.vii)

A sample weight of 5mg was used for most of the studies and if the weight was different from 5mg it is written on the appropriate graphs or tables. Generally a heating rate of 20°Cmin⁻¹ was used to heat the furnace in conjunction with a chart speed of 20cm hour⁻¹

The typical experimental run procedure was as follows: a sample of clay was placed in the sample bucket and preheated

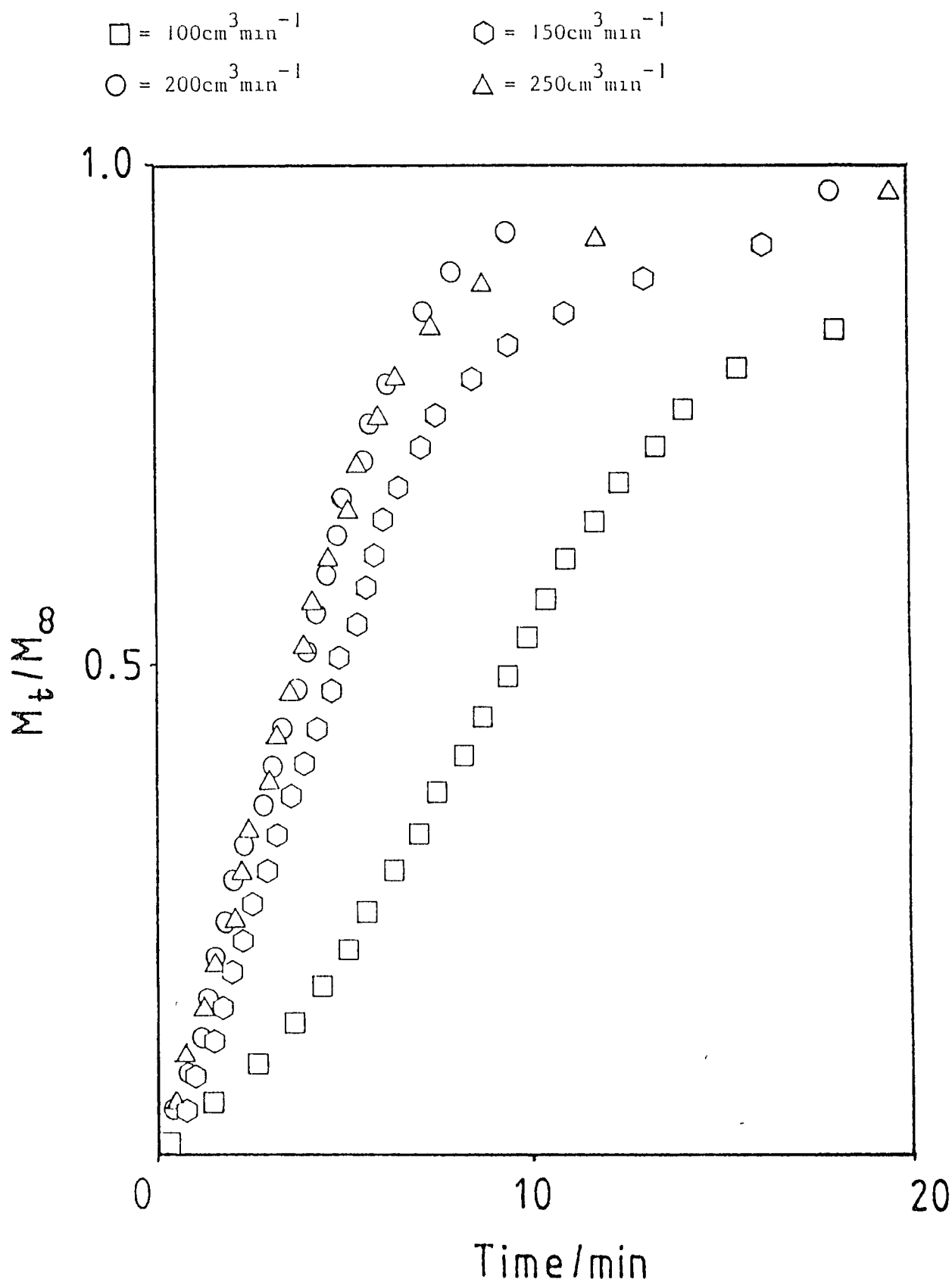


Fig 3.vii Optimization of the flow rate for the uptake of 1-propanol upon Cr^{3+} -montmorillonite at 18°C .

to 120°C at 5°Cmin⁻¹ in a flow of dry nitrogen of >250cm³ min⁻¹. The temperature of the sample was maintained at 120°C for 15min or until no further weight change occurred. The sample was then allowed to cool to a known temperature (18°, 43°, 72° or 105°C), and by the turn of a tap the dry nitrogen was directed through the alcohol reservoir. This time was taken as zero for the mass uptake experiment.

Between runs (particularly when a change of alcohol was necessary) the thermobalance was purged with dry nitrogen at a flow rate in excess of 1000cm³ min⁻¹, whilst heating the furnace to 500°C over a 30min period and then allowing it to cool. After cooling the furnace, a clay sample was added to the sample pan and, if no deviation from the baseline occurred within 15min, further purging was considered unnecessary. (eg. typical trace from an experimental run as described above is shown in Fig 3.viii.).

3.6. Temperature Programmed Desorption (IPD)

The studies were carried out on essentially the same experimental setup as the IGA studies. The output from the thermobalance was relayed to the chart recorder using a derivitising unit (this gives the derivitised weight loss signal (Fig 3.ix.)). Also the dry nitrogen flow is not run through the bubble chamber, so it is never saturated with solvent vapour. The nitrogen flow was 50cm³ min⁻¹ for the IPD experiments. The furnace was heated to 800°C at 20°Cmin⁻¹ and the chart recorder was run at 20cm hour⁻¹. A sample weight of 7-8mg was used for all of the IPD experiments.

Sample preparation for a IPD investigation was as follows. Approximately 0.1g of a <45µm fraction of a previously prepared clay was used. This was labelled and placed in a small vial, this was then placed in a gas-jar (the atmosphere of which was saturated with the solvent vapour required), for 48 hours (Fig 3.x.). After this time

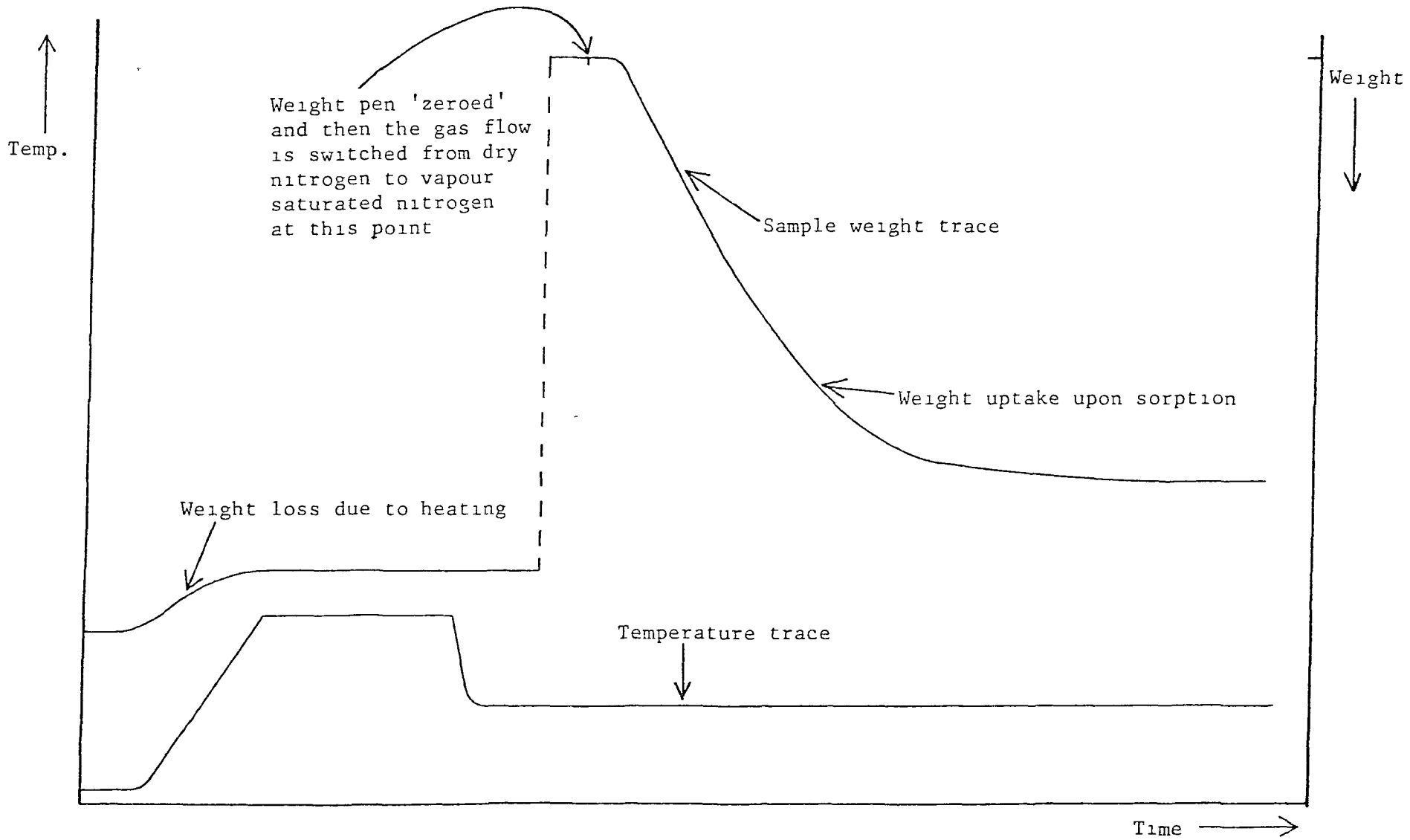


Fig 3 viii. Example of an experimental trace from a typical sorption uptake experiment.

a 7-8mg clay sample is quickly placed in the thermobalance, and its TPD profile obtained under the conditions outlined above. It should be noted that a small portion of physisorbed solvent is lost during the transfer of the sample from the gas-jar to the thermobalance. This was not a problem since the more tightly bound, chemisorbed species were of more interest.

3.7 Infa-Red Investigations.

These studies were used primarily to corroborate and aid the interpretation of the lower portion, (up to 200°C) of the TPD profiles. Consequently, the samples were prepared in the gas-jars in the same way as the TPD samples, the difference being that a previously prepared I.R. film (section 3.3) replaced a clay powder sample.

The infa-red spectrometer used was a Perkin Elmer 983.IR. equipped with presample chopping and with quoted accuracies at 1600cm^{-1} of 2% (ordinate) and $\pm 3\text{cm}^{-1}$ (abscissa). The I.R. spectra were recorded using an evacuable variable temperature cell, at room temperature initially, and then after evacuation for 1 hour at 50°C, 100°C, 150°C and finally 200°C (200°C was the maximum operating temperature of the variable temperature cell). The I.R. range scanned was 4000cm^{-1} to 600cm^{-1} , however certain ranges were expanded as required, eg, the range 1800cm^{-1} to 1300cm^{-1} for the alcohol investigations.

3.8. X-Ray Diffraction Studies (XRD).

The XRD slides were prepared in the same way as the I.R. films, and the TPD samples, using a gas-jar saturated with the required solvent vapour. The XRD traces were recorded using a Jeol JDS-8X. Diffractometer operating at 40kV and 20mA.

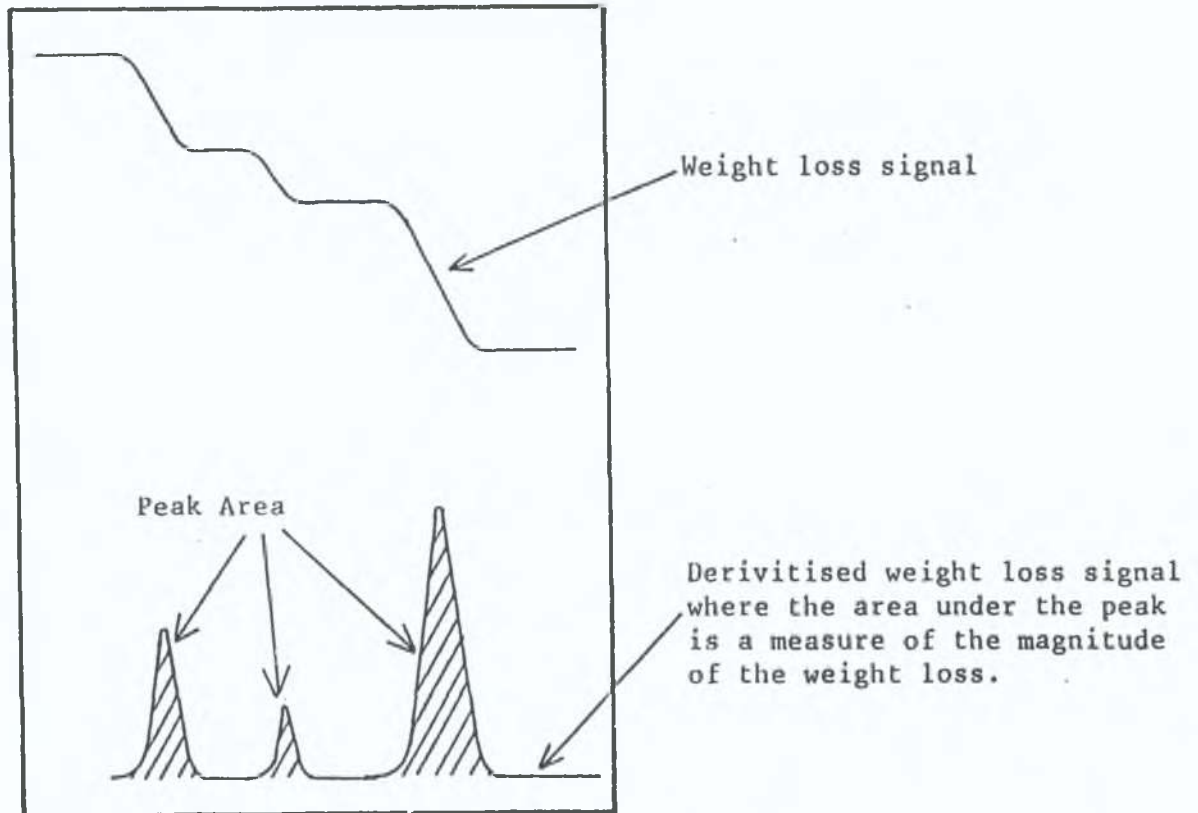


Fig 3.ix. Example of a TPD weight loss profile.

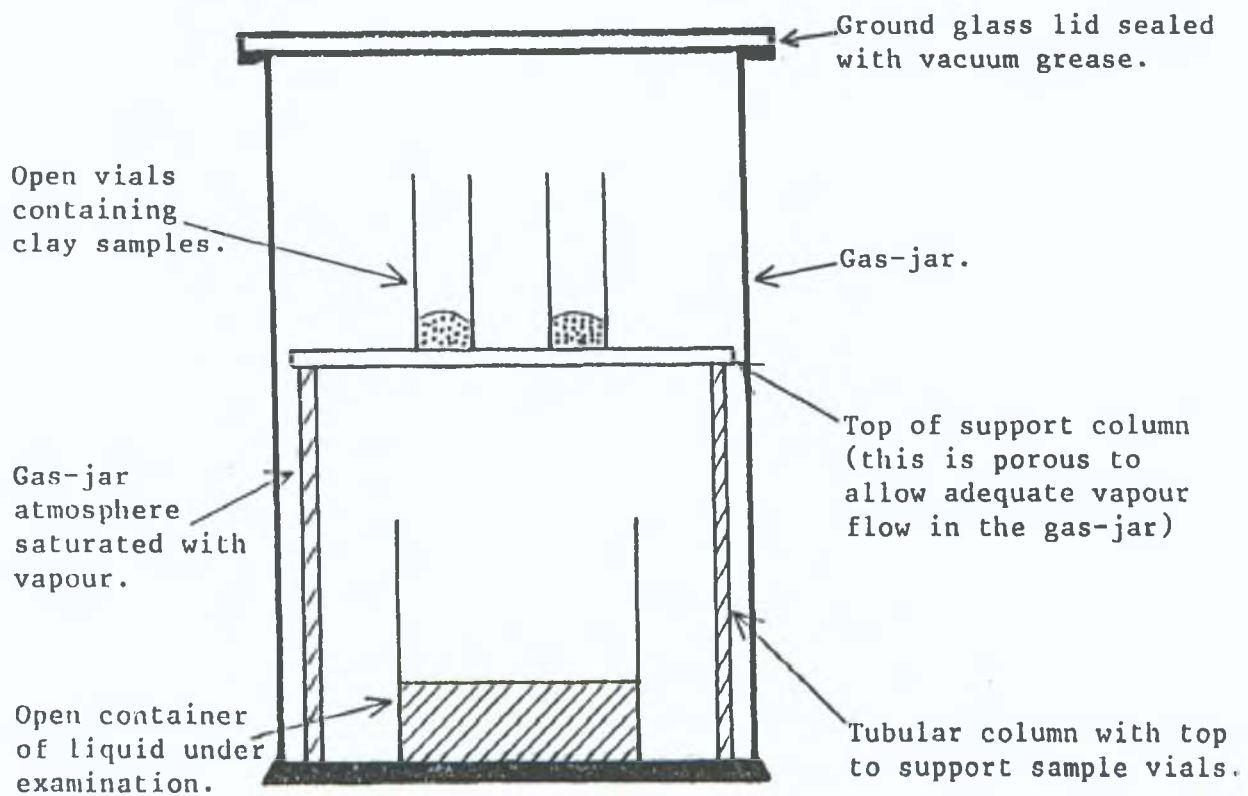


Fig 3.x. Schematic diagram of the gas-jar used to saturate clay samples

3.9. Quantification of the exchangeable cations

To measure quantitatively the concentration of interlayer cations in a cation exchanged montmorillonite, a back-exchange technique is used. A 1g sample of dry, finely ground clay is added to 25cm³ of a 0.5M Ca²⁺ solution, (Calcium chloride is suitable as neither Ca²⁺ or Cl⁻ ions will interfere with the atomic absorption spectroscopy (AAS) spectra of the cations of interest in this work, (Al³⁺, Fe³⁺, and Cr³⁺). This mixture is shaken vigorously to ensure thorough mixing, covered and left to equilibrate for at least 48 hours. The very high concentration of Ca²⁺ ions will replace the exchangeable interlayer cations, forcing them into solution. After 48 hours the mixture is centrifuged, the supernatant collected, and the clay slurry is re-suspended, re-centrifuged, and the supernatant is again collected. The volume of combined supernatant is carefully noted and the solution is then analysed using AAS, for the concentration of the exchangeable cations of interest. This will give the result in millimoles of cation per gram of clay.

In order to quantify the cation content of the silicate sheets a similar method is used. Firstly take a 3g sample of a dry finely ground clay and divide it into two portions of 1g and 2g respectively. The 1g sample is then assayed using the back exchange method described above to quantify the interlayer cation content. The 2g sample is assayed using a sodium fusion method⁴⁴. The results are combined, and the total cation content minus the interlayer cation content, gives the concentration of cations in the sheet structure, again in mmol g⁻¹. These techniques are useful when assessing a newly made clay, to see if the exchange process has worked and the exchange cations have actually filled the interlayer sites, or to check for batch to batch variations in a cation exchanged montmorillonite.

3.10. Theoretical Background

A model is presented below for a gas diffusing isothermally at constant pressure into a cylindrical clay pellet through its curved lateral surface, in the absence of chemical reactions. The flat circular faces of the cylinder are assumed to be impermeable and the gas is assumed to be initially absent from the pellet. Subsequently the cylinder is exposed to an atmosphere with a uniform concentration of the gas, the surface concentration approaching the value of this ambient concentration.

In this analysis, $c(r, \theta, z, t)$ denotes the concentration of the gas at time t at the point with the cylindrical co-ordinates (r, θ, z) . The pellet occupies the fixed right-circular cylinder $0 \leq r \leq a$, $0 \leq \theta \leq 2\pi$, $-\ell \leq z \leq \ell$. The diffusion of the gas is assumed to be Fickian, and the diffusivity D of the gas is assumed to be independent of concentration. The concentration then satisfies the diffusion equation,

$$\frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} + \frac{\partial^2 c}{\partial z^2} \right] \quad (1)$$

Initially the concentration satisfies,

$$c(r, \theta, z, 0) = 0 \quad (2)$$

On the flat impermeable surfaces,

$$\frac{\partial c}{\partial z}(r, \theta, \pm \ell, t) = 0 \quad (3)$$

The concentration on the lateral surface is given by

$$c(a, \theta, z, t) = c_{\infty} (1 - e^{-\beta t}). \quad (4)$$

Here, $\beta > 0$ is expected to be large, so that the concentration on the curved surface rapidly approaches c_{∞} .

The solution of the equations (1) - (4) is given in §5.3 of Crank⁵⁵. Note that there is a misprint in Crank's equation (5.28).

It is fairly straightforward to show that,

$$c(r, \theta, z, t) = c_{\infty} \left[1 - e^{-\beta t} \frac{J_0(rd)}{J_0(ad)} \right] - \frac{2\beta c_{\infty}}{a} \sum_{n=1}^{\infty} \frac{1}{n(\beta - D\alpha_n^2)} \frac{J_0(\alpha_n r)}{J_1(\alpha_n a)} e^{-\alpha_n^2 D t} \quad (5)$$

Where $d = (\sqrt{\beta}/D)$, and (α_n) is the increasing sequence of positive roots to the equation $J_0(a\alpha) = 0$. In equation (5), β cannot take the values $D\alpha_1^2, D\alpha_2^2, \dots$, and J_0 and J_1 are the Bessel functions of the first kind of order zero and one respectively.

Due to equation (2), the mass M_t of the gas adsorbed by the clay during the time interval $(0, t)$ is given by

$$M_t = \int_{-\ell}^{\ell} \int_0^{2\pi} \int_0^a c(r, \theta, z, t) r \, dr \, d\theta \, dz$$

Equation (5) can be substituted into this expression to obtain

$$\frac{M_t}{M_{\infty}} = 1 - 2e^{-\beta t} \frac{J_1(ad)}{adJ_0(ad)} - \frac{4\beta}{a^2} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 D t}}{\alpha_n^2 (b - D\alpha_n^2)} \quad (6)$$

Where $M_{\infty} = 2\ell\pi a^2 c_{\infty}$ is the limiting value of the mass of gas adsorbed by the clay particle. As in equation (5), it is required in equation (6) that $\beta \neq D\alpha_1^2, D\alpha_2^2, \dots$. From kinetic absorption data for M_t/M_{∞} , which was obtained using a gravimetric method, the constants D and B can be determined using equation (6). Note that $M_0 = 0$.

In practice, the series in equation (6) must be truncated in order to be evaluated numerically, and this truncated solution will be inaccurate for small times. Because data for M_t/M_{∞} were not obtained at such times, the truncated solution was satisfactory. An approximation that is accurate for small times can be found using the techniques reported by Carslaw and Jaeger⁵⁶

If the diffusion coefficient $D(c)$ varies with concentration, the value \tilde{D} found using equation (6) represents a mean value, termed

the integral diffusion coefficient Crank⁵⁵ gave in §11.6 the relation

$$\tilde{D} = \frac{1}{c_{\infty}} \int_0^{c_{\infty}} D(c) \, dc$$

The ambient temperature, T , is a parameter in the isothermal experiments that has thus far been suppressed. Diffusion in porous crystals is normally assumed to obey the Arrhenius equation

$\tilde{D} = \tilde{D}_0 \exp(-\Delta E/RT)$. Consequently, if D is determined over a range of temperatures, the activation energy ΔE and \tilde{D} can be calculated.

CHAPTER 4Literature survey4.1 General Introduction

For many centuries now, clays have been used to make products varying from earthenware vessels and ceramics to bricks and building materials. Today the use and applications of clay minerals are much more extensive and technically demanding. Clays are no longer taken straight from the earth for use, instead they undergo extensive processing to yield a range of structurally similar clays with a variety of properties.

These processed clays have been used in a number of applications including molecular sieves where the clay is used to separate compounds on the basis of molecular size. Another application of clay that has expanded in recent years is its use in electrochemistry. This is demonstrated by Oyama and Anson²⁵, where sodium-montmorillonite was used to coat a graphite electrode, and the clay plays a primary role in catalysing the reduction of hydrogen peroxide at the electrode surface. The reason suggested for this, is that iron cations (Fe^{3+}) which isomorphously substitute some of the Si^{4+} and Al^{3+} cations in the montmorillonite structure, (specifically the octahedral sites) may greatly enhance the activity of the electrode towards the reduction of hydrogen peroxide in solution. Rudzinski and Bard²⁶, examined the ability of montmorillonite to transport electrons within its structure. They concluded that for clays with large metal complexes in their interlayer space, (ie metal trisbipyridyl complex ions) the electron charge transport mechanism is primarily due to diffusion of externally adsorbed species. For smaller metal complexes (ie $\text{Ru}(\text{NH}_3)_6^{3+}$) the transport mechanism is via diffusion through and around the clay sheets. This gives cation exchanged montmorillonite the potential for a wide

range of electrochemical applications.

In recent years pillared clays have been developed, these are clays which have been modified so that the interlayer cation is replaced by a large robust cation. The most commonly used pillaring agents are aluminium based, such as $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ which is thought to be uniformly distributed on the interlayer surfaces. The large cations give large basal spacings in the clays, and reactant molecules can diffuse more quickly to the active interlamellar sites, so where the reaction rate is diffusion controlled reaction can occur more quickly. Also Diddams et al²⁷ has shown that pillared clays can change the selectivity for certain reactions, ether synthesis from pentanol among others, with the selectivity differing significantly from those for non-pillared clays. Other examples of pillaring agents would be niobium and tantalum $\text{M}_6\text{Cl}_{12}^{n+}$ cluster cations, ($\text{Nb}_6\text{Cl}_{12}^{2+,3+}$ and $\text{Ta}_6\text{Cl}_{12}^{2+}$) however such examples are rare and aluminium based pillaring cations are more commonly used.

Cation exchanged clays and especially montmorillonites have proven useful as selective catalysts for organic synthesis²⁸ (section 4.2). The acidic nature of cation exchanged montmorillonite is what gives it a wide potential degree of utility in acid catalysed and other reactions, with shape selectivity and product distribution ratio engineering also possible²⁸. Cation exchanged montmorillonites provide a source of protons to catalyse reactions, and choosing the optimum clay-solvent system is important. This will allow the maximum product yield and the shape selective nature, reduces the amount of side reactions occurring, (Table 1.1. list some of these reactions). An example is a study by Adams et al^{7,29} where the reaction of methanol and isobutene over Al^{3+} , Fe^{3+} and

Cr^{3+} clays using a range of solvents to produce methyl-t-butyl ether (MTBE) as the major product was investigated. MTBE is used as an alternative non-lead based additive to petrol, to increase its octane rating. When producing MTBE choosing the correct solvent-cation exchanged clay system is very important to get the optimum yield at the lowest temperatures

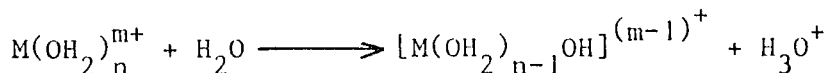
4.2 Catalysis by Clays

A brief outline of the types of reaction for which solid acid catalysts have been used is given in Table 1.1 This is a very short synopsis from a long list of reactions for which clays may be used. Before examining these reactions in detail it is worth considering some of the factors influencing the catalytic process. In most cases the clay appears to be acting purely as a solid source of protons⁹ However to date it has not been possible to produce a set of guidelines for catalysis by montmorillonites, which would help to decide whether a particular acid-catalysed reaction would succeed over a clay or which would suggest procedures to optimise yields for a particular reaction. As protons are responsible for the acidic character of the clay, and are produced by polarization of interlayer water³⁰, Adams et al⁵ have confirmed experimentally that M^{3+} -montmorillonites are more active than divalent or monovalent ion-exchanged clays. Consequently Cr^{3+} , Fe^{3+} and Al^{3+} are the more usual interlayer cations used in catalytic processes.

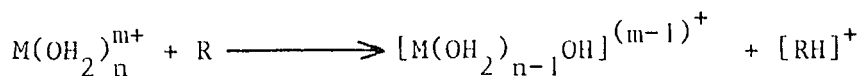
4.2.1 Reaction Sites

Although the protons necessary for acid catalysis are produced in the interlayer region, reaction need not occur there. The mobile proton can easily migrate to a more convenient location for reaction. It is important to note, that when the water is polarized about the interlayer cation, it can exert enormous

polarizing power on any molecule in the neighbourhood. Hence, immediately on production, the proton (H^+) will protonate a molecule present in the interlayer space and this process may be described as,



or in the case of an organic molecule being present in the interlayer then,



and the protonated species can move to the site where reaction occurs. The relative probability of the forward reactions occurring depends on the number of water and organic molecules in the interlayer space. The fact that the reaction need not occur in the interlayer was demonstrated using cation-exchanged montmorillonite, and the equivalent heat collapsed clay⁸, (ie it has no interlayer region as the layers have collapsed). When products were formed by the collapsed clay, this showed that the carbocations $[RH]^+$ can react at two possible sites, either with (i) oxygenated polar species such as alcohols and water on the clay surface, or (ii) hydrocarbons also in the interlayer region. Thus the active sites in the clay are not confined to the interlayer region exclusively.

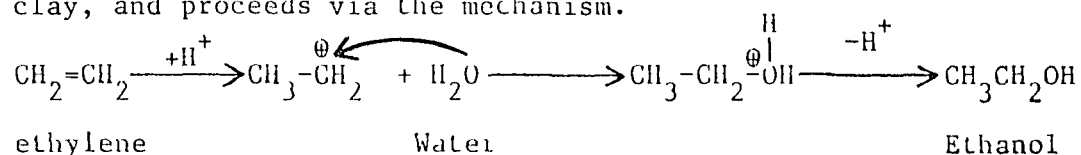
4.2.11 Solvent Effects

It was first (erroneously) thought that saturated hydrocarbon solvents should be used in acid catalysed reactions to avoid the possibility of coordination of the solvents to the interlayer cations. However Adams et al⁶ found cyclic ether type solvents to give comparable yields of MIBE at temperatures $\sim 30^\circ C$ lower than when hydrocarbon solvents are used. The lower temperature minimised the yield of side products, and for the specific example of 1,4-dioxan, (this was found to give the best result),

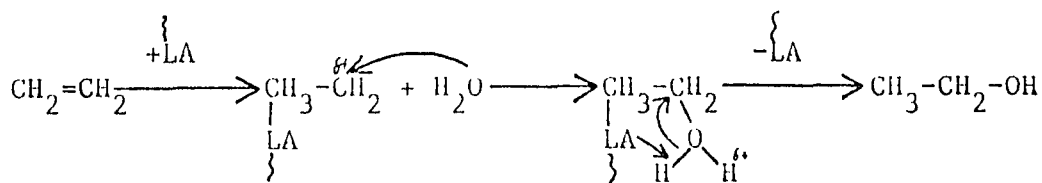
it is miscible with all the reactants and products, thus enabling the reaction to proceed more rapidly. Also some displacement of interlayer water by 1,4-dioxan may increase the interlayer acidity. Further to this Adams et al.³¹ studied the clay catalysed lactonization of cyclo-octene-5-carboxylic acid, a reaction that occurs at temperatures above 100°C. The increased temperature is thought to remove some of the interlayer water, effectively generating a stronger acid. However oxygenated solvents such as 1,4-dioxan reduce the efficiency of reaction by competing with interlayer water for the cation coordination sites, thus reducing the number of free protons. Hydrocarbon solvents such as xylene do not have this effect so above 100°C the cations are not fully hydrated and the clay behaves as a strong acid, (reactions with primary and secondary carbocations occur readily), and saturated hydrocarbon solvents are more efficacious. For low temperature reactions, when the cations are fully hydrated, and only a relatively low acidity is required, (protonation to form tertiary or allylic carbocations is feasible), the use of a solvent to promote miscibility (ie 1,4-dioxan) is advantageous.

4.2.111 Clay Catalysed Reactions

Some of the reactions listed in Table 4.1 will be considered here. Atkins et al.⁴ has studied the hydration of alkenes to alcohols using ethylene, to give ethanol. It is suggested that reaction occurs via protonation at a bronsted acid site in the clay, and proceeds via the mechanism.

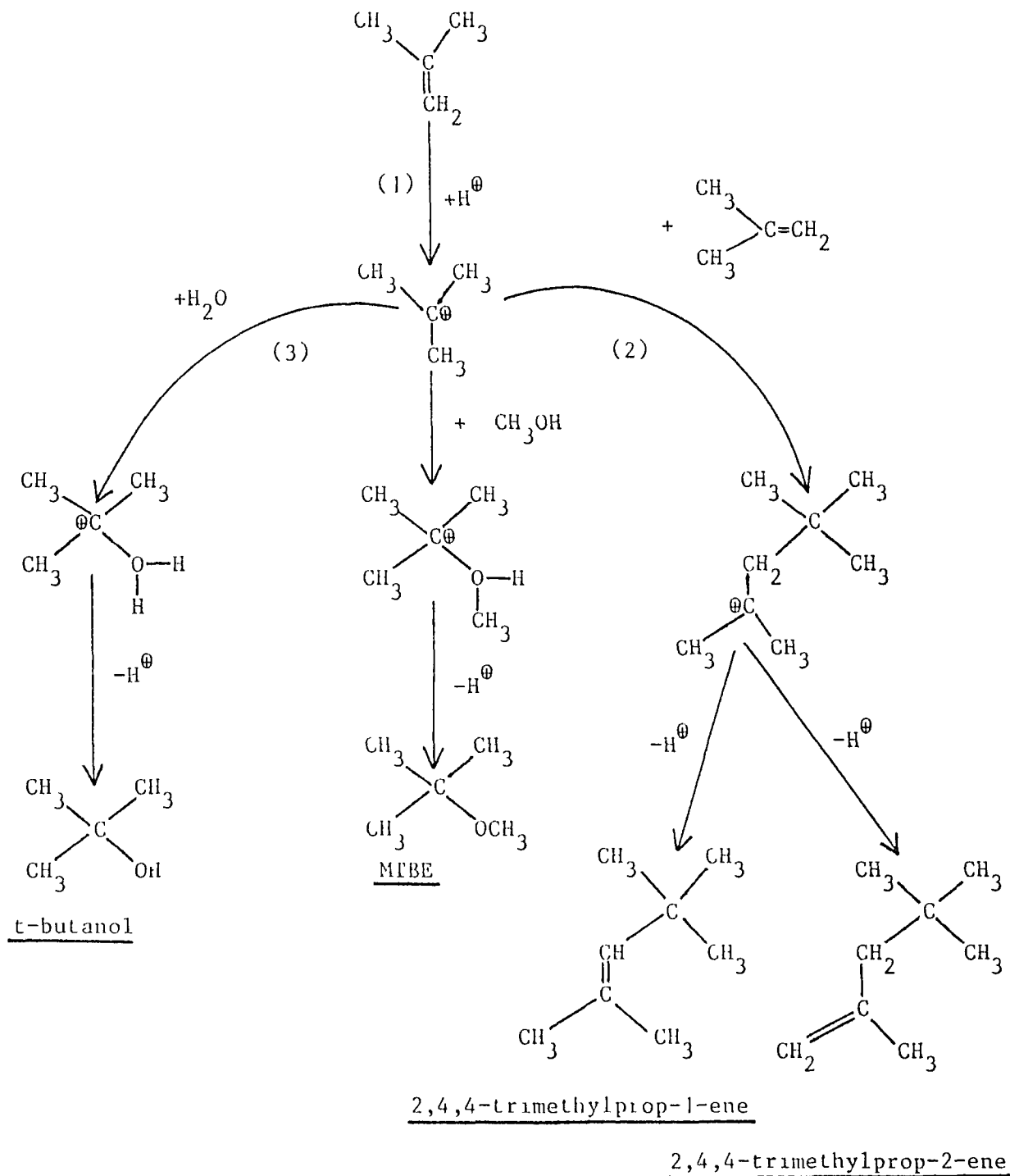


This mechanism may also be written by invoking a lewis acid site within the clay



However it should be noted that reactions occur mainly on bronsted sites. It was found that Al^{3+} -montmorillonite gave the highest conversions to ethanol, with the order of reactivity for the cation-exchanged montmorillonites, being $\text{Al}^{3+} \gg \text{Fe}^{3+} > \text{Cl}^{3+} > \text{H}^+ > \text{calcined clay}$. The poor yields from calcined clays indicated that the reaction is, at least in part, an interlamellar process. Now as the choice of cation influences the polarity of the interlamellar environment and the binding of the alcohol to the cation, two types of interactions are suggested. These are (1) the interaction of the empty electronic orbitals of the cation with the lone pair of electrons of the alcohol molecule, (ii) strength of the hydrogen bonding between the alcohol molecules. Consequently the arrangement of the ethanol about the cation influences the reaction. Hence the overall rate of hydration is effected by the the strength of the alcohol-cation dipole attraction and this may hinder the approach of the reactants to the interlamellar catalytic sites. Hence the observation that different interlayer cations give different yields of product.

The clay catalysed reaction of alcohols with alkenes to give ethers is of some importance, not the least because some sorption studies in this thesis were based on some of the work on this reaction. Adams et al examined the reactions of various alcohols (ie primary alcohols (C_1 - C_{18})) with alkenes (2-methyl pent-2-ene) over an Al^{3+} -montmorillonite. However the production of MIBE from methanol and isobutene will be discussed in detail as an example of this group of reactions. The suggested reaction pathways are as follows



The cation exchanged montmorillonites were compared with some commercially available acid catalysts, which gave good yields of MTBE (>50%), which is not surprising as these catalysts are based on smectite clays. The K10 and KSF catalysts probably have Al^{3+} cations leached from their octahedral sites into the interlayer and consequently behave as Al^{3+} -montmorillonite. All three cation exchanged clays Al^{3+} , Fe^{3+} and Cr^{3+} -montmorillonite gave yields of

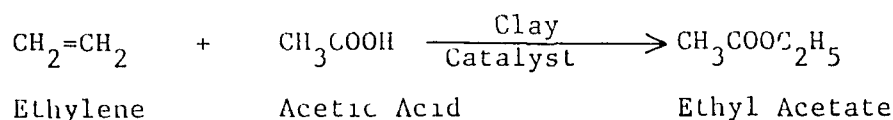
>50% MTBE with low yields of t-butanol these results were obtained using alkane solvents (eg n-pentane), however further studies with oxygenated solvents (ie tetrahydrofuran, tetrahydropyran (THF, THP), and 1,4-dioxan), demonstrated that they were just as effective, and in the case of 1,4-dioxan and Al^{3+} -montmorillonite, the highest yield of MTBE was obtained.

In the hydration of ethylene, it was shown that an interaction between an organic species (either reactant, solvent, or product molecule) and interlayer cation can influence the reaction yield. In an attempt to elucidate this effect a number of parameters were examined. The basal spacings of the different cation exchanged clays with the solvents, showed the effect was not due to the ease with which the reactant could enter between the layers, because the clay solvent system with the largest basal spacings (Fe^{3+} and Cu^{2+} -montmorillonite with 1,2-dimethoxyethane), gave the lowest yield of MIBE. The miscibility of the reactants and products in the solvent effects their distribution, however this cannot be the sole explanation as the observed effect depends on both solvent and cation, and not the solvent alone. The conclusion was that the effect was due to solvent-interlayer cation interaction, which modifies the efficiency of the reaction. It can influence the competition between, water, solvent, reactant and product for sites in the hydration shell of the active cations.

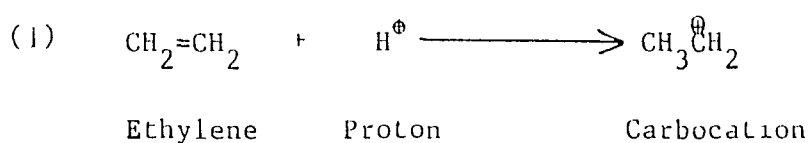
Adams et al⁷ investigated this reaction further by studying the reaction of alcohols (methanol, propanol, and 1-propanol) with t-butanol to produce t-butylethers at low temperatures (<100°C), using Fe^{3+} -montmorillonite and 1,4-dioxan as the solvent. It was found that the yield of t-butylethers from the alcohols was of the order methanol>propanol>1-propanol>>t-butanol. This trend

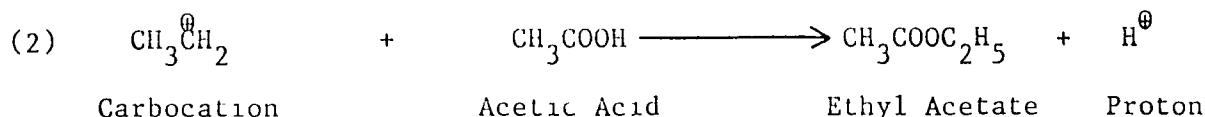
correlates well with the rate of diffusion for these molecules within the clay, or inversely with the steric hinderance which would occur during the reaction step when the alcohol attacks the carbonium ion, (see MPBE reaction pathway) So based on these studies, the investigations in this thesis were carried out. The rate of diffusion of the alcohols (methanol, 1-propanol and t-butanol) upon various cation exchanged montmorillonites (Al³⁺, Cr³⁺ and Fe³⁺) were measured to see if the rate of reaction was controlled by the diffusion coefficient of the alcohol, (which would be expected to depend on steric factors) Also the diffusion of the solvents (THF, THP and 1,4-dioxan) upon Cr³⁺ and Al³⁺-montmorillonite was examined. This was to see if diffusion of these solvent molecules, could influence the rate of reaction by propping the layers apart, for the smaller reactant molecules to enter the active sites more easily. Also infared studies of both the alcohols and cyclic ether solvents were used to see how these molecules may interact with the clay surface and interlayer.

Gregory et al¹⁰ investigated the addition of acids to alkenes to produce esters or more specifically



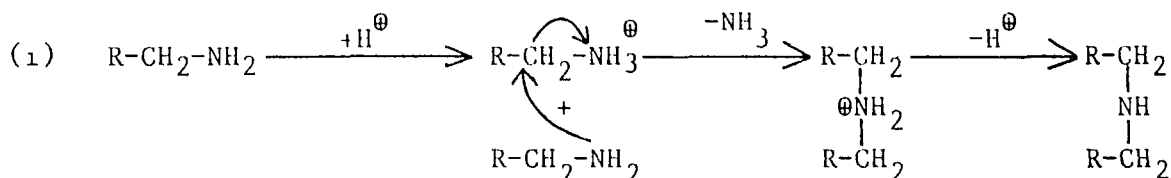
This reaction is known to occur in the interlayer region, since little or no product is formed using a collapsed clay catalyst. The reaction mechanism is thought to begin by protonation of an ethylene molecule at a bronsted acid site (1), and the carbocation then reacts with an acetic acid molecule within the interlayer region.





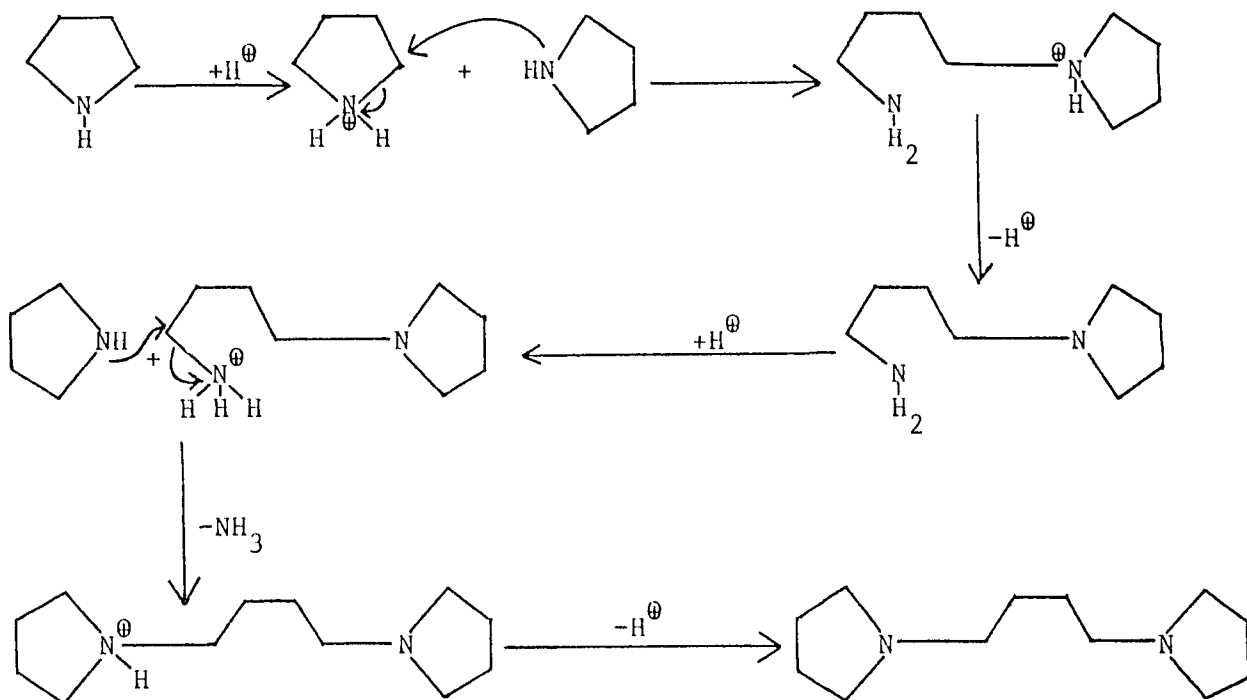
Also the selectivity for conversion to ethyl acetate was >99% for each of a range of ion-exchanged bentonite (H^+ , Al^{3+} , Fe^{3+} , Cr^{3+} , Cu^{2+} , and Na^+). Further to this Ballantine et al⁹ studied the addition of acids to a range of alkenes. The conclusion was that ion-exchanged clays were highly efficient for reactions with alkenes, when compared with sulphuric acid catalysed reactions, and the clays have a high selectivity for a specific product, eg the above reaction of ethylene with acetic acid over Al^{3+} -montmorillonite will yield ethyl acetate as the sole product.

Ballantine et al¹³ have also been investigating some elimination reactions involving clay catalysts. One of the interesting features of these elimination reactions, is that they are novel clay catalysed reactions, and have no counterparts in proton catalysed solution chemistry, (although similar reactions have been observed using finely divided nickel, palladium and ruthenium catalysts). A range of solid acid catalysts have been examined, (Al^{3+} -montmorillonite, Al^{3+} , H^+ , and NH_4^+ -bentonite), and two of the reactions studied were the elimination of ammonia from (i) alkyl-1-amines, and (ii) cyclo-alkylamines. The reaction mechanism is as follows.

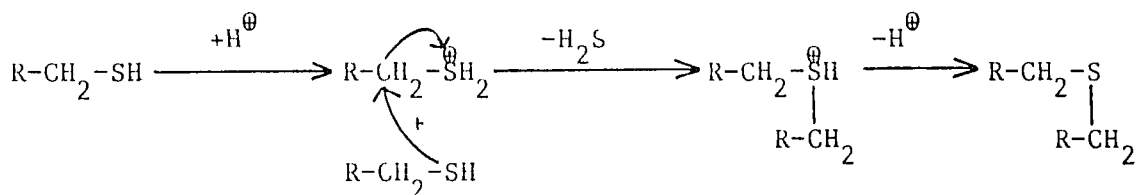


This type of reaction involves the use of an unprotonated amine to act as a nucleophile to displace ammonia from a protonated amine molecule, and such reactions are quite unknown in solution chemistry. The source of highly acidic protons in the interlayer region,

(reaction occurs at $>200^{\circ}\text{C}$), ensures that both protonated and unprotonated species can co-exist in proximity close enough for substitution reactions to occur, making clay catalysts almost unique for this type of reaction.

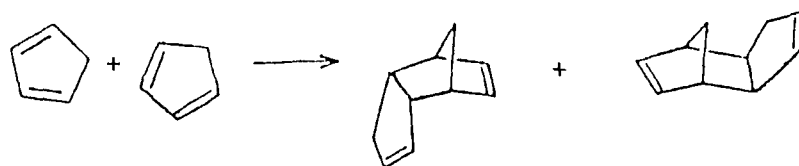


Similar reactions involving the elimination of hydrogen sulphide from thiols have also been reported¹⁵, and these reactions are similar to the amine reactions in almost every respect, eg.



Catalysis of diels-alder cycloaddition reactions by ion-exchanged montmorillonite, have been reported¹¹ It was found that while Cr^{3+} and Fe^{3+} -montmorillonite were effective catalysts non-transition metal ions such as Na^+ , Mg^{2+} and Al^{3+} were not. Where as it has been suggested that the clays are not acting as lewis acid or proton donor catalysts, but rather a one electron transfer process is involved, leading to a radical cation catalysed process.

As an example the dimerization of cyclopentadiene using Fe^{3+} -K10, (see page 48), Fe^{3+} and Cr^{3+} -montmorillonite catalysts will be considered. The reaction may be described as follows.



It was found that Fe^{3+} and Cr^{3+} have activities similar to that of Fe^{3+} -K10 even though this material has a much larger nitrogen surface area, (250 compared with $50\text{m}^2\text{g}^{-1}$). So it appears that the reactions are not catalysed solely by surface Fe^{3+} or Cr^{3+} cations, but must also involve those cations in the interlayer region of the K10 or montmorillonite (note, the cation exchange capacities of these materials are similar). If this is true, it implies that diffusion between the clay layers is not the rate determining process. The fact that transition metal cations are active, while Al^{3+} cations are not, suggests that one electron processes are as important here as they are in radical cation catalysed diels alder reactions. One further observation is that reactions catalysed by Fe^{3+} -K10 and Fe^{3+} -montmorillonite contained numerous unidentified by-products, but Cr^{3+} -montmorillonite gave a much 'cleaner' product yield. Indicating that the acidity of the clay appears to effect the product yield and purity.

In conclusion, cation exchanged montmorillonites may be used to catalyse a great variety of reactions, and the clay can behave as a solid source of protons, or it may be involved in

electron transfer process catalysis. The choice of interlayer cation can influence the activity of the clay for a specific reaction, and it can also effect the selectivity for, and purity of the product required. The temperature and solvent used can influence the acidity of the clay, (usually by displacing interlayer water), and so effect the reaction. Clay catalysts are easy to use, efficient, selective and in some cases unique acid catalysts for synthetic organic reactions.

4.3. Acidity of Clays.

The proton-donating or acid-catalysing abilities of a cation exchanged montmorillonite is one of its most significant features. It is this acidic nature that has led to the use of ion-exchanged clays as solid acid catalysts. The acid catalytic reactions are thought to take place at active sites within the clay structure, and these may be divided into two types of site³², the bronsted acid site and the Lewis acid site. The bronsted acid sites, basically behave as a bronsted-lowery acid which may be defined as a substance which supplies protons. Therefore any substance that increases the concentration of hydrated protons (H_3O^+) above that due to the autodissociation of the water, is an acid³³. In the case of an ion-exchanged montmorillonite, it is the effect of the polarizing power of the interlayer cation upon its sphere of hydration that polarizes the water molecules generating a source of protons within the clay interlayer. So generally bronsted acid sites are associated with the interlayer cations of the montmorillonite^{30,34}. Bronsted acid catalysis is involved in reactions where nucleophilic attack on a protonated species occurs²⁸, and although these reactions primarily occur within the interlayer space, when polar oxygenated species are involved, reaction may also occur on the surface of the clay.

In the case of ion-exchanged montmorillonite catalysed reactions, bronsted acid sites are thought to be the major source of the clays acidity, although in some cases the second type of acid site is thought to be involved. The lewis acid sites, may be defined as a lewis acid, which is a general definition of an acid, as an electron pair acceptor³³. (this definition includes the bronsted-lowry definition as a special case). This definition includes many systems where protons are not involved at all. In the case of montmorillonite the lewis sites are associated with the Al^{3+} and Fe^{3+} cations within the octahedral sheet of montmorillonite, and the coordination sphere of these cations is likely to be made up of water and hydroxyl groups, when they are exposed at crystal edges²⁸. Lewis acid sites are thought to be involved in reactions where the clay is heated in excess of $100^{\circ}C$ and so dehydrated. (also when the clay is dehydrated by vacuum) It is possible that the lewis sites may be more significantly involved in catalysis due to the lack of water as a source of protons for the bronsted sites.

The ability to measure the acid strength of a clay catalyst, in the same way the PH of a liquid can be measured, is a useful tool when applying these acids to various catalytic reactions. So a very brief mention of the various methods that have been developed over the years will be given. It should be noted that these methods are not specifically for ion-exchanged montmorillonites, but apply equally well to most solid acid catalysts, (ie zeolites, silica-alumina oxides, kaolins, etc.).

One of the earliest methods was the use of Hammett indicators, (developed by Hammett and Deyrup in 1932,³⁵). These work like a conventional acid base indicator, by forming a coloured complex with the acidic clay and changing colour when the clay

is mixed with a strong base such as an amine. (n-butylamine is commonly used^{36,37}). The colour change occurs once the amine has filled all of the acidic sites on the clay, (ie is in an excess). This method however is cumbersome to perform and it is difficult to accurately note the colour change on a dark medium such as a clay. Although in the 1960's Drushel and Sommers³⁸ developed a system of fluorescent indicators where the acid-base change in the indicator could be measured using a spectrometer. More recent instrumental methods include a temperature programmed desorption technique, developed by Nelson et al³⁹, although today a more commonly used technique is infra red spectroscopy (IRS). This has the advantage of not only being fast and easy to use but it can distinguish between bronsted and lewis sites within the clay^{40,41}

4.4 The Interaction of Organic Molecules with Acid Catalysts.

Adams et al^{6,31} has shown that for catalytic reactions involving cation-exchanged montmorillonites, the nature of the reactant, product and solvent molecules, influence the overall reaction dynamics. An understanding of how these molecules interact with the clay surface would help in determining how the choice of these molecules can influence the diffusion rate, product formation, and overall reaction rate. For the purpose of this study the discussion will be restricted to the interaction of alcohols, ethers and alkenes with the catalyst surface, (as these are the type of molecules of primary interest this study). For this work the most commonly used techniques are infrared spectroscopy and temperature programmed desorption, as they complement each other, which aids in interpreting the data.

Throughout the literature very little work has been done on the interaction of alcohols, ethers and alkenes with trivalent cation-

exchanged montmorillonite. The work in this area has centered mainly on Ca^{2+} , Na^+ , and Cu^{2+} -montmorillonite, although some work has been carried out on Al^{3+} -montmorillonite. By examining the mechanisms of interaction of various clay-organic systems, it is hoped that this will aid in the interpretation of the data for the adsorption of the alcohols and cyclic ethers on the various trivalent cation-exchanged montmorillonites studied in this thesis.

When the intercalation of alcohols in montmorillonite is considered several general trends begin to become apparent:

- (i) The alcohols are adsorbed by displacement of water molecules in the primary hydration shell of the cations⁶¹
- (ii) Primary aliphatic alcohols form single-layer complexes in the interlayer, but smaller molecules such as methanol and ethanol can form double-layer complexes⁶⁶
- (iii) For these small alcohol molecules, the cation-dipole interactions are far more important than any surface-molecule interaction.
- (iv) For larger alcohol molecules (ie longer carbon chain), Van der Waals interactions with the silicate surface become more significant.

The application of these principles is evident in Dowdy and Mortlands⁶² study of the adsorption of ethanol on Na^+ , Ca^{2+} , Al^{3+} and Cu^{2+} -montmorillonite, using infrared techniques. When considering the Al^{3+} -montmorillonite, it was suggested that the ethanol interacted with the water and hydroxyl groups of the Al^{3+} -hydration sphere, and that the $\text{Al}(\text{OH}_2)_6^{3+}$ octahedral complex undergoes spontaneous hydrolysis to $\text{Al}(\text{OH})_x(\text{H}_2\text{O})_{6-x}^{(3-x)+}$ so that the ethanol be bonded as shown in Fig 4.1. The mechanism of interaction shown is suggested by the infrared data. The C-H stretching frequencies of ethanol at (2984, 2936, and 2898cm^{-1}), are not detectably lowered on adsorption,

hence C-H---O hydrogen bonding of the alcohol to the silicate surface seems unlikely.

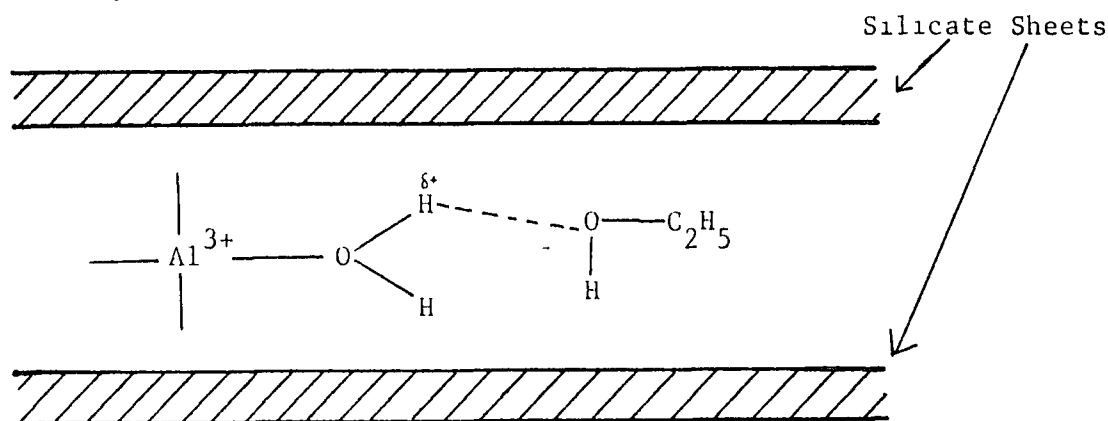


Fig 4.1. A schematic diagram of the interaction of ethanol with the Al^{3+} hydration sphere in Al^{3+} -montmorillonite.

Also the deformation band of water at 1635cm^{-1} shifted to a higher frequency in Al^{3+} -montmorillonite on exposure to the ethanol vapour suggesting the above mechanism of interaction.

This emphasizes the importance of the cation-dipole interaction in adsorption on cation-exchanged montmorillonites. However if the interaction of n-propanol on Na^+ -montmorillonite is considered, a further type of interaction appears to occur⁶³ The n-propanol is thought to form a single-layer complex of molecules orientated perpendicularly to the silicate sheets in the interlayer space. The n-propanol interacts with the surface oxygens via OH-----O hydrogen bonds, and also simultaneously interacts with the interlayer Na^+ ions via its oxygen atom. At the other end of the molecule the methyl groups are thought to interact with the surface via Van der Waals interactions and hydrogen bonds, (Fig 4.11.). For branched chain alcohols the situation is similar with single-layer complexes being formed⁶⁴.

To summarise the adsorption of alcohols on montmorillonite is influenced by both cation-dipole and surface-dipole interactions, as there is an insufficient number of cations to which organic molecules

can coordinate so surface interactions (OH-----O-Si) can and most probably do occur.

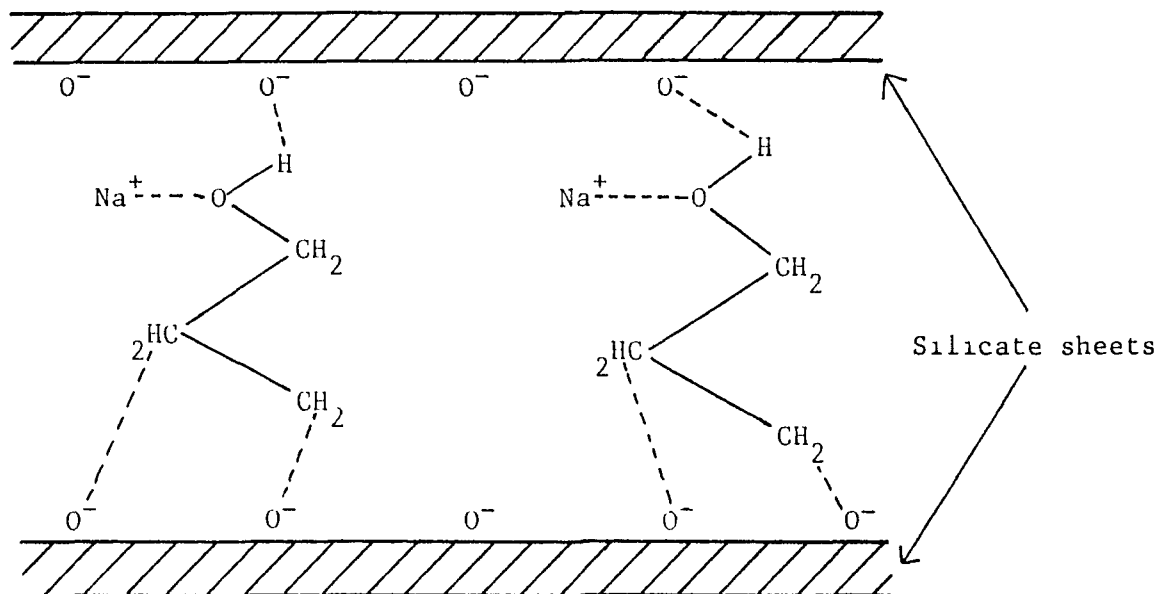


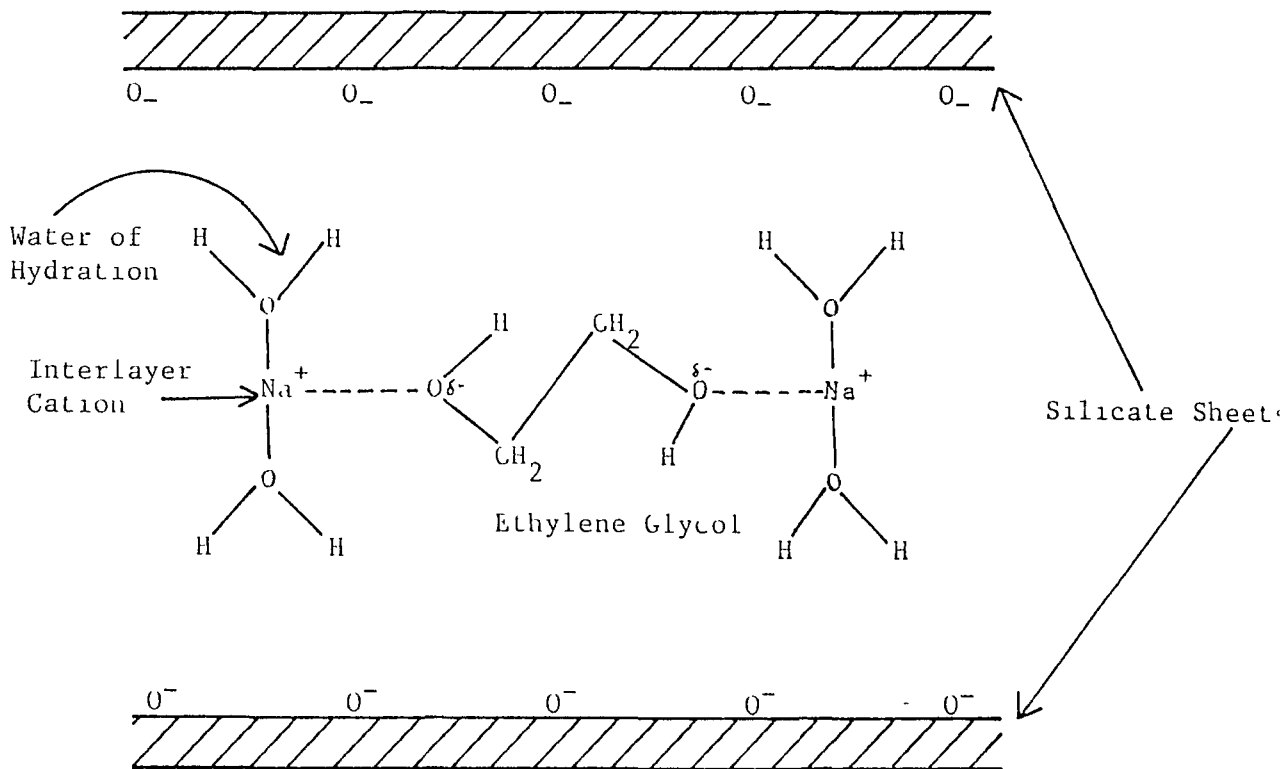
Fig 4.11. A schematic diagram of the interaction of propanol with Na^+ -montmorillonite (----- = Van der Waals interactions).

Studies of the intercalation and interaction of ethers with cation-exchanged montmorillonites are not well documented in the literature, however studies on the interactions of glycols have been carried out. If ethylene glycol is taken as an example, it resembles 1,4-dioxan in that it has an oxygen molecule at each end separated by a distance of two carbon units.



However it does not have the ring structure and overall size of 1,4-dioxan, and this must be considered when drawing analogies between the two compounds. Dowdy and Mortlands,⁶⁵ investigation of the interaction of ethylene glycol with Cu^{2+} -montmorillonite, showed that ethylene glycol and water compete for the same ligand sites around

the cation. Using the 1632cm^{-1} infra-red water absorption band, they showed that this band intensified when the clay-ethylene glycol complex was exposed to atmospheric air for increasing lengths of time, and the intensity of the bands due to adsorbed ethylene glycol decreased. Also bands at 2750 and 2650cm^{-1} were attributed to stretching vibrations of the hydroxyl groups in the glycerol molecule which are directly coordinated to the interlayer copper ion. These bands were thought not to be due to C-H stretching vibrations, as absorption in this region is weak or absent in the spectra of ethylene glycol complexes with montmorillonite containing cations other than copper, and in the spectra of ethanol-montmorillonite systems. Also no lowering of C-H stretching frequencies was observed on adsorption, as may be expected if the methyl groups were interacting with the surface, so based on this the suggested mechanism of interaction for ethylene glycol is as follows¹⁰⁴,



A single-layer complex with the plane of the carbon chain perpendicular to the silicate sheets, and based on the C-H stretching data above no C-H-----O-Si interactions are thought to occur. Also the ethylene glycol is known to form a double-layer complex via a similar mechanism under certain conditions⁶⁹

In general for ethers, one or two layer complexes can exist with cation-exchanged montmorillonite, and for the specific example of 1,4-dioxan a single layer complex is formed^{64,70}, with the plane of the ring lying normal to the plane of the surface, and again for ethers the interaction is primarily a cation-dipole and not a surface-dipole interaction.

Finally a brief mention of the interaction of alkenes with montmorillonite. Not a great deal is known about the interaction of these molecules with cation exchanged clays. However it is known that unlike polar organic species, they do not occupy similar sites to water at the silicate surface or satisfy the coordination requirements of the interlayer cations. Non-polar compounds are thought to be adsorbed by relatively weak, non-specific London Van der Waals forces, and ion-dipole effects are not generally important. The π electrons of the alkene double bond are thought to interact with the clay surface so enhancing adsorption, (this effect is well known for benzene type compounds (ie they have large π electron groups)), making π electron interactions an important mechanism in the intercalation of alkene molecules⁸¹⁻⁸³.

In conclusion it appears that cation-dipole interactions are of primary importance for intercalation on cation-exchanged montmorillonite, and interactions with the silicate surface are only of secondary importance. Also the packing of the diffusive or the number of layers formed, depends greatly on the actual diffusing

molecule, (its size, shape, and polarity), and on the specific cation-exchanged form of montmorillonite being used.

4.5. Diffusion in Clays

The diffusion or sorption uptake of various organic compounds in cation-exchanged montmorillonite was investigated for this thesis, however very little work of this nature has been published. In a brief overview, some of the of the studies to date are as follows.

In an early study by Barrer and MacLeod⁷¹ in 1954, the sorption of polar (methanol, ethanol and pyridine), and non-polar (oxygen, nitrogen and benzene), gases were studied. The results showed that both polar and non-polar molecules could be intercalated by montmorillonite, and that greater than monolayer coverage of the surface could be obtained if a sufficiently high pressure was used. Later in the 1960's Palmer and Bauer⁷² in a paper on the sorption of amines by montmorillonite, reached some conclusions that still hold today. Using weight uptake measurements they found the sorption rate to be of the order methylamine > ethylamine > dimethylamine >> trimethylamine, so confirming that steric hinderance influenced the rate of sorption. Also an average local temperature increase of 1°C upon sorption in the sample was noted, and the effect of the heat of sorption on the rate was suggested, (ie. the uptake occurs under non-isothermal conditions). Finally the authors were examining the effect of particle size in the rate of sorption, but this work was incomplete and no firm conclusions were reached. More recent studies have tried to determine the rate limiting step of diffusion in montmorillonites and in a review by Breen et al⁷³, it is suggested that at lower partial pressures of water, the rate limiting step is the rate of diffusion of the vapour in the lower spacing intercalate, (ie in the system studied two basal spacings were found to exist 23 Å, and 14.4Å respectively).

It is clear that a number of factors influence diffusion.

in cation-exchanged montmorillonites, however due to the lack of studies on montmorillonite it will be necessary to consider some studies on zeolites. Similar factors (ie molecular size, polarity and heat of adsorption) effect diffusion in zeolites, and a considerable number of studies have been carried out. A detailed examination of this work should provide a good basis for interpreting the results for the diffusion in montmorillonite studied in this thesis.

Montmorillonite clays have a lamellar sheet structure, that may be expanded by intercalation of organic molecules. Zeolites on the other hand have a series of channels and pores, that provide a robust network, which allows no loosening or opening of the framework upon sorption. The two major types of zeolite considered here, are zeolite A and zeolite Y. The difference between the framework of these zeolites is that zeolite A has an eight membered oxygen ring window, with a free diameter of about 4.2 \AA in the unobstructed Ca^{2+} or Mg^{2+} form (5A zeolite), and the channels do not contain cations. The 4A zeolite has a smaller free diameter as the channels are obstructed by Na^+ cations. The Y zeolite has a window constructed of a twelve membered oxygen ring, making its free diameter larger, so it can intercalate larger molecules. It is worth noting that the two very different structures of zeolite and montmorillonite minerals, mean that direct comparisons of the sorption rates for the two systems are not possible. The diffusing molecule must diffuse through the zeolite window to enter the pore, and this will remain a constant obstacle throughout the sorption process. In montmorillonites however the initial diffusing molecules must prise open the silicate sheets to reach the interlayer. This process becomes progressively easier as more molecules diffuse in and prop the layers apart, until the clay is saturated. Hence direct comparisons of the diffusion coefficients

for the two systems are not possible, but the diffusion processes may be similar.

As with montmorillonites it is possible to have different cation exchanged forms of a zeolite. Barrer and Brook⁷⁴ have examined the influence of the exchange cation on the rate of sorption of nitrogen, oxygen, hydrogen, krypton, and argon onto cation-exchanged zeolites. It was found that the cation influence on the sorption rate followed the general trend $\text{Ca} < \text{K} < \text{Ba} < \text{Na} < \text{Li}$ for all sorbates, and this suggests the radius of the cation influences the rate of sorption, and the interlayer cation is known to influence the equilibrium sorption in montmorillonite also²¹.

It is worth considering the effect of steric hinderance, as this can influence the rate of diffusion. The structural differences between zeolites and montmorillonite must be borne in mind when discussing the influence of steric hinderance on the sorption rate. Such studies generally consider the size, shape and polarity of the sorbate. Moore and Katzer⁷⁵ while studying the counterdiffusion of hydrocarbons in Y zeolite, observed that the movement of the sorbate molecule through the pore apperture may be the rate limiting step in the diffusion process. This observation was confirmed when Barrer and Clarke⁷⁶ studying the diffusion of n-paraffins in zeolite A, noted that the diffusion coefficient decreased as the carbon chain length increased, (ie, the \tilde{D} values decreased $0.26 > 0.19 > 0.11 (10^{17} \text{ m}^2 \text{ s}^{-1})$ as the carbon chain length increased $\text{n-C}_4\text{H}_{10} < \text{n-C}_6\text{H}_{14} < \text{n-C}_9\text{H}_{20}$ respectively). So the larger the sorbate molecule the more slowly it passes through the zeolite window. Moore and Katzer's⁷⁵ paper also considered the effect of the polarity of the sorbate molecule. While considering the aromatic diffusate-zeolite interactions, they found the effective diffusion coefficient for toluene to be four orders of

magnitude larger than that for phenol, although the critical molecular diameter for the aromatics is the same, (0.64 nm). It appears that the polar hydroxyl group of the phenol is in some way interacting with the zeolite and so retarding its progress through the pore channel, thus reducing its diffusion coefficient, and a similar effect might be expected in montmorillonites.

The effect of the particle or crystal size on the rate of diffusion in zeolites has also been examined. Yucel and Ruthven^{51,52} considered this effect using the sorption of CF_4 and $n-C_4H_{10}$ in zeolite 5A⁵² and nitrogen, methane, and ethane in zeolite 4A⁵¹. These studies found no significant difference in the diffusion coefficients for the different crystal sizes when the thermal effects were taken into account. Bulow et al.⁷⁶ also looked at the uptake of *n*-hexane on different crystal sizes of MgA zeolite. Here it was noted that for crystals in the size range 33-43 μm the uptake rate seemed to be limited by intracrystalline diffusion. However some dependence of the apparent diffusion coefficient on zeolite crystal size was observed. In a more recent paper by Bulow et al.⁷⁷ the effect of crystal size is examined in more detail. Using NaX zeolite of different crystal sizes, two factors were noted, (i) the sorption kinetics in larger crystals (120 μm) is mostly controlled by intracrystalline diffusion, and (ii) the uptake on the smaller crystals ($\sim 18 \mu m$) is limited by intercrystalline transport. This study also confirmed the Yucel and Ruthven^{51,52} observation that heat transfer effects need to be considered when calculating the diffusion coefficient, \tilde{D} .

The effect upon the diffusion coefficient due to the heat of adsorption was observed by Palmer and Bauer⁷⁸ in sorption onto montmorillonites. A number of papers have considered this effect and its influence in zeolite sorption. Firstly it is worth considering

how an increase in temperature will influence the rate of sorption. Barrer and Clarke⁷⁶ showed that increasing the temperature of sorption causes an increase in the measured diffusion coefficient, and a decrease in equilibrium loading (Q_{∞}) of the zeolite, (Table 4.1.).

Table 4.1. The diffusion coefficients and equilibrium loadings for the uptake of some n-paraffins in zeolite A at various temperatures⁷⁶

<u>Diffusivative</u>	<u>Temperature</u>	<u>Equilibrium Loading</u>	<u>Diffusion Coefficient</u>
	(K)	$Q_{\infty}(\text{mgg}^{-1})$	$D (10^{17} \text{m}^2 \text{s}^{-1})$
n-C ₄ H ₁₀	348	87.2	0.74
	363	80.2	1.64
	373	73.5	2.60
n-C ₉ H ₂₀	373	136.0	0.32
	393	134.2	1.11
	408	132.6	2.40

So any alteration in the local temperature of the zeolite could influence the observed sorption rate. Consequently heat transfer processes must be properly accounted for in the diffusion coefficient determination.

Attempts to measure the heat generated during sorption in zeolites have been made by Egan et al⁴⁵ and Ilavsky et al⁷⁹. Egan and co-workers measured a maximum temperature rise of 15°C for the sorption of nitrogen in 4A zeolite, and 50°C for the sorption of propane in 5A zeolite, and both experiments were conducted isothermally at -78°C. The effect of this heat of adsorption on the rate uptake curve was then considered, (Fig 4.111.). When the temperature maximum occurs early in the uptake process no pronounced effect on the rate curve is observed (curves A and B, Fig 4,111.), although it would be erroneous to assume that the data was obtained under isothermal conditions. However when the temperature maximum occurs later in the

uptake process (curve C, Fig 4.iii.) the uptake curve is altered (curve D, Fig 4.iii.), so the effect of the heat of adsorption will influence the observed value of the diffusion coefficient. The authors note however that the distribution of particle sizes within the sample could cause a similar effect, ie. the smaller crystals saturate first and no longer contribute to the rate, so the observed rate is reduced as the sample approaches equilibrium loading. The Ilavsky⁷⁹ study confirmed much of this work using a different technique. Using thermocouple wires of 0.1mm diameter, the temperature on the surface and in the centre of a zeolite pellet could be measured, and for the sorption of n-heptane on a zeolite, a temperature gradient of more than 20°C above isothermal was observed.

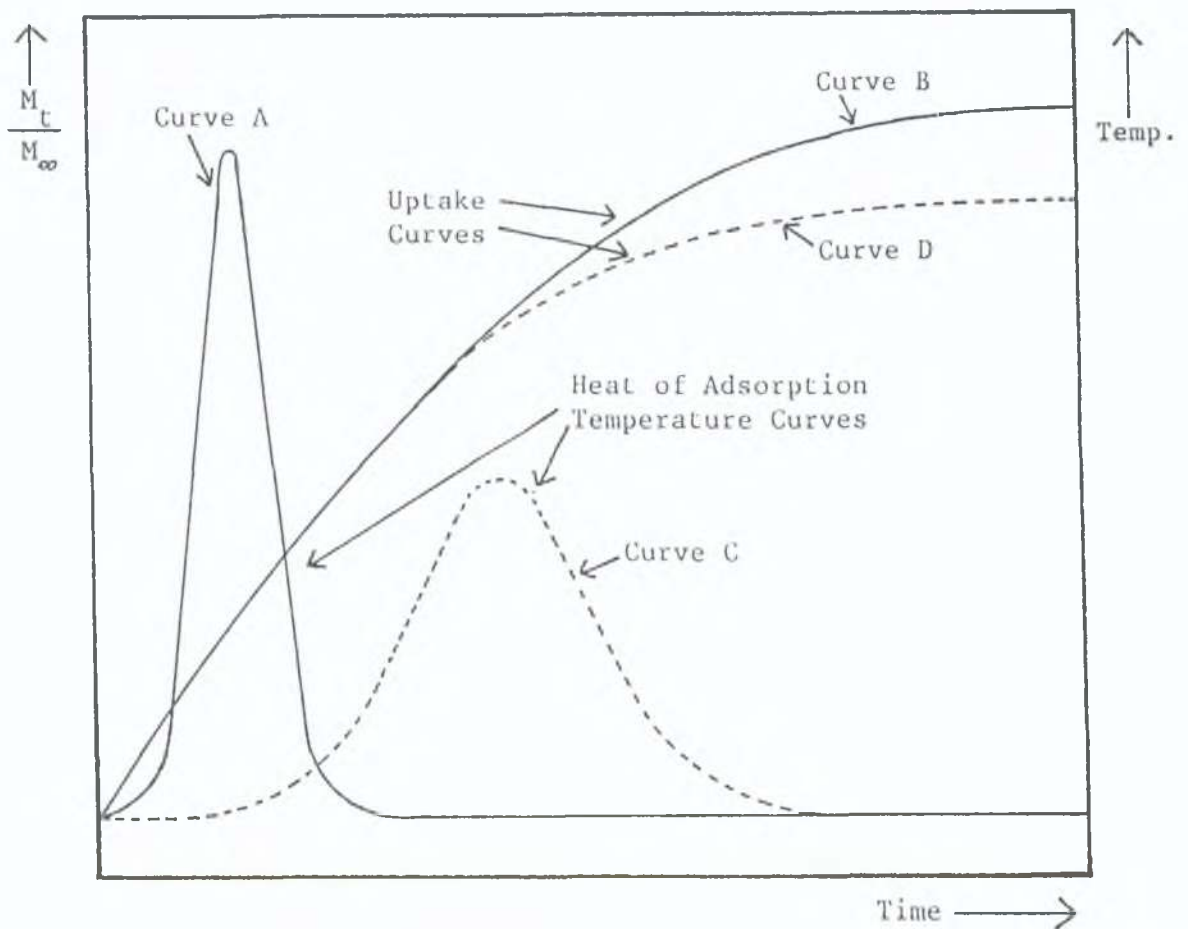


Fig 4.iii. Diagram illustrating the effect of the heat of adsorption on the isothermal rate uptake curve.

In recent years the use of nuclear magnetic resonance techniques to measure diffusion coefficients, have been applied to the study of thermal effects in zeolite crystals. Some points worth noting about nuclear magnetic resonance studies are that they have the advantage of not being influenced by thermal effects⁵³. Also the mineral samples used for nuclear magnetic resonance studies are previously equilibrated with sorbent, and so they are a study of the sorption dynamics at equilibrium. Sorption rate studies use non-equilibrated samples, and so are dynamic studies of a non-equilibrium system. A further point is that the nature of the nuclear magnetic resonance studies, means that the sample and grain size usually have an influence, this however is a problem in sorption rate studies, so the results from the two techniques may not be directly comparable. However Bulow et al⁸⁰ found that by comparing nuclear magnetic resonance and sorption rate results, the rate uptake curves deviated from an isothermal uptake curve, being faster in the initial region and slower in the final approach to equilibrium in accord with observations previously made by Egan et al⁴⁵ and Lee and Ruthven⁵⁵. This is attributed to thermal effects primarily due to heat transfer from the external surface of the sample. In conclusion diffusion in zeolites may be summarised by the findings of Doelle and Riekert⁴⁶. Processes other than diffusion in crystals, but coupled with sorption, namely flow in the intercrystalline voids and heat transfer, can have considerable influence on the rate of mass transfer between the gas phase and a zeolitic sorbent.

Before discussing the type of diffusion that might occur in a clay system it is worth mentioning counterdiffusion briefly. This may be considered as a second molecule diffusing within the clay in the opposite direction to the first, i.e. the reactant diffusing to

and the product diffusing away from the active site. Moore and Katzer⁷⁵ showed that diffusion of products out of zeolite catalysts may interact with the reactant molecule and contribute to a reduction in the rate of diffusion. Such influences on the sorption rate must be borne in mind when interpreting the data.

Before the experimental results can be evaluated properly it is important to have an understanding of the diffusion processes involved in adsorption on clays. When sorption rate studies on zeolites are carried out the theoretical model can be based on the fact that each zeolite pellet is a single crystal and may be approximated to a sphere, consequently a diffusion model may be designed on this basis. However with clays such as montmorillonite a very different situation exists (Fig 4.1v.), each grain of clay is comprised of many different particles of a non-uniform shape and size, and varying diameters. The grain itself is a non-uniform shape, but by sieving the clay a uniform size range may be obtained (see chapter 3.) The diffusion model for a clay must be based on an idealised representation of the actual packed bed of clay grains. So the physical characteristics of the clay sample must be borne in mind considering diffusion in such a system (Fig 4.1v.).

Diffusion in macropores^{50a}, is known to influence the overall kinetics of heterogeneous catalytic reactions, and is generally controlled by a combination of four different diffusion processes. Two of the four mechanisms will only contribute slightly in the case of the samples used in the studies here. Molecular diffusion is when the resistance arise from collisions between the diffusing molecules, and is dominant whenever the mean free path of the gas, (the average distance travelled between molecular collisions), is small relative to the pore diameter, and with montmorillonites this

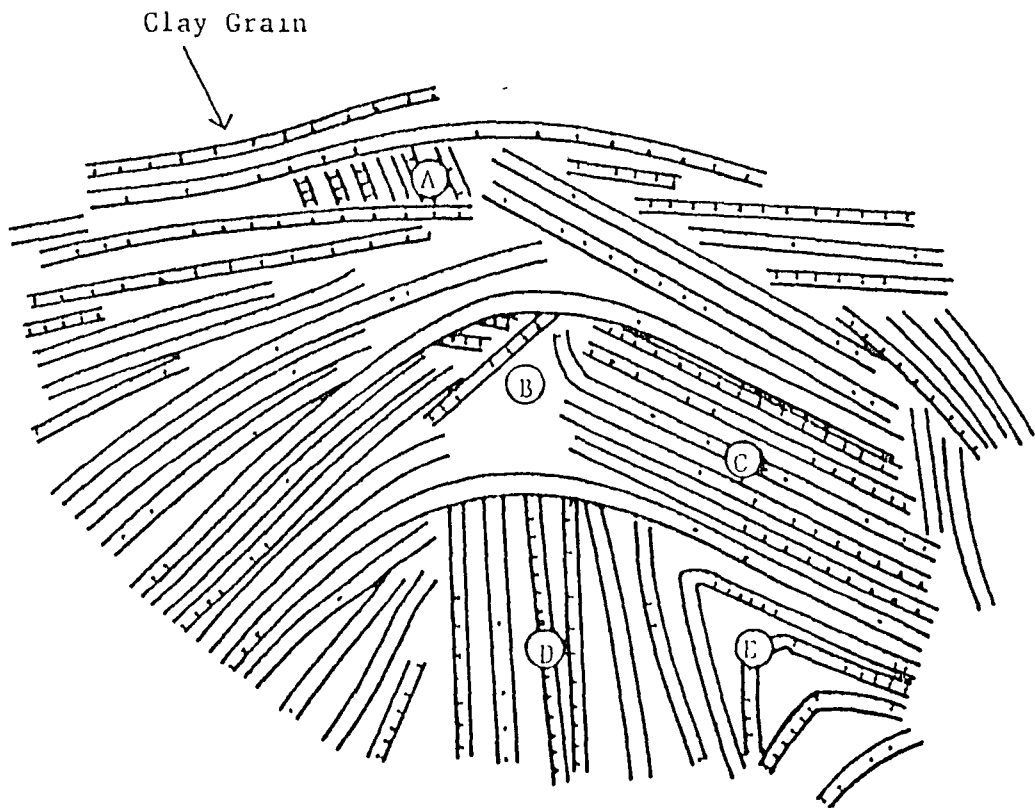
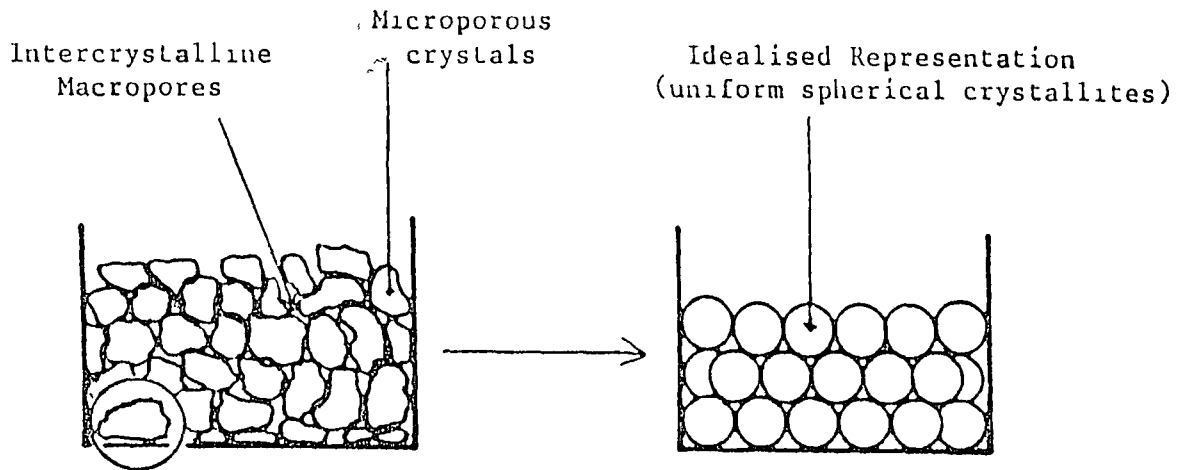


Fig 4.iv. Schematic representation of the structure of a clay grain.

Some of the common structural defects are shown A - E.

Where A = Edge to face stacking.

B = Voids.

C = Ordered Domains.

D = Regions of disordered stacking.

E = Regions of gross folding. (adapted from Cebula et al⁸⁶).

is unlikely to be a significant factor. Poiseuille flow is only a contributing factor, when the differences in total pressure across a particle directly contributes to the adsorption flux from forced laminar flow through the macropores. This effect is generally negligible in a packed bed since the pressure drop over an individual particle is very small, and packed bed systems were used in these studies.

The two diffusion controlling factors of more interest for this study are, firstly, Knudsen diffusion, this occurs in low pressure systems where the mean free path is greater than the pore diameter. So collisions of the molecules with the pore walls occur more frequently than collisions between diffusing molecules. The characteristic feature of Knudsen diffusion is its randomness. When a molecule strikes the pore wall it is not bounced off like a tennis ball, rather it is instantaneously adsorbed and re-emitted in a direction random to its original direction before collision. Knudsen diffusion may be estimated from the equation,

$$D_k = 9700u \left(\frac{1}{M} \right)^{1/2} \quad (\text{cm}^2 \text{s}^{-1})$$

u = the pore radius (cm)

T = temperature (K)

M = the molecular weight of the diffusing species

One of the features of Knudsen diffusion is that each species diffuses independently so it is independent of composition or total gas concentration. There is a slight temperature dependence and an inverse dependence on the square root of the molecular weight. The second influencing factor is Surface diffusion, as it is a direct contribution to the flux from transport through the physically sorbed layer on the surface, and may be applicable in the case of montmorillonite clays. This effect is temperature dependent, as a temperature above the boiling

point of the sorbed species, would cause the thickness of the adsorbed layer to decrease, so flux through the surface layer becomes small compared with flux through the gas phase. It is also usually concentration dependent as this can influence the adsorbed layer thickness, and as a good general rule, surface diffusion is only significant in small diameter pores in which flux through the gas phase can be attributed entirely to knudsen diffusion.

In conclusion, it is clear that many factors influence diffusion in zeolites and other clay minerals, and these factors will also be important when considering diffusion in trivalent cation-exchanged montmorillonite. So when considering the following studies it is important to bear in mind the effects of size, shape, polarity, and partial pressure of the diffusivative, and its interactions with the clay sheets or the interlayer cations, as these may influence the rate of diffusion. Other factors such as the heat of adsorption and the magnitude of such a thermal effect will also influence the rate uptake curve. The clay sample itself is also important, as the nature and type of interlayer cation, and the grain and sample size being used in the packed bed of the sample pan are important. So bearing all of these influencing factors in mind a study of the diffusion and interactions of alcohols and cyclic ethers on trivalent cation-exchanged montmorillonite will be considered in the following chapters.

CHAPTER 5Vapour Phase Sorption Kinetics for Alcohols and Cyclic Ethers on
Cation Exchanged Montmorillonite5.1 Introduction

The study of sorption dynamics, or the diffusion of organic compounds towards, and product molecules away from the active sites of a cation exchanged clay, can play an important role in the rate of reaction, and may even be the rate limiting stage. In this investigation the direct measurement of sorption kinetics was used, as this determines the rates in practical applications. In section 4.5 it was shown that the sorption dynamics are influenced by several factors, and the effect of these factors on the rate of uptake will be examined. By using various forms of cation exchanged montmorillonite such as Al^{3+} , Fe^{3+} , and Cr^{3+} , the effect of size and charge of the cations will be examined. The cation can influence the selectivity of the clay for a specific reaction¹¹, and the cation can interact with organic molecules in the interlayer⁶, thus effecting reactions occurring in the clay interlayer. The physical size of the hydrated cation will determine the basal spacing of the clay and this can influence the rate of diffusion of organic compounds to the active sites, as larger basal spacings can help to reduce steric hinderance in the diffusion process. Also the choice of cation can influence the number and yield of side products for a specific reaction¹¹.

The cationic form of the clay will to a certain extent influence the geometry and dimensions of the channel network, as will thermal pre-treatment of the clays. The size shape and flexibility of the diffusing molecule can be examined using two different solvent types. The alcohols used increased in physical size as methanol < propan-2-ol < 2-methyl-propan-2-ol, whereas the cyclic ethers used

1,4-dioxan, tetrahydrofuran (THF), and tetrahydropyran (THP), are all of similar physical dimensions and have no bulky substituents, so that all three might be expected to interact with the exchange cation in a similar manner.

The effect of sample and particle size was investigated by using clays divided into known grain size ranges and using different sample sizes of these groups for the studies. Based on studies by Egan et al⁴⁵, and Doelle and Riekert⁴⁶, the effect of a temperature rise caused by exothermic heat of adsorption, on the sorption kinetics was also measured. Hence the study may be divided into five sections, (although many of these influencing factors are interrelated).

- (i) An investigation of the influence of sample size.
- (ii) An investigation of the influence of grain size.
- (iii) An investigation of the influence of the cation exchange form of the clay.
- (iv) An investigation of the effect of the molecular size and shape of the diffusate.
- (v) The effect of temperature on the rate of adsorption.

The choice of the compounds for the investigation was to some extent based on studies by Adams et al⁷, where the influence of steric hinderance on the rate of reaction of methanol, propanol, and 1-propanol with t-butanol was considered, and this suggested the choice of alcohols for this study. In another study by Adams et al⁶ the influence of the oxygenated solvents THF, THP, and 1,4-dioxan on the reaction to produce MTBE was considered, and the authors found 1,4-dioxan to give the highest yield of product. Hence it was decided to investigate the diffusion of these cyclic ethers and three of the alcohols listed above upon various cation exchanged montmorillonites, (Al³⁺, Fe³⁺, and Cr³⁺).

Experimental limitations dictated that the rate of sorption may only be studied at the room temperature partial pressures of the diffusing compounds. The vapour pressure considerations allow the direct comparison of the sorption rates for, 1,4-dioxan, 1-propanol, and t-butanol as one group, and methanol, THF, and THP as the other group. This allows additional information on the effect of molecular size and shape on the relative rate of diffusion of these compounds into clays to be obtained.

5.2. Optimization of the Experimental Conditions.

Before undertaking sorption kinetic investigations it is important to ensure that the experimental conditions are optimised prior to making any measurements.

5.2.i. Optimising Vapour Flow Rates

The flow of solvent vapour over the sample essentially generates a saturated atmosphere about the sample. Fig 5.1. shows that by increasing the flow rate of the vapour the rate of sorption increased to a point where increasing the vapour flow any further does not effect the rate of sorption significantly. If however a flow of $100\text{cm}^3\text{min}^{-1}$ had been used the derived rate of sorption, would have been limited by the concentration of the vapour in the furnace atmosphere about the sample. Therefore an unsaturated atmosphere will give an artificially low diffusion coefficient. The trend shown in Fig 5.1. is for the uptake of i-propanol upon Cr^{3+} -montmorillonite, and is indicative of the trend for the other clay-vapour systems studied.

5.2.ii. Optimising the Grain and Sample Sizes.

Fig 5.11. illustrates the influence of grain size on the rate of adsorption. The system illustrated is the sorption of

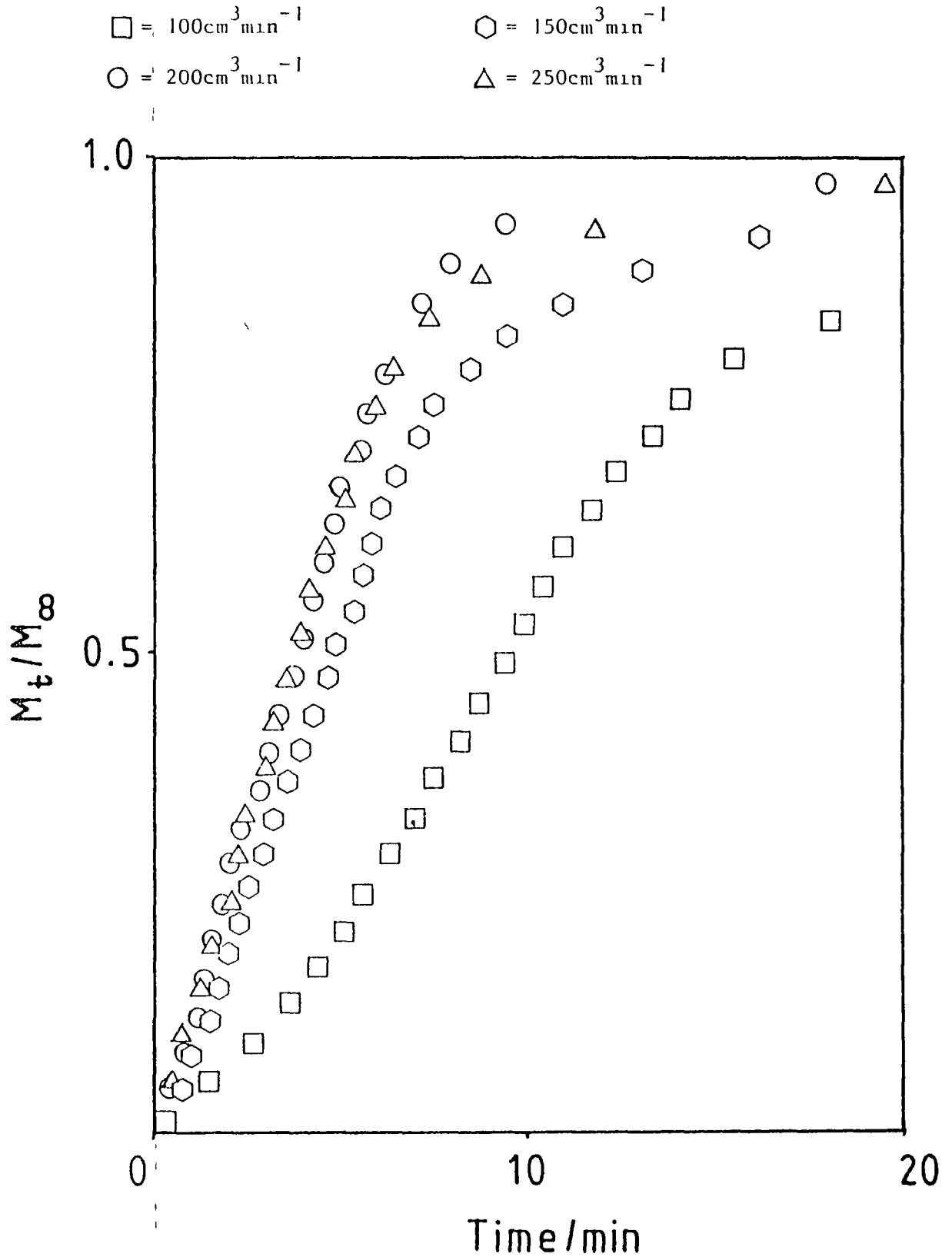


Fig 5.1. Optimization of the flow rate for the uptake of 1-propanol upon Cr^{3+} -montmorillonite at 18°C .

i-propanol upon Cr^{3+} -montmorillonite at 18°C . The clay was divided into different grain size groups (see section 3.4.), and the rate of sorption for each group plotted, (Fig 5.11.). As can be seen the rate of sorption increased with increasing grain size until a grain size of $<45\mu\text{m}$ was reached, as this was the smallest sieve available at the time, and this grain size group was chosen as optimum. Using the $<45\mu\text{m}$ grain size the optimum sample size was investigated, using different sample weights. Fig 5.111. shows that the rate of sorption increased with decreasing sample size, to a weight of 2.5mg as this was the minimum weight with which the thermobalance could be operated. It should be noted that the adsorption of i-propanol upon Cr^{3+} -montmorillonite used in these investigations is representative of the other clay-vapour systems.

Finally Fig 5.1v. illustrates the effect of a mixed grain size sample on the sorption rate. This shows that for a mixture of large and small grains the early part of the curve is unaffected, but the effect is much more pronounced at longer times, with the time required to reach equilibrium loading significantly longer than that required by a sample containing the smaller grain sizes only.

5.2.111 Determining the Optimum Thermal Pre-treatment of the Clay.

The hydration state of the clay effects its acidic or catalytic nature, and was discussed in section 4.3. A fully dehydrated clay will have a lower amount of bronsted acidity than a partially dehydrated clay³⁴. Ensuring the water content or hydration state of the clay is reproducible from sample to sample is important. This may be done by pre-heating the clay to a set temperature before each experimental run, ensuring a consistent water content each time. The effect of thermal pre-treatment at a series of temperatures, on the adsorption of i-propanol upon Cr^{3+} -montmorillonite system,

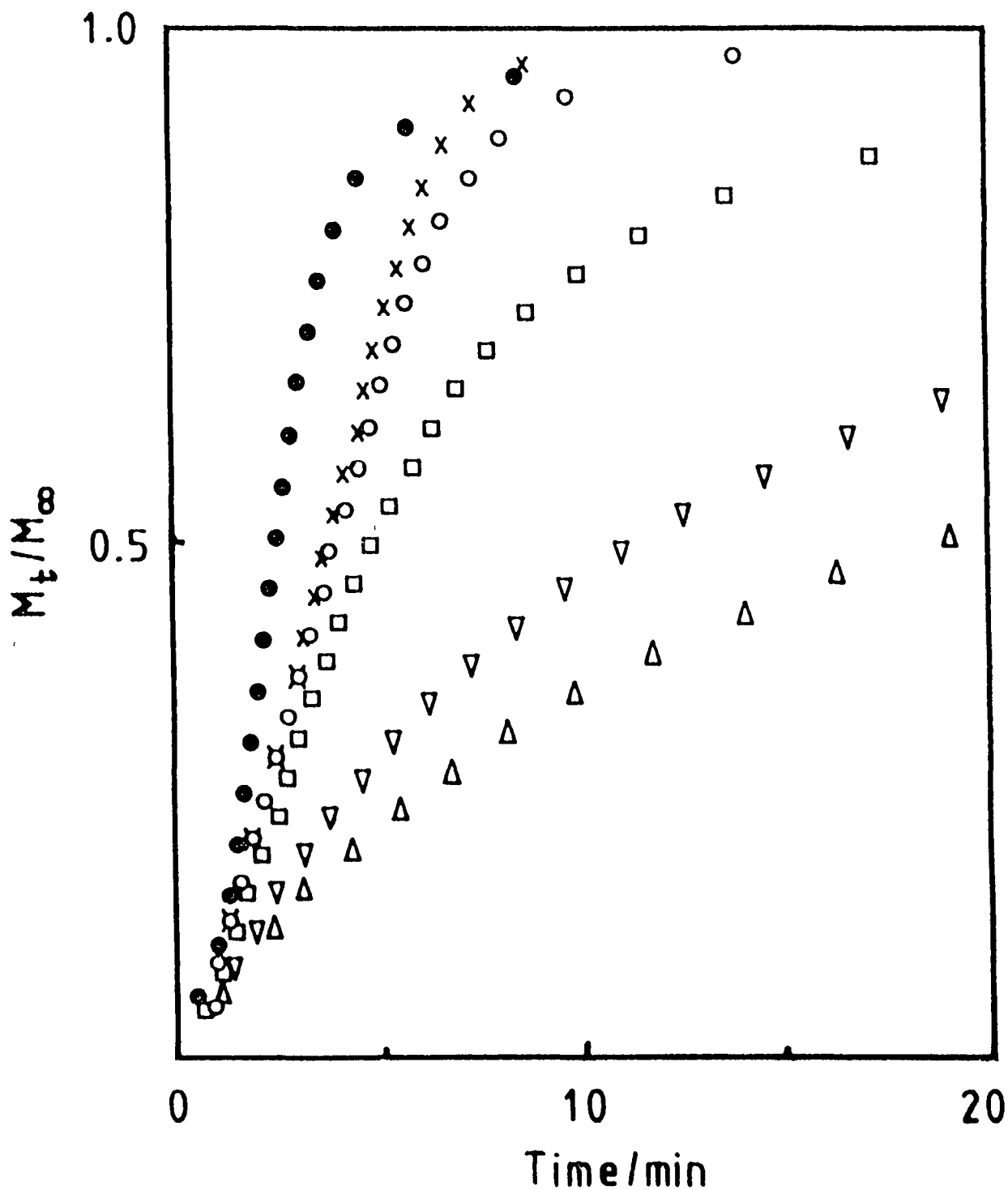
Δ = 5mg, >250um ∇ = 5mg, 125-250um \square = 5mg, 63-125um \circ = 5mg, 45-63um \times = 5mg, <45um \bullet = 2mg <45um

Fig 5.i1. Optimization of the grain size groups using the uptake of 1-propanol upon Cr^{3+} -montmorillonite at 18°C .

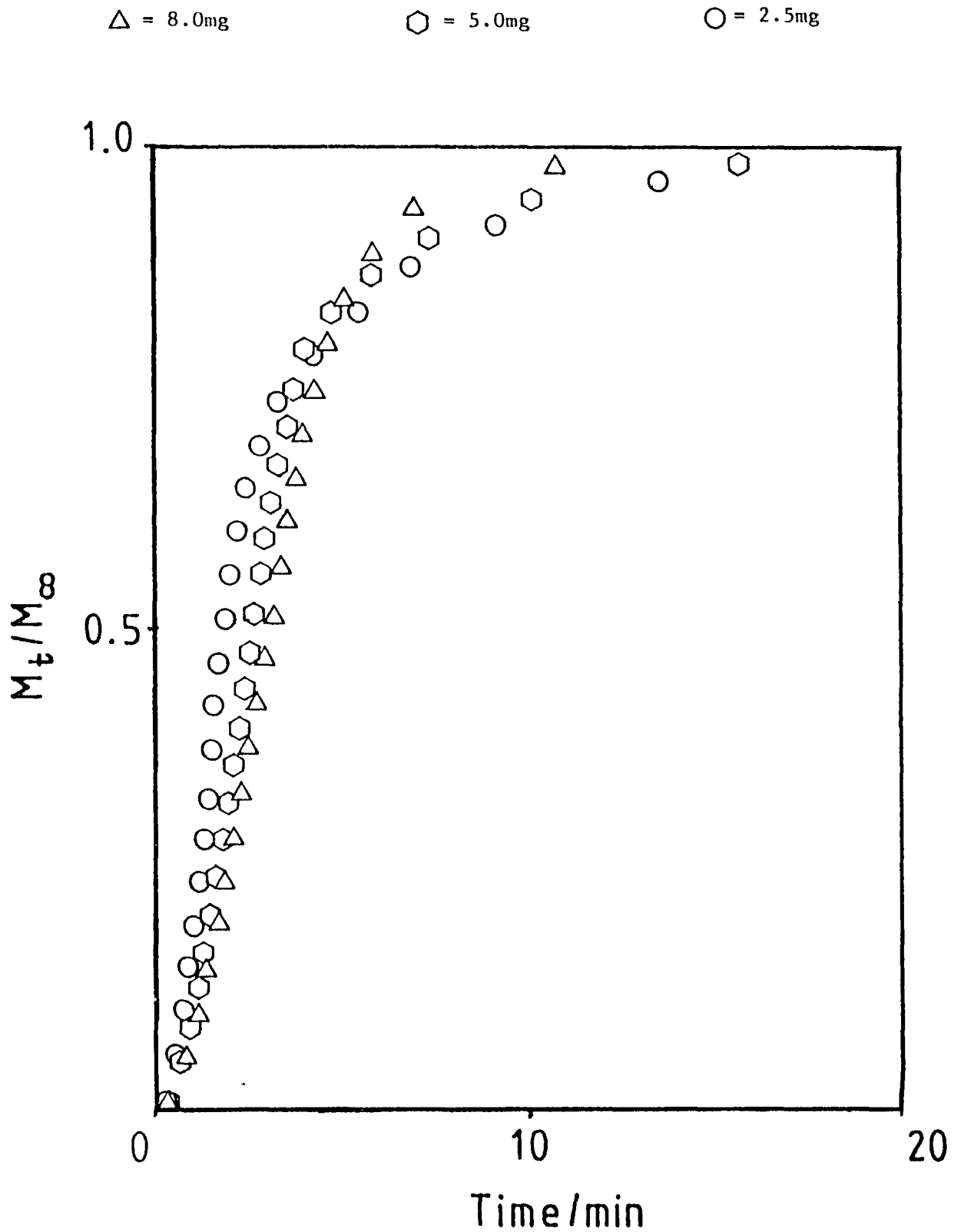


Fig 5.iii. Optimization of the sample weight using the uptake of i-propanol upon Cr^{3+} -montmorillonite at 18°C .

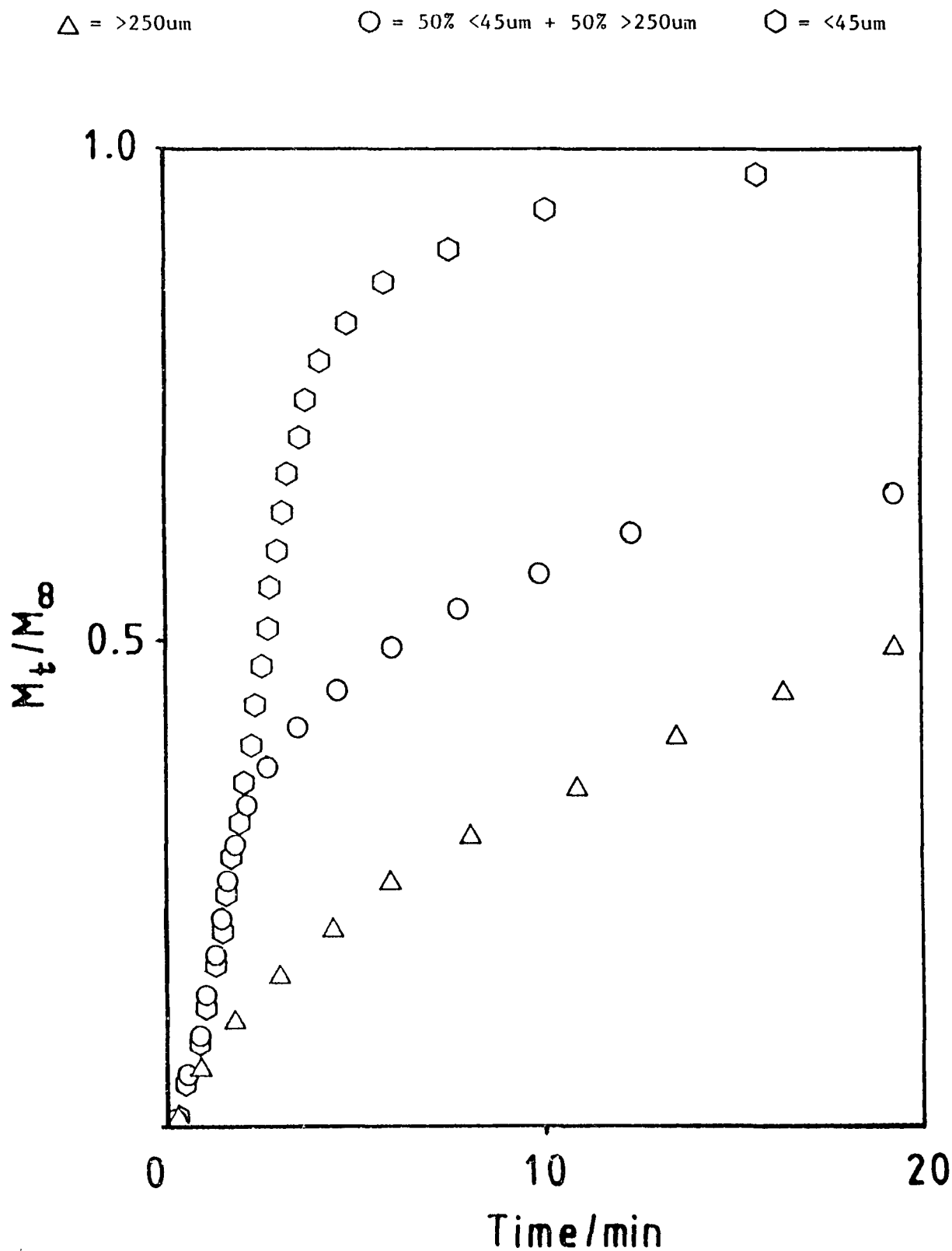


Fig 5.1v. Mixed grain size study using the uptake of i-propanol upon Cr^{3+} -montmorillonite at 18°C

(fig 5.v.). The rate of sorption decreases as the temperature is increased beyond 120°C, consequently a thermal pre-treatment temperature of 120°C was chosen, and again the 1-propanol-Cr³⁺-clay system is representative of the other vapour-clay systems studied. Also this pre-treatment ensures that the clays should have a representative amount of water in the hydration sphere of the interlayer cations, thus mimicing the hydration state of the clays used in catalysis

5.3. Fitting the Experimental Data.

Fig 5.vi. shows a theoretical curve fitted to the experimental data points. This is done by first plotting the experimental data on a set of axes, and then different values of the diffusion coefficient D are supplied to the two-dimensional model of the uptake process. Using this information the computer plots a curve for the rate of uptake independent of the experimental data. The curve is then checked to see if it fits the experimental data points. If the experimental and calculated curve do not fall on the same line a better estimate of D is given to the computer, and a second calculated curve is drawn. This process is repeated until the two lines coincide. It is important to note that there is an initial time lag in the uptake data, this is due to experimental limitations as the furnace atmosphere about the sample does not become saturated with the vapour instantly upon switching the nitrogen through the solvent reservoir. This is taken into account when calculating the best fit curve, a second variable parameter B which represents the time lag is given to the computer, which then calculates \sqrt{B}/D the value of which is used to obtain values for the Bessel functions J_0 and J_1 , from standard tables and these values are

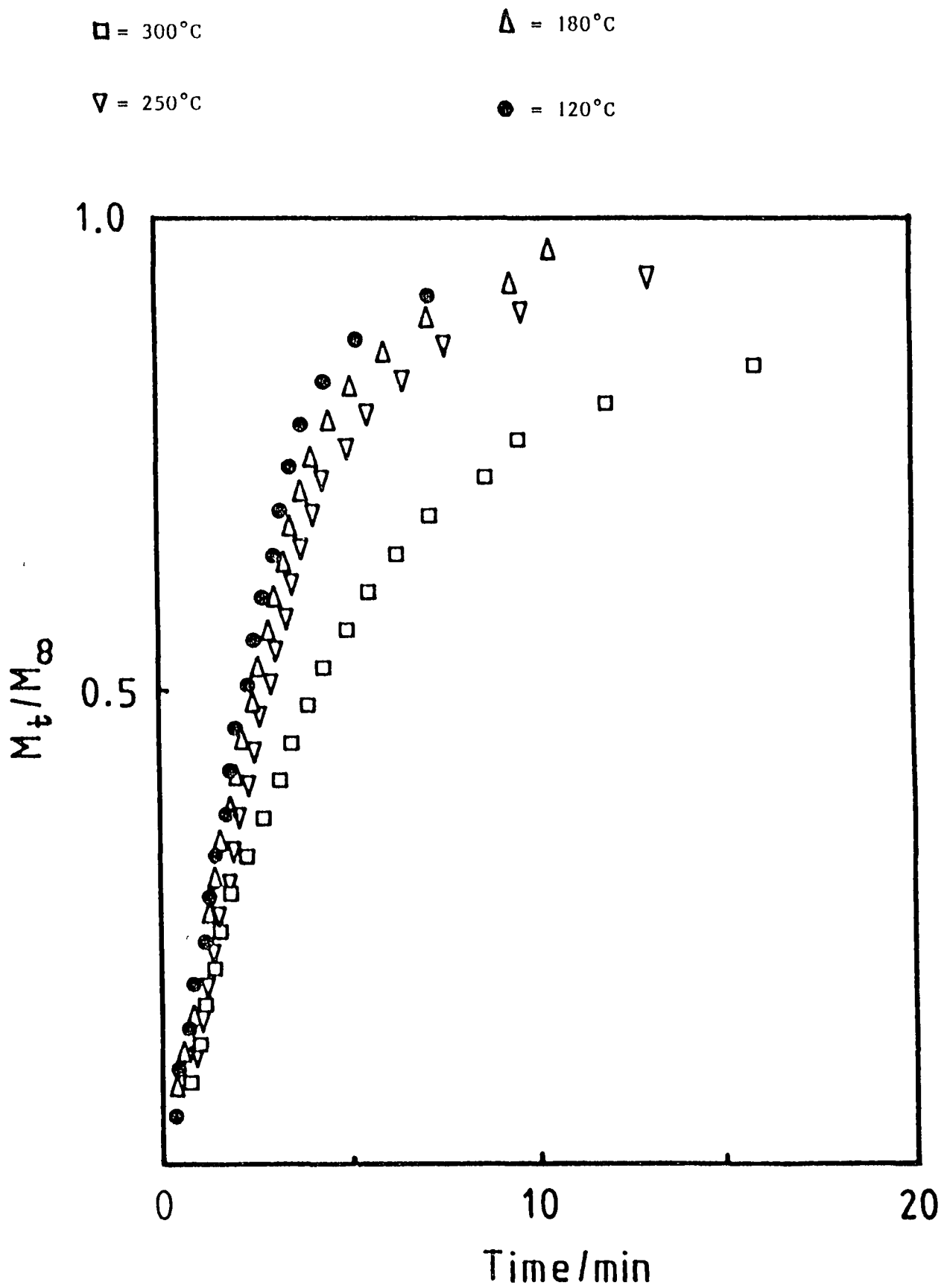


Fig 5.v. The effect of thermal pretreatment on the uptake of 1-propanol upon Cr^{3+} -montmorillonite at 18°C.

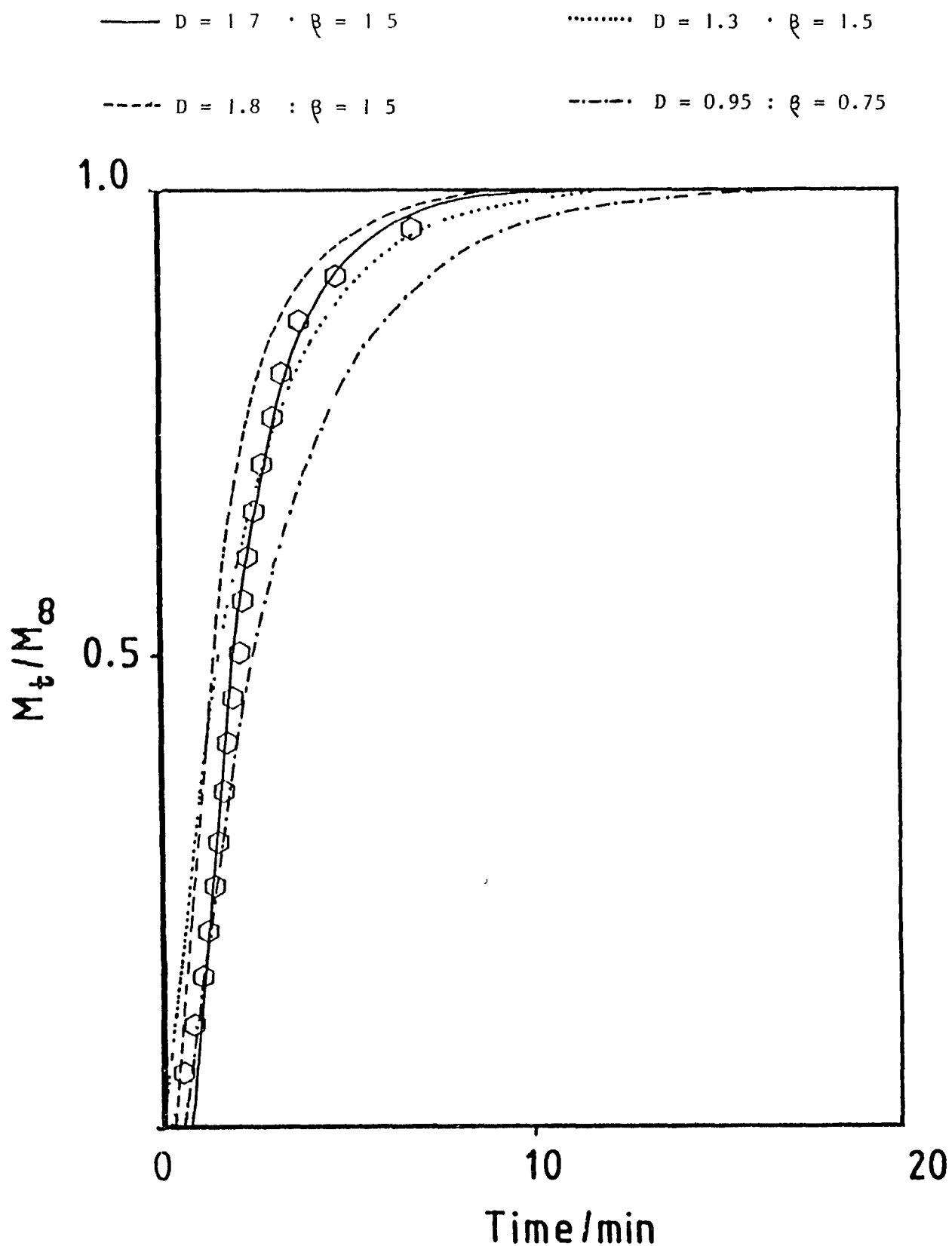


Fig 5.vi. Fitting of the calculated curve to the experimental data for the uptake of 1-propanol on Cr^{3+} -montmorillonite at 18°C .

inputed to the computer to slightly alter the theoretical curve shape to fit the experimental data profile more closely, thus obtaining a more accurate value of \tilde{D} . The values of \tilde{D} and corresponding β values are shown in Fig 5.vi

5.3.1 Experimental Errors on the Data Points.

In order to have some idea as to when a best fit of the data has been obtained, an indication of the errors involved in the experimental data points is useful. Fig 5.vii. shows the errors on the various data points for the uptake curve of i-propanol on Cr^{3+} -montmorillonite. Taking the error on the measured time to be 10 min. \pm 12sec. which is \pm 2% error, for the weight measurement the error was taken to be 10mg \pm 0.2mg which is again 2% error, so the area surrounding the data points in Fig 5.vii. represents a 2% error on both axes. This error measurement is useful when using the \tilde{D} values to obtain the activation energies for the clay-vapour systems.

5.3.11. The Effect of Particle Size Distribution on Curve Fitting.

As mentioned in section 5.2 the particle size distribution within a given clay sample can effect the rate of sorption, and the shape of the uptake curve (Fig 5.iv). The sample which consisted of 50% $<45\mu\text{m}$ grains and 50% $>250\mu\text{m}$ grains had an uptake curve that was unaffected in the early portion but the uptake became much slower than the $<45\mu\text{m}$ sample as time progressed, and the time required to reach equilibrium loading was much greater.

Fig 5.vii illustrates the particle size distributions of the clays, and shows that each of the $<45\mu\text{m}$ fractions of the different clay types has a different median particle size. From this it might be expected that the clay types with the larger particle sizes might deviate slightly from the calculated curves, towards the latter part of the uptake curve. So the uptake curves were the calculated and

• = Experimental data point \pm = region of error

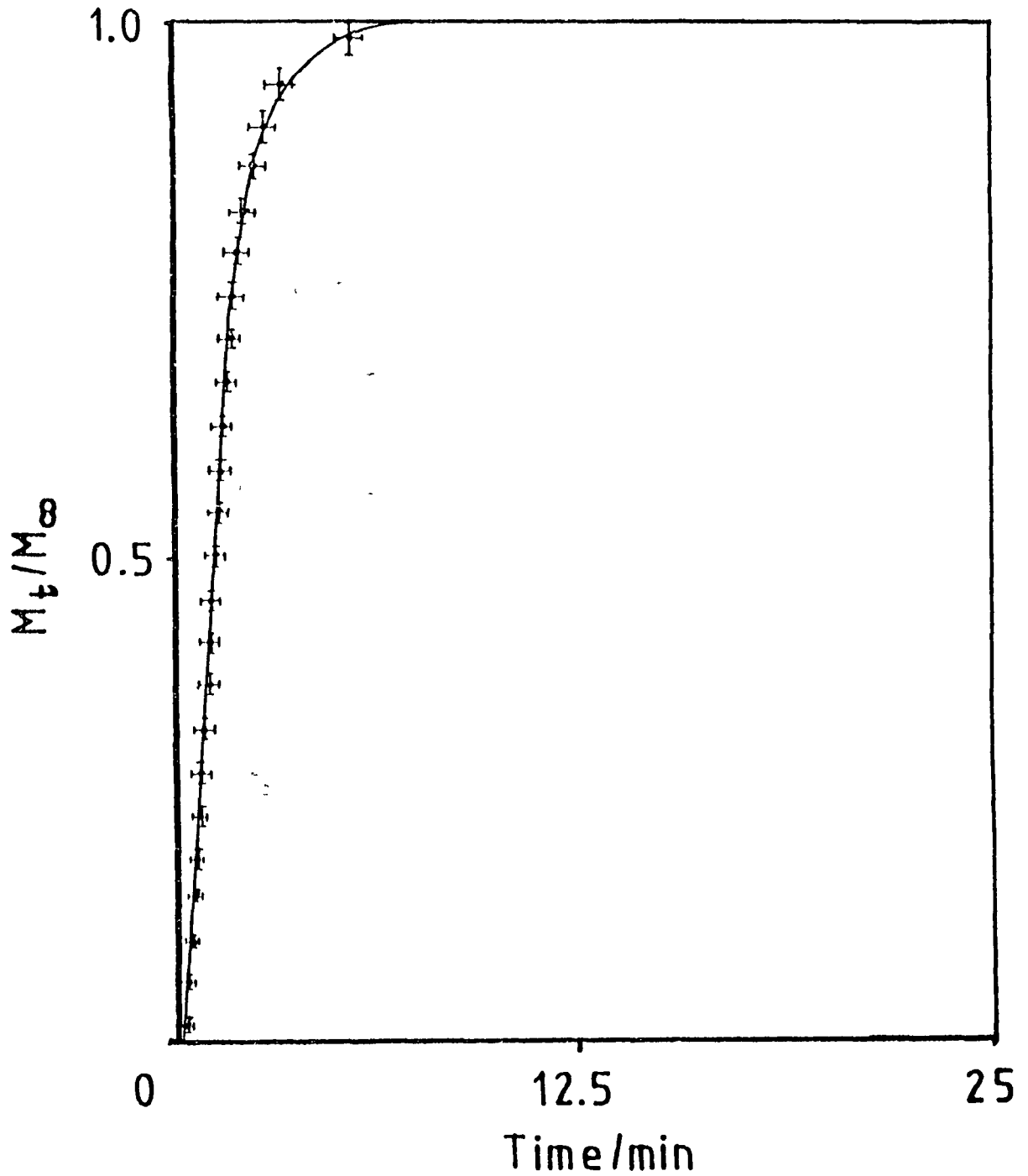


Fig 5.vii. The experimental error bars on the data points for the uptake of 1-propanol on Cr^{3+} -montmorillonite at 18°C .

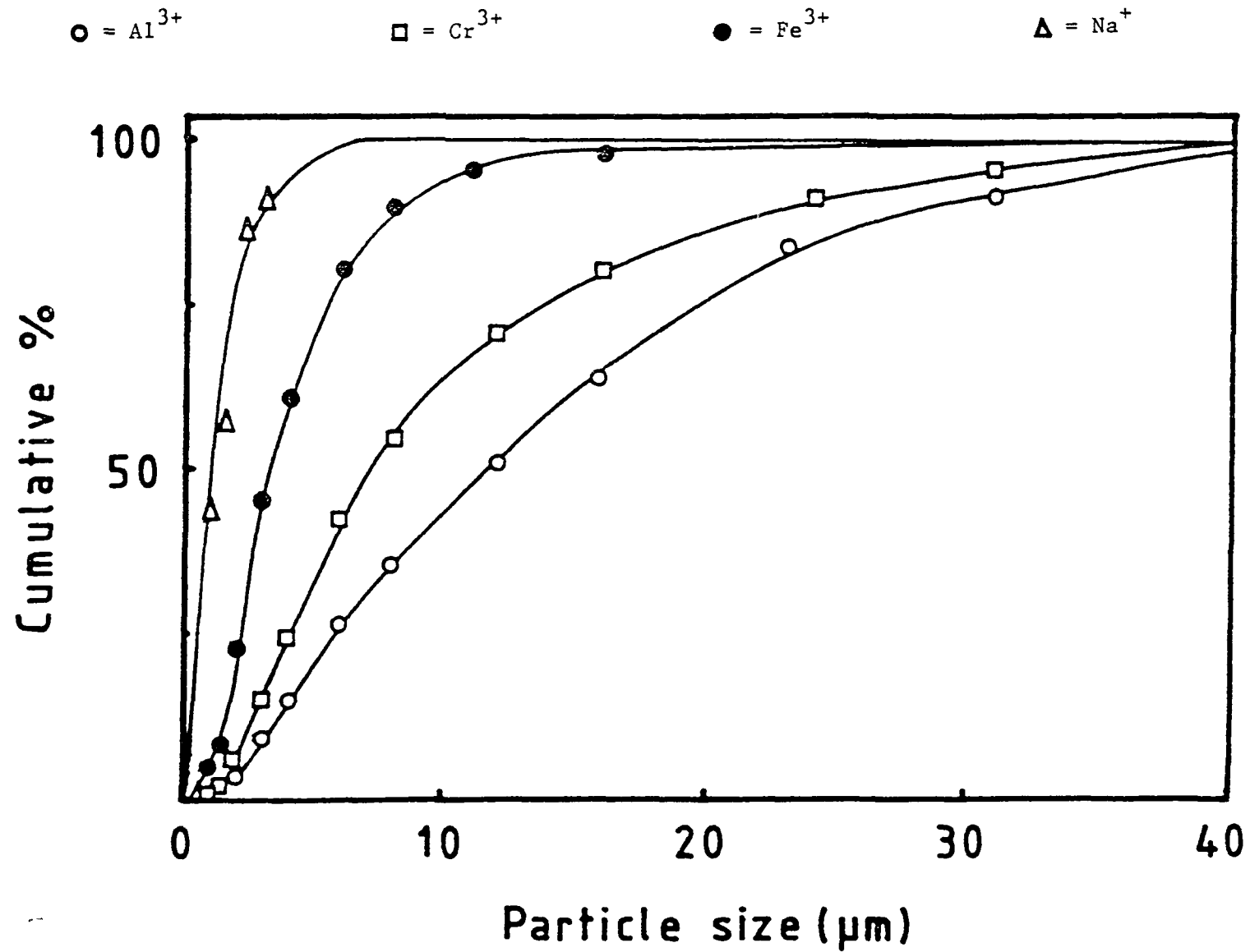


Fig 5.v111. Particle size distribution for the various cation-exchanged montmorillonites.

experimental values which deviate only towards the end of the uptake, may be due to this effect.

5.4 Sorption Kinetics Results.

5.4.1. The Cation Exchanged Clay Parameters.

The optimum grain size used was <45 μ m for each of the clay types, and these grains contained a median particle size that increased in the order Na < Fe < Cr < Al (Table 5.1. and Fig 5.viii.). The amount of water lost by the clay when preheated to 120°C is listed in Table 5.ii., and is expressed as a percentage of the total water lost by heating to 500°C, (this temperature is just below the dehydroxylation temperature for the clays). Table 5.iii. lists the basal spacings for the clays after pretreatment at 120°C, cooling in a desiccator, and exposure to the vapour for 16 hours. This gives the equilibrium loading or saturation with vapour of the clay.

Table 5.1. The median particle size distribution of various cation-exchanged montmorillonite clays.

<u>Cation</u>	<u>Vapour</u>	<u>Median Particle Size (μm)</u>
Al ³⁺	H ₂ O	11.7
Cr ³⁺	H ₂ O	7.2
Fe ³⁺	H ₂ O	2.0
Na ⁺	H ₂ O	1.2

Table 5.ii. The water loss on preheating at 120°C for various cation-exchanged montmorillonite clays.

<u>Cation</u>	<u>Vapour</u>	<u>Water removed by 120°C (%)</u>
Al ³⁺	H ₂ O	70 ^a
Cr ³⁺	H ₂ O	71 ^a
Fe ³⁺	H ₂ O	76 ^a
Na ⁺	H ₂ O	83 ^a

note: a = expressed as a percentage of the total water lost by heating to 500°C.

Table 5.111. The saturated vapour basal spacings for various cation-exchanged montmorillonites over a range of vapours

Cation	Vapour	Basal Spacing (Å)
Al ³⁺	Water	12.5 ^a
	Methanol	14.0 ^b
	1-Propanol	14.3 ^b
	t-Butanol	15.3 ^b
	1,4-Dioxan	15.6 ^b
	1HF	14.5 ^b
	THP	15.0 ^b
Cr ³⁺	Water	12.5 ^a
	Methanol	15.0 ^b
	1-Propanol	13.8 ^b
	t-Butanol	17.4 ^b
	1,4-Dioxan	15.8 ^b
	THF	14.3 ^b
	THP	15.0 ^b
Fe ³⁺	Water	9.6 ^a
	Methanol	15.5 ^b
	1-Propanol	16.0 ^b
	t-Butanol	17.7 ^b
Na ⁺	Water	9.6 ^a

note: a = 120°C pretreated and cooled in a desiccator prior to analysis.
 b = As for footnote 'a', then exposed to solvent vapour for 16 hours.

5.4.11. The Rate of Sorption Data.

Sorption kinetics data is usually expressed as plots of,

$$\left(\frac{Q_t - Q_0}{Q_\infty - Q_0} \right) \text{ versus Time.}$$

Where Q_t = the amount of vapour adsorbed at time $t=t$.
 Q_0 = the amount of vapour adsorbed at time $t=0$
 Q_∞ = the amount of vapour adsorbed at time $t=$ equilibrium.
 t = time

In this system Q_0 was taken as zero, hence this equation may be written as,

$$\left(\frac{M_t}{M_\infty} \right) \text{ versus Time.}$$

Where M_t = the mass of vapour adsorbed at time $t=t$.
 M_∞ = the mass of vapour adsorbed at time $t=$ equilibrium.

Using methanol as the vapour the cation dependence of the rate of sorption was found to increase as $Fe^{3+} < Cr^{3+} < Al^{3+}$ (Fig 5.1x), and this is representative of the sequence for the other vapours. The solid lines in the subsequent graphs are the theoretical curves generated by the computer using the two-dimensional diffusion model, (described in section 3.10.) The value for the diffusion coefficient was obtained from the calculated curve, (assuming a particle size of $1\mu m$), and is included along with the others derived here in Table 5.1v. The rate of alcohol uptake observed is shown in Fig 5.x., and the rate of uptake decreased as methanol \gg 1-propanol $>$ t-butanol, and for the cyclic ethers the observed rate of uptake decreased as THF \gg THP \gg 1,4-dioxan, (Fig 5.xi). The effect of temperature on the uptake of methanol on Al^{3+} -montmorillonite is illustrated in Fig 5.xii., and a temperature variation in the range 18° to $72^\circ C$, has little effect on the observed diffusion coefficients. This observation was further investigated using the uptake of 1-propanol on Cr^{3+} -montmorillonite, (Fig 5.xiii), the diffusion coefficients for the uptake at various temperatures, (18° , 43° , and $72^\circ C$) were measured. An Arrhenius plot of these diffusion coefficients was drawn, and from this the activation energy for the uptake of 1-propanol on Cr^{3+} -montmorillonite was determined (~ 4 kJ mole $^{-1}$). The derived activation energy was extremely low, and is indicative of all of the alcohols. Similarly for the cyclic ether vapours, the effect of varying the temperature on the cyclic ether vapour, the effect. The uptake of THF and 1,4-dioxan on Al^{3+} -montmorillonite was studied, (Fig 5.xiv.). (note, the solid lines on this figure are not the best fit of the data points as is usually the case, instead, they represent the best fit lines for the sorption of THF and 1,4-dioxan on Cr^{3+} -montmorillonite). This shows that there is little cation dependence of the uptake of these vapours, when the results from each set of

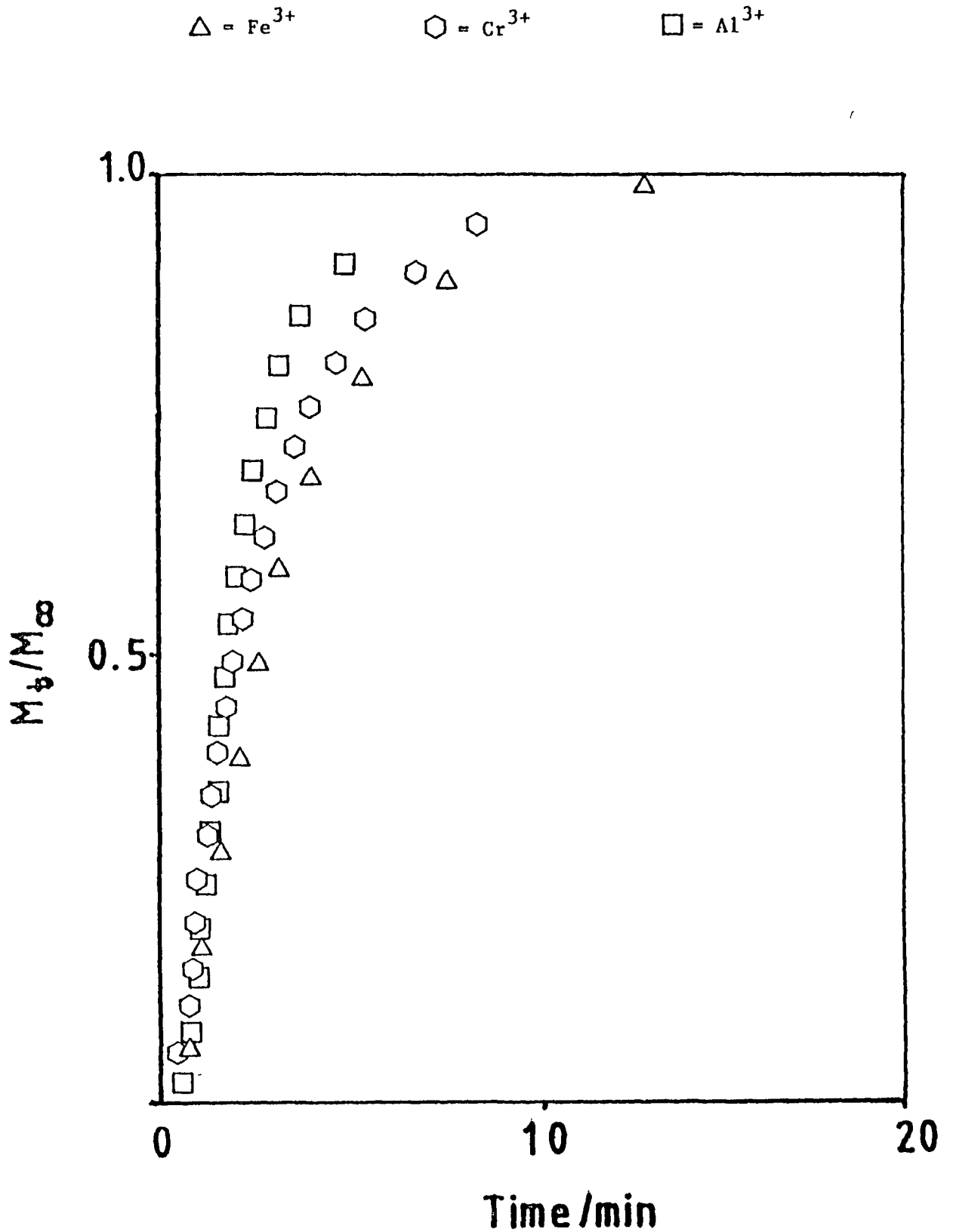


Fig 5.ix. The cation dependence of the uptake of methanol on the three cation-exchanged montmorillonites at 18°C.

\triangle = t-Butanol \circ = Methanol \square = i-propanol

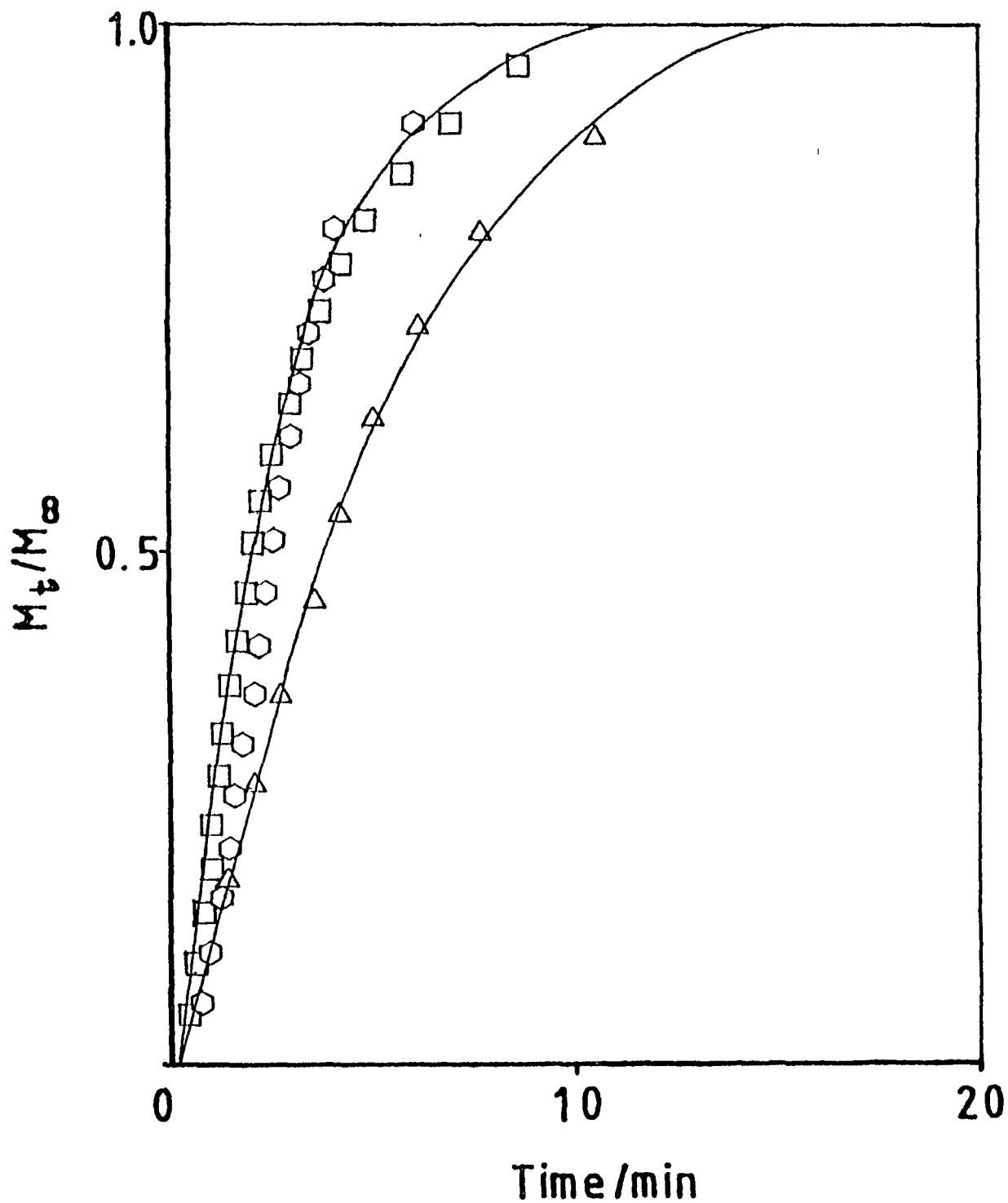


Fig 5.x. The uptake of the three alcohols on Cr^{3+} -montmorillonite at 18°C .

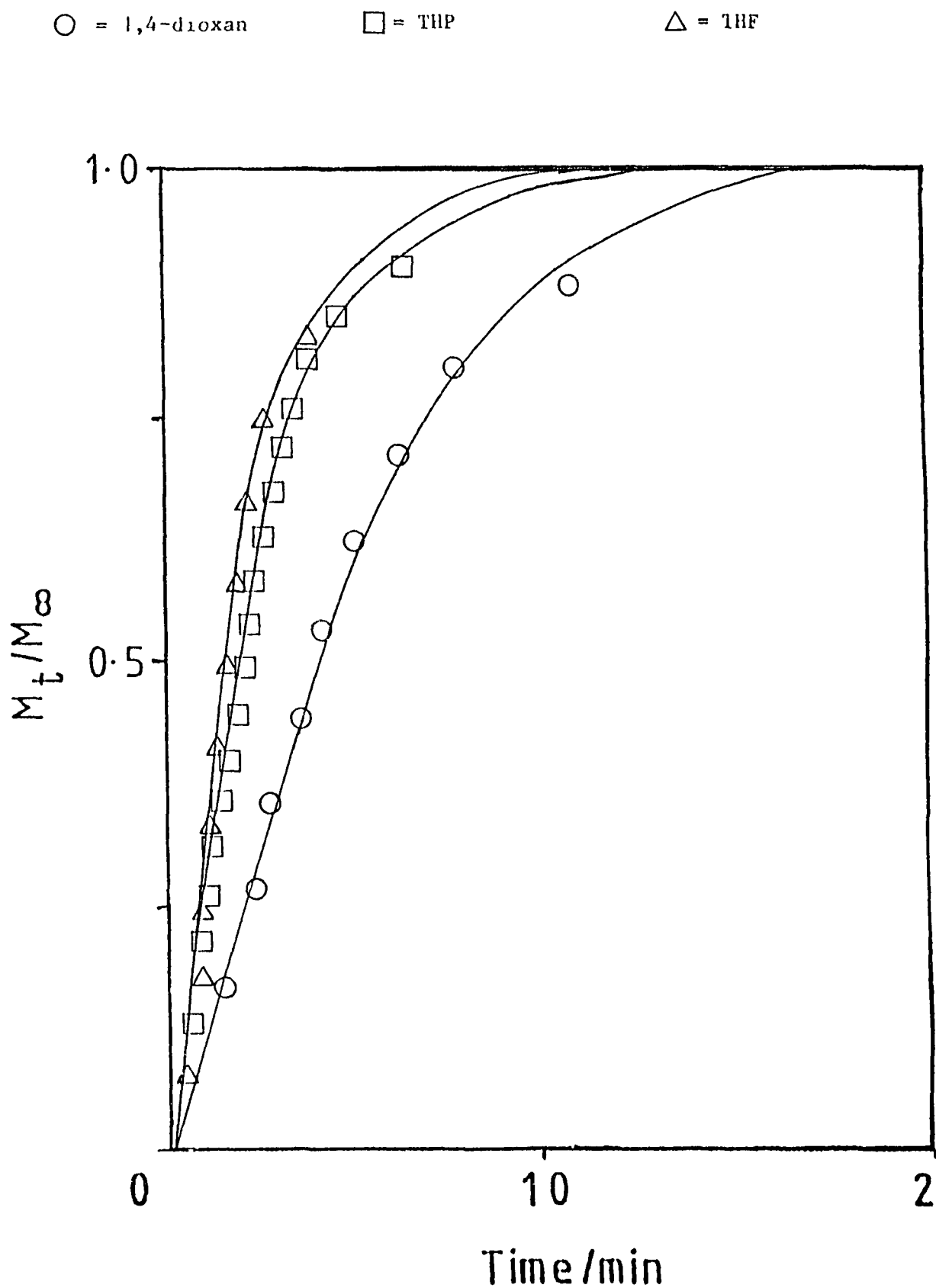


Fig 5.x1. The uptake of the three cyclic ethers on Cr^{3+} -montmorillonite at 18°C . (The full lines are theoretical curves generated by the two-dimensional model)

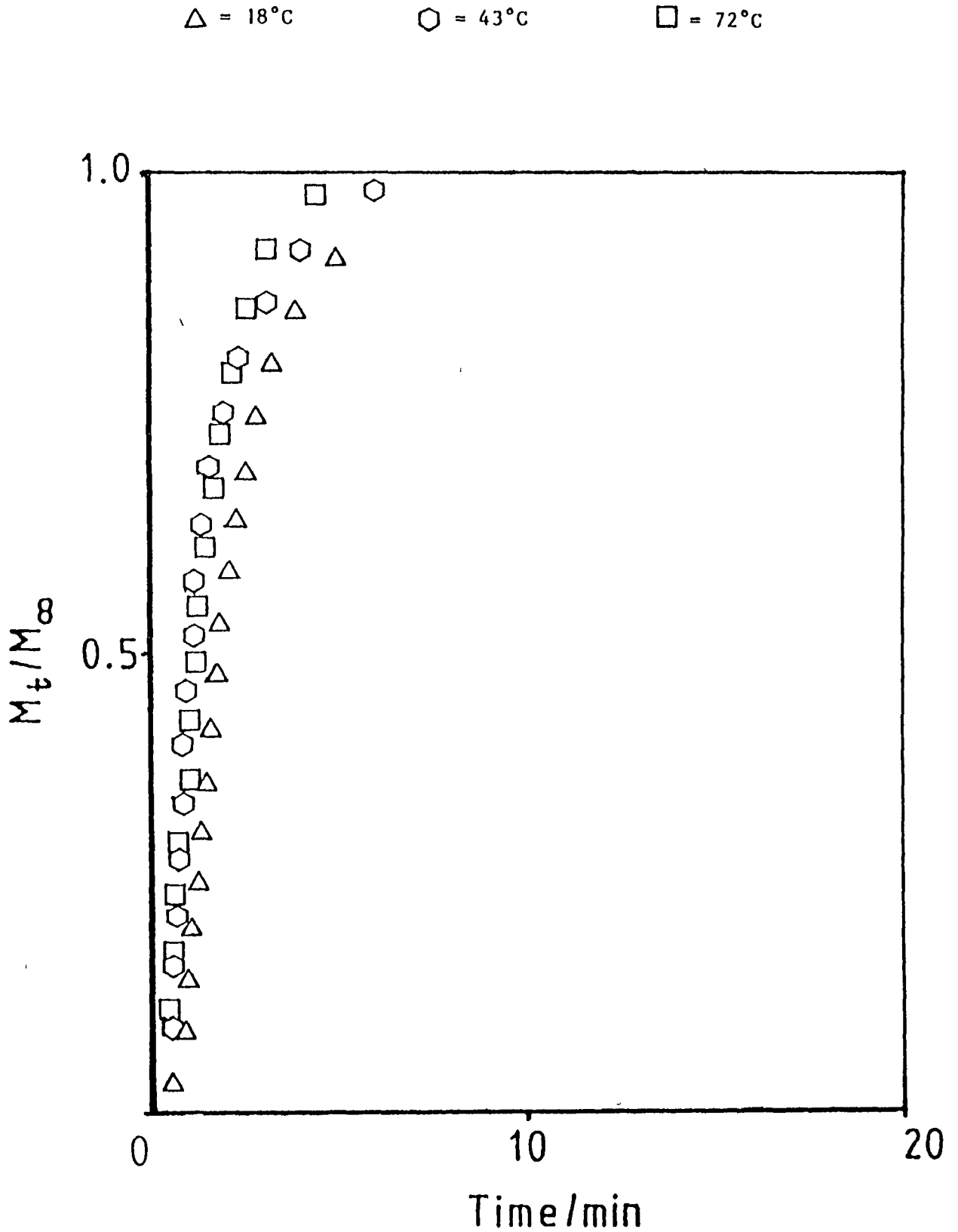


Fig 5.xii. The temperature variation of the sorption rate using the uptake of methanol on Al^{3+} -montmorillonite.

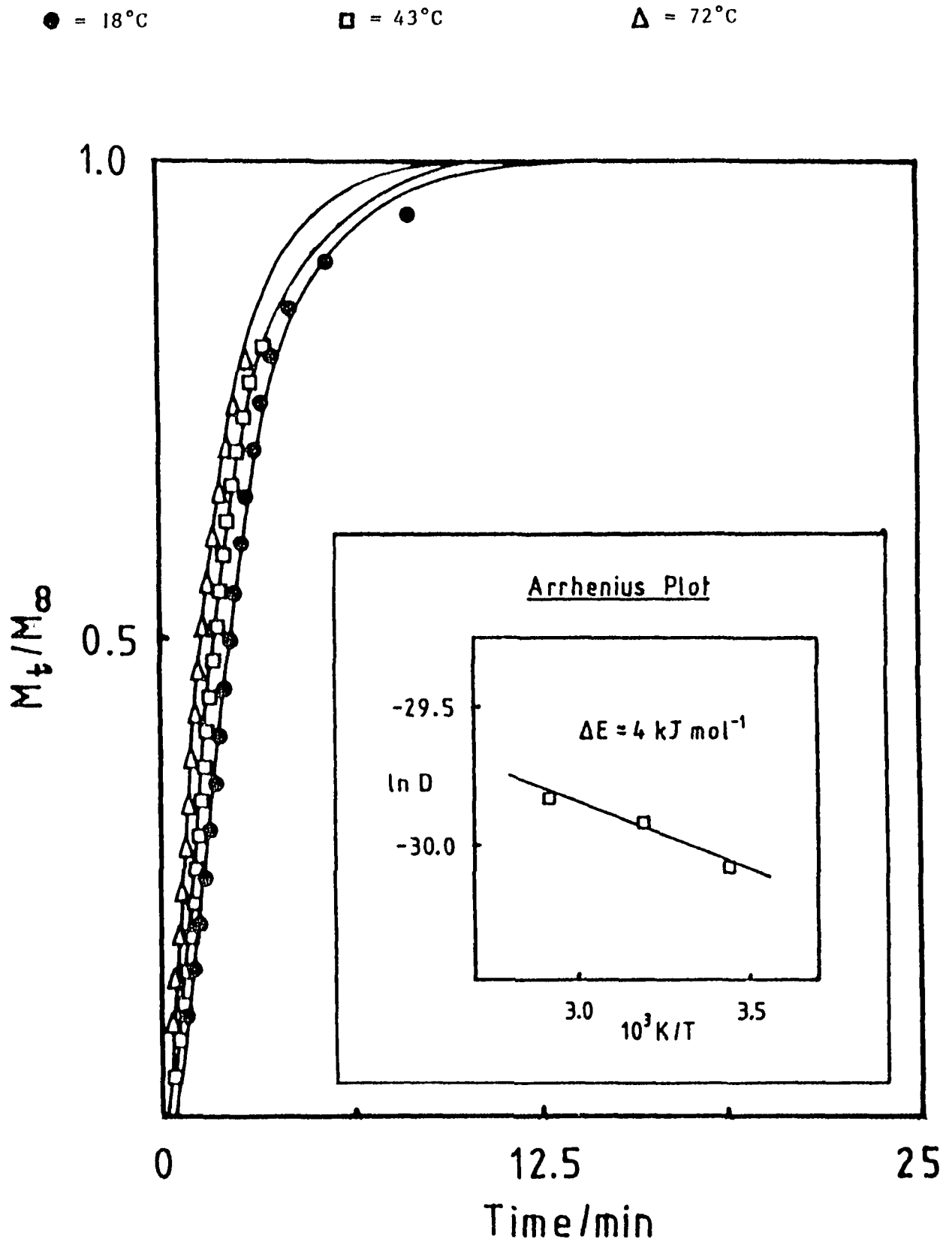


Fig 5.xiii. The effect of temperature on the sorption rate of 1-propanol on Cr^{3+} -montmorillonite. (insert is the Arrhenius plot of the data, and the full lines are the theoretical curves generated by the two-dimensional model)

▲ = 1,4-dioxan/18°C ● = 1,4-dioxan/ 40°C ■ = 1,4-dioxan/105°C

△ = THF/ 18°C ○ = THF/40°C □ = THF/105°C

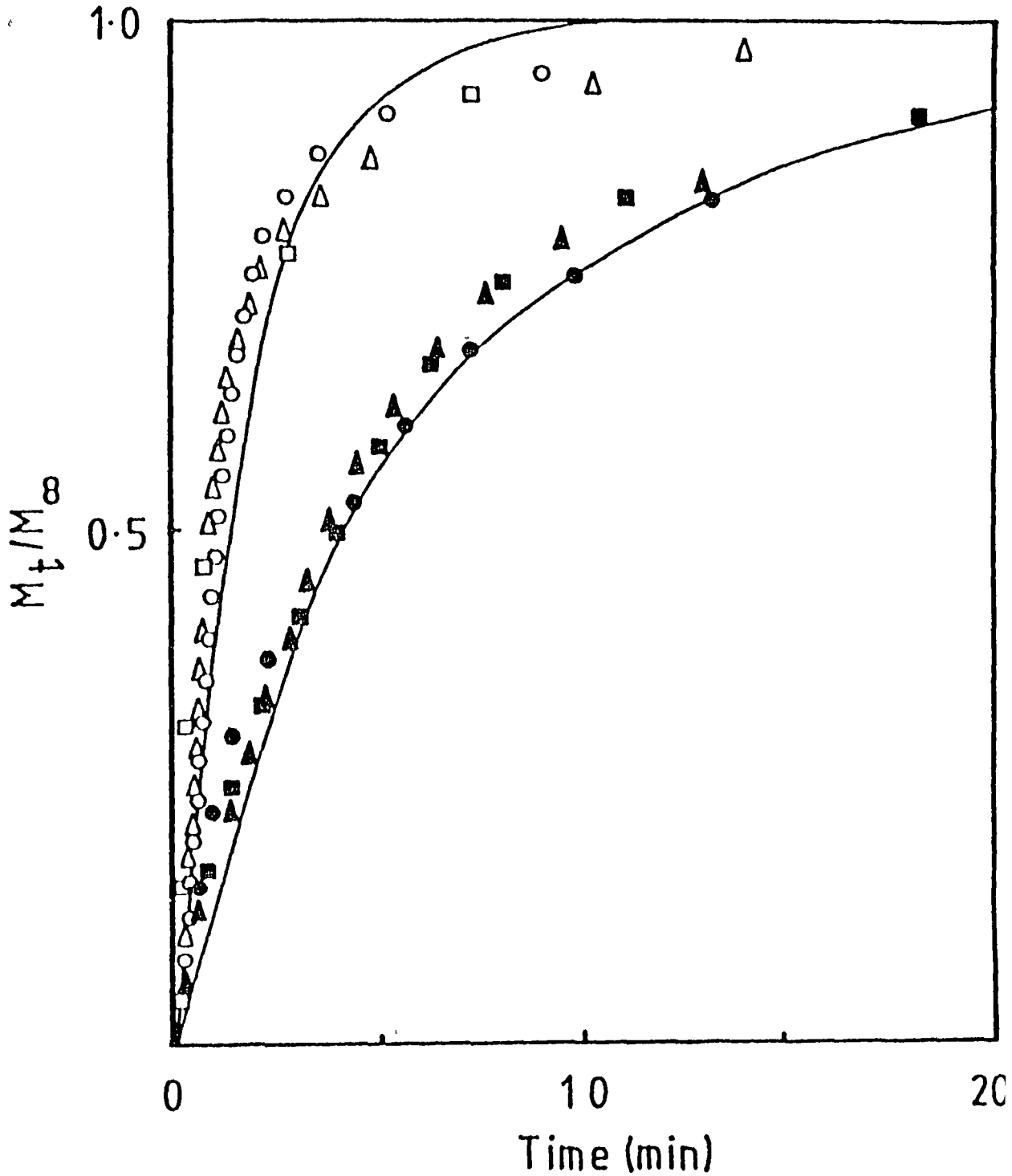


Fig 5.xiv. The uptake of THF and 1,4-dioxan on Al^{3+} -montmorillonite as a function of temperature.

data are superimposable in this manner. Also from the tight bunching of the data points for the different temperatures, it may be assumed that like the alcohol vapours, the cyclic ether sorption rates are not significantly affected by temperature. Fig 5.xv. shows the uptake curves for all six compounds on Cr^{3+} -montmorillonite, and it can be seen that THF, THP, methanol and 1-propanol all have sorption rates of a similar magnitude, while t-butanol and 1,4-dioxan have similar sorption rates, but these are different to those for the first group of compounds. So the sorption rates for the vapours may be collected into these two distinct groups.

Table 5.iv. The diffusion coefficients and equilibrium loading values for various cation-exchanged montmorillonites using a range of vapours.

<u>Cation</u>	<u>Vapour</u>	<u>Equilibrium loading</u> (mMoles/gram)	<u>Diffusion Coefficient</u> ($D \times 10^{14} \text{ m}^2\text{s}^{-1}$)
Al^{3+}	Methanol	6.0	2.0
	1-Propanol	2.9	2.0 ^a
	t-Butanol	1.8	---
	1,4-Dioxan	1.5	0.6
	THP	1.3	2.4
	THF	3.5	3.5
Cr^{3+}	Methanol	7.0	1.7
	1-Propanol	3.3	1.7
	t-Butanol	2.2	1.1
	1,4-Dioxan	1.6	0.5
	THP	1.3	1.9
	THF	3.5	2.8
Fe^{3+}	Methanol	6.3	1.3
	1-Propanol	1.9	1.3 ^a
	t-Butanol	1.3	---

note: a = uptake of t-butanol was slower than the other vapours, but did not fit the two dimensional model well.

Finally measurements of the temperature rise associated with the adsorption of solvents are listed in table 5.v. The magnitude of the temperature rise is small in comparison with the temperature of the sample in each case, and thus is unlikely to have much effect on

the rate of sorption.

Table 5.v. The peak heat of adsorption data for the uptake of various vapours on Al³⁺-montmorillonite at 18°C.

<u>Clay</u>	<u>Vapour</u>	<u>Peak Heat of Sorption (°C)</u>
Al ³⁺ -montmorillonite	Methanol	1.0
	1-Propanol	2.0
	THF	3.0
	1,4-Dioxan	0.25

5.5 Discussion of the Experimental Results.

5.5.1. The Clay Grains.

The use of cation-exchanged montmorillonite clays in catalysis has been discussed at length in this work, however when using these clays it is important to ensure that, for example an Fe³⁺-montmorillonite is a clay in which the interlayer cations are actually Fe³⁺-cations so that a correct interpretation of the results can be made. It is possible that on heating the clay, the interlayer environment of the clay may alter, with some of the cations leaching to the edges of the clay layers causing the clay to behave as a partially H⁺-montmorillonite. Hence the basal spacings shown in Table 5.iii. indicate that thermal pretreatment at 120°C causes the Fe³⁺-montmorillonite to essentially collapse, whereas the Al³⁺-montmorillonite and Cr³⁺-montmorillonite are still partially expanded, (ie some H₂O remains in the interlayer as suggested by Carr³⁴). However the results in Table 5.iii. show that on equilibrium loading during the sorption kinetics experiments the Fe³⁺-montmorillonite form is re-expanded to a basal spacing similar to that of the Al³⁺, and Cr³⁺-montmorillonites. Breen et al⁴⁷ have shown that the number of bronsted acid sites increases following thermal pretreatment at 120°C for all three forms of the clay. Also Tennakoon et al²¹ postulated that upon heating Al³⁺-montmorillonite at a temperature as low as 50°C a dimerization and subsequent release

of a proton occurred. Combined with this some mossbauer studies by Halsen⁴⁹ on Fe³⁺-montmorillonite showed that on drying the iron precipitated as an oxyhydroxy form between the clay sheets, and on increased heating this iron diffused to the edge of the platelets causing the clay to collapse.

Based on this the Fe³⁺-montmorillonite reported here may behave as a H⁺-montmorillonite with an oxy or oxyhydroxy coating, and the Al³⁺, and Cr³⁺-montmorillonite may be partially H⁺-exchanged.

5.5.11. The Effect of Sample and Grain Size on Sorption Kinetics.

In recent studies it has been shown that the rate of sorption at the surface of a porous solid is usually so high that the overall rate of sorption is controlled by the heat or mass transfer rather than by intraparticle diffusion kinetics^{50a,50b}. So to confirm the dominance of intracrystalline diffusion both the sample and grain size must be varied.

It is now well established that the initial portion of the uptake curve is sensitive to any resistance to diffusion in the sample bed, or macropore resistance. As initially the diffusing molecules would not only be expected to penetrate the clay layers, but also would meet additional diffusional resistance associated with transport through the crystal bed^{50b}, because it is not possible to have a single isolated particle. The longtime region of the curve is sensitive to the effects of finite heat transfer resistance and crystal size distribution. As a buildup of localized heat in the sample can effect the rate of diffusion. Although as shown in Fig 5.xii. and 5.xiv. the clay-vapour systems considered here show little variation with temperature and the peak heats of adsorption (Table 5.v.) are low relative to the temperature of sorption. Another possible cause of any deviation in the latter part of the experimental data points from the calculated curve

may be due to the particle size distribution as a grain comprised of larger particles will have a decreased rate uptake at longer times, (Fig 5.1v.). Egan et al⁴⁵ showed that the rate limiting heat transfer process in a batch sorption experiment is controlled by the dissipation of exothermic heat of adsorption from the external surface of the adsorbent sample, rather than, by conduction of heat through the sample.

Based on this Fig 5.iii. shows that the rate of sorption increases with decreasing sample size and this indicates that resistance to diffusion in the bed is occurring. Also Fig 5.11. shows that the rate of sorption increases with decreasing grain size which constituted the sample bed, suggesting that there is resistance to mass transfer between the various size particles, (ie Fig 5.vii.), which formed the grain. Note this trend was observed despite the fact that grains of >63um packed easily into the sample pan, whereas grains <63um were of a more powdery nature and increased the physical size of a given sample weight. This observation removes any concern about the interlayer cation form (discussed in section 5.5.1.), Since these cations seem to contribute little to the rate limiting process.

However if Fig 5.1x. is considered the observed cation dependence of the alcohol sorption rate is difficult to identify, although the rate parallels the observed sequence of the median size of particles which contribute to the grains (Table 5.1.). This implies that the measured rate probably reflects the tortuosity of the channel network within the grains. Consequently this combination of factors indicate that inter-particle and not intra-particle diffusion is the rate controlling influence.

5.5.iii The Sorption Rates of the Alcohols and Cyclic Ethers.

The sorption rate of the alcohols shown on Fig 5.x., generally

decreases as methanol \gg 1-propanol $>$ t-butanol and could be due to steric effects, if the rate determining process was interlamellar transport. But as bed diffusion appears to be the rate controlling stage, the sequence conforms to the required $1/\sqrt{\text{mass}}$ dependence required if Knudsen diffusion was the major contributor to mass transfer resistance. Knudsen diffusion occurs where resistance to the flow arises from collisions between diffusing molecules, and is independent of concentration with only a slight dependence on temperature, but it is inversely dependent on the square root of the molecular weight.

$$D_k = 9700u \left(\frac{T}{M} \right)^{1/2} \quad (\text{cm}^2 \text{s}^{-1})$$

Where u = the pore radius (cm)

T = temperature (K)

M = molecular weight of the diffusing species.

When the cyclic ethers are studied the sorption rate decreased as THF \gg THP \gg 1,4-dioxan, (Fig 5.x1.). However the sequence does not conform to the $1/\sqrt{\text{mass}}$ dependence required for the limiting Knudsen diffusion. This trend may reflect a concentration dependence of the sorption rate insofar as THF and THP yield higher vapour pressures than 1,4-dioxan. Also it may simply be that the 1,4-dioxan sorption process is retarded due to bidentate coordination of the ether to the Al^{3+} -ions at the clay edges. A similar binding for methyl acrylate which inhibited its reaction with cyclopentadiene is discussed by Adams et al.²⁸. Also the difference between the alcohols and cyclic ethers is reflected in the cationic dependence of the alcohol group, which increased as $\text{Fe}^{3+} < \text{Cr}^{3+} < \text{Al}^{3+}$, (Fig 5.ix.), whereas no cationic dependence of the cyclic ether sorption rate was observed, (Fig 5.xiv.).

The values for the effective integral diffusion coefficients \tilde{D} for the alcohols and cyclic ethers were of the same order of magnitude, (Table 5.iv.). This combined with the temperature independence of the sorption rate (Fig 5.xii. and 5.xiv.), and small temperature increase

associated with the sorption process indicates that bed diffusion is also the rate controlling influence in the sorption of cyclic ethers.

If the diffusion rates for cation-exchanged montmorillonites are compared to those for zeolites in the literature, the zeolites would be expected to have slower diffusion rates than montmorillonites, due to the restrictive nature of the zeolite channel network (section 4.5.). This was found to be the case as diffusion in zeolites of molecules of a similar size and shape to those used in this study, gave diffusion rates considerably slower⁵¹⁻⁵⁴ than those for the montmorillonites.

5.5.iv. Other Factors Influencing the Sorption Process.

The temperature variation of the sorption rates for 1-propanol on Cr^{3+} -montmorillonite (FIG 5.xiii.), is just discernable, and the Arrhenius plot to calculate the associated activation energy is also shown. The activation energy was found to be $\sim 4 \text{kJmole}^{-1}$, and for such a small potential barrier, the sorption process should have been almost instantaneous. However for all the clay-organic systems studied several minutes were required for the clays to reach equilibrium loadings. The reason for this may well be explained by the inter-crystalline macropore diffusion resistance (section 5.5.ii.). This delayed time to reach equilibrium loading could also be due to the finite time required to dissipate the exothermic enthalpy of intercalation of the vapour molecules.

This may be examined as follows, if the dissipating time is wholly or partly rate limiting, it would effect the uptake curve in two ways. Firstly the initial uptake rate would be increased due to the temperature difference of the diffusivity, and secondly, the latter part of the sorption rate would be retarded due to the temperature dependence of the equilibrium position⁵⁵. Table 5 v. shows that experiments conducted to quantify the temperature rise associated with the sorption

- ▲ = 1,4-Dioxan ● = i-Propanol ■ = THP
- △ = t-Butanol ○ = methonal □ = THF

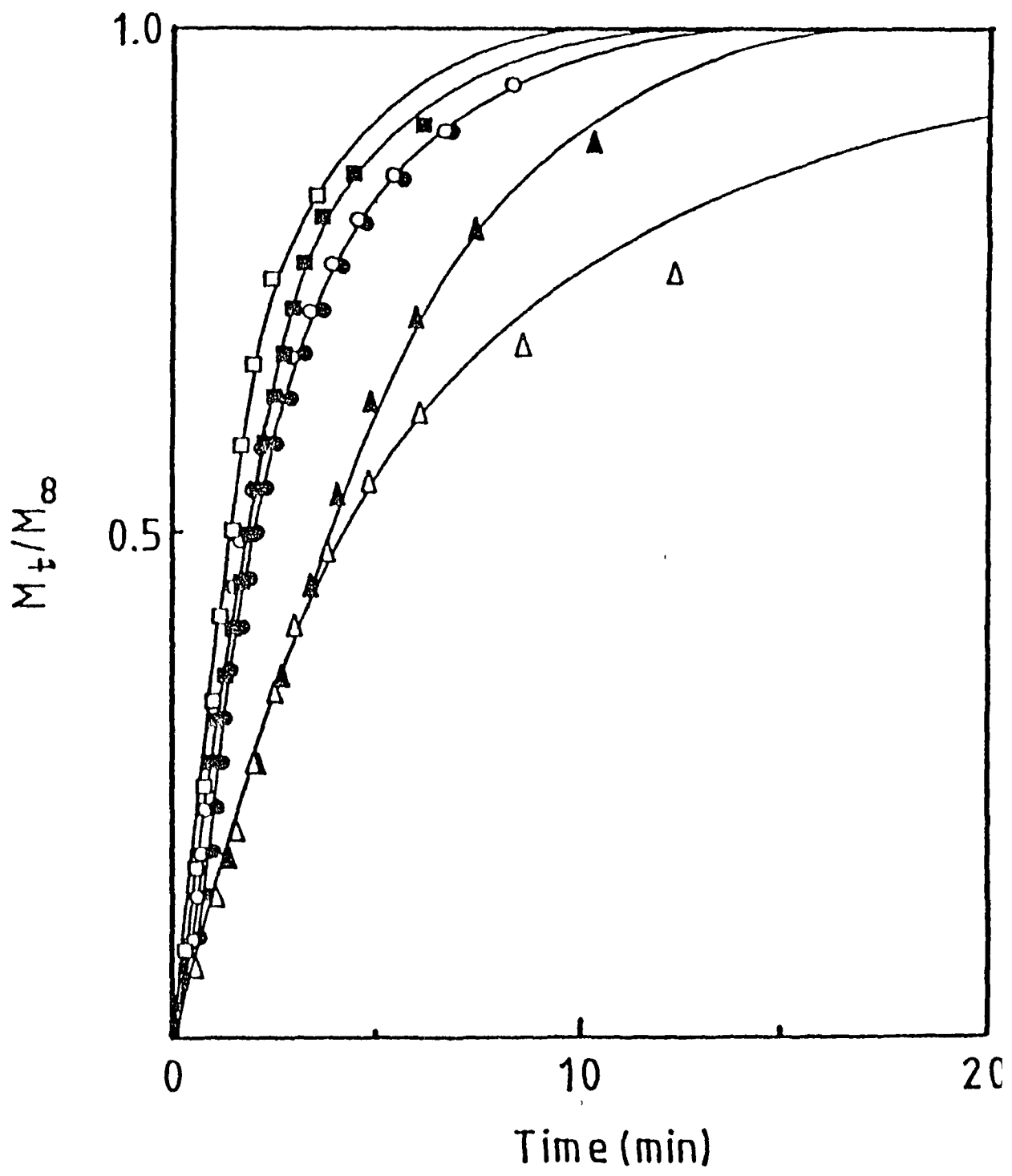


Fig 5.xv. A comparison of the sorption rates for the cyclic ethers and alcohols on Cr³⁺-montmorillonite at 18°C.

Δ = Reservoir temperature 17°C \circ = Reservoir temperature 19°C
Furnace temperature 15°C Furnace temperature 15°C

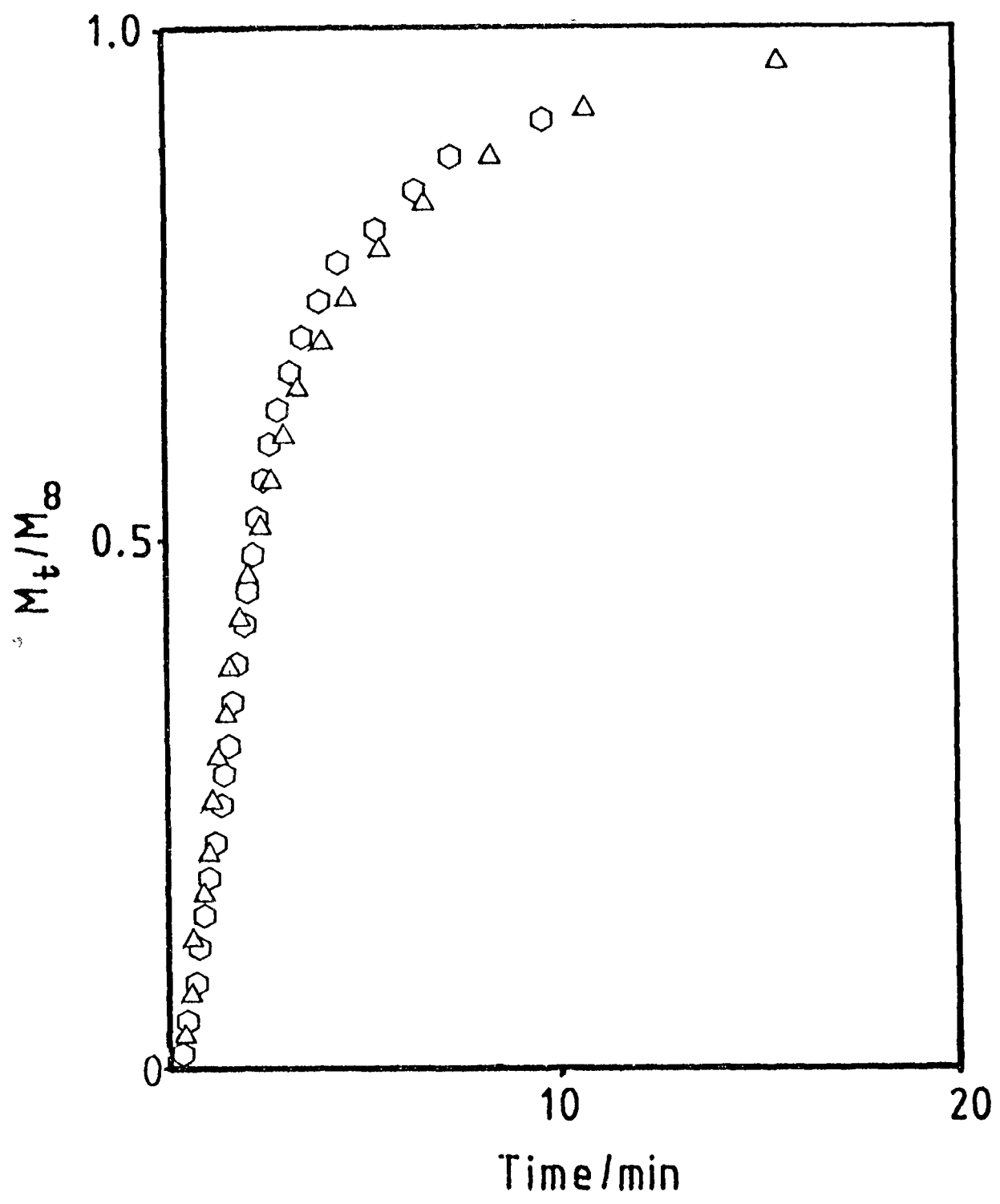


Fig 5.xvi A comparison of the effect of a temperature difference between the liquid reservoir and the furnace on the uptake of THF on Al^{3+} -montmorillonite at 18°C.

of the vapours on various cation-exchanged montmorillonites, however yield values of up to 3°C (this is the largest value). These temperature increments are negligible compared with the values of 50°C for the sorption of propane on synthetic 5A zeolite at -78°C⁴⁵, and 15°C for butane on synthetic NaX zeolite at 25°C⁴⁶, and, thus, confirm the overall isothermal nature of the uptake process. However when considering this, it is possible that the magnitude of the temperature rise may reflect the fact that the heat of sorption of the vapour molecule may in part be utilized to desorb a water molecule. If this were the case the observed weight change may only be an incremental change equal to

$$\left(\text{Mass}_{\text{vap.}} - \text{Mass}_{\text{water}} \right).$$

The effect of different temperatures in the liquid reservoir and the thermobalance furnace (this is because the running water used to cool the furnace was often colder than the ambient temperature in the room). This is especially important for the 18°C sample runs. When the furnace temperature is lower than the liquid reservoir temperature the vapour may condense onto the sample and the sample pan causing an apparent high rate of sorption, (or high rate of mass increase as this is what is actually measured). However Fig 5.xvi. shows that there does not appear to be any significant difference in the sorption rates under these conditions, so the temperature difference between the liquid reservoir and the furnace does not appear to have any effect.

The equilibrium loading of the clay is a measure of the total amount of the diffusing compound that has been adsorbed by the clay, and Table 5.iv. shows that a general trend for equilibrium loading of the alcohols and cyclic ethers on all three cation-exchanged montmorillonites used. The equilibrium loading decreased in the order methanol >> THF > i-propanol > t-butanol > 1,4-dioxan and THP.

The amount of vapour adsorbed depends to a large extent on the packing

of the molecules within the interlayer space. Hence the small compact molecules such as methanol, would be expected to pack tightly into the interlayer space, (methanol is known to form a double-layer complex with cation-exchanged montmorillonites⁶⁶) The progressively larger molecules would be expected to have a lower equilibrium loading due to steric hinderance of the packing, and this is the trend observed in the experimental results, with the exception of THF. THF might be expected to have an equilibrium loading similar to that for THP and 1,4-dioxan as it is similar in physical size, however it has an equilibrium loading similar to that of 1-propanol. This may be explained by the fact that ethers are known to form one and two layer complexes with cation-exchanged montmorillonites, and 1,4-dioxan is reported to form only mono-layer complexes with montmorillonites⁶⁴. So THF may form a double layer and THP may behave like 1,4-dioxan forming a mono-layer and so explaining the observed trend. However if the basal spacings are considered (table 5.111.) it is similar for all three cyclic ether vapours, and this would not be the case if THF formed a double layer. So the equilibrium loading difference is probably due to some structural difference between the molecules. The most obvious difference is that THP and 1,4-dioxan are six-membered ring compounds, whereas THF has a smaller five-membered ring, and it may be that the smaller ring structure allows a more dense packing of the THF molecules and hence a higher equilibrium loading value. Also it is possible that the THF molecules do not orientate themselves perpendicular to the silicate sheets, but instead lie parallel to the silicate sheets, thus allowing a more dense packing. This combined with the smaller size of THF may account for the higher equilibrium loading on the clay.

The effect of temperature on the equilibrium loading was as expected with the equilibrium loading decreases as the temperature

increased. This is because increasing the temperature would impart greater mobility to the adsorbed compounds owing to an increase in thermal energy, and the weakening of the intermolecular Van der Waals attractions. Also since the adsorption process is an exothermic process increasing the temperature would disfavour an exothermic process and the equilibrium loading would be expected to decrease. This was observed for all six compounds on the various cation-exchanged montmorillonites used.

Finally the overall significance of the diffusion results will be considered. The rate uptake curves for all six diffusivatives on Cr^{3+} -montmorillonite at 18°C are shown in Fig 5.xv. The observed sequence in this diagram reflects the general trend for all the montmorillonites and is $\text{THF} \gg \text{THP} > \text{methanol} \gg \text{i-propanol} > \text{t-butanol} > \text{1,4-dioxan}$ with respect to the sorption rate. If these vapours are grouped by comparable vapour pressures, the following trends are revealed, $\text{THF} \gg \text{THP} \gg \text{methanol}$ in one group and $\text{i-propanol} > \text{t-butanol} > \text{1,4-dioxan}$ in the other group. However when experimental imprecision is taken into consideration the vapours fall into two distinct groups each having about the same sorption rate. Group (i) THF, THP, methanol, and i-propanol have a faster sorption rate than group (ii) t-butanol and 1,4-dioxan. If steric factors are considered, t-butanol would be expected to have a slower sorption rate than the other molecules due to the bulky side group substituents on this molecule. However 1,4-dioxan might be expected to have a sorption rate similar to that for THP and THF, since 1,4-dioxan is known to interact with the clay surface and the interlayer cations^{6,31}, it is possible that these interactions slow down the rate of sorption, and it falls into the same group as t-butanol and is not in the group with THF and THP.

In this study a better distinction between the sorption rates

of the six diffusivities would have been expected, as methanol is a very different molecule to THP in terms of its size and shape, and so methanol would be expected to diffuse faster than THP, however this was not found to be the case. This assumption is based on the fact that the molecules are diffusing between the silicate sheets of the montmorillonite, (ie intraparticle diffusion). Since the rate controlling influence is bed diffusion (see section 5.5.iii.), this may not necessarily be the case. Hence only very bulky molecules such as *t*-butanol or molecules that interact with the clay, 1,4-dioxan might be expected to have a significantly different sorption rate. It is also worth noting that the cyclic ether compounds show some evidence of a slight concentration dependence, (ie the sorption rate for the THP and THF was faster than for 1,4-dioxan, and THF and THP have a higher partial pressure than 1,4-dioxan). This may influence the observed trend in the sorption rates to some extent, as a reduced concentration of 1,4-dioxan in the furnace atmosphere due to its lower partial pressure would cause a reduced sorption rate to be observed

One final point worth noting is, that cation-exchanged clay is used as solid acid catalysts, and all clay catalysed reactions are carried out in the liquid phase, however diffusion coefficients derived from studies on sorption in the vapour phase may not apply. However Bulow et al⁶⁷ have shown that there are only slight differences ($\ll 10^1$) in the diffusion coefficients for *n*-decane into zeolite A, from the liquid and the vapour phase. So the results from these studies may be applicable to liquid phase studies in certain circumstances.

CHAPTER 6

The Interaction of Alcohols and Cyclic Ethers with Trivalent

Cation-Exchanged Montmorillonite.

6.1. Introduction

In chapter 5 the diffusion of alcohols (methanol, 1-propanol, and t-butanol), and cyclic ethers (tetrahydropyran (THP), 1,4-dioxan, and tetrahydrofuran (THF)), on various trivalent cation-exchanged montmorillonite, was examined. In this chapter the interaction of these diffusivatives with the clay surface or in the interlayer space about the cations will be examined. Again for the purpose of discussing the results the compounds will be considered in two groups, the alcohols and the cyclic ethers.

Ballantine et al¹² has shown that primary aliphatic alcohols such as ethanol, propanol, and butanol when intercalated in Al³⁺-montmorillonite react preferentially via intermolecular nucleophilic displacement of water to give high yields (30-65%) of di-(alk-1-yl) ethers, rather than undergo competitive intramolecular dehydration to the appropriate alkenes. In contrast, the reactions of secondary aliphatic alcohols (propan-2-ol, butan-2-ol, and pentan-2-ol) gave high yields (~80%) of the corresponding alkene, except for propan-2-ol which was converted to both the di-(alk-2-yl) ether (30%), and alkene (40%). The formation of di-prop-2-yl ether has also been reported by Adams et al⁷, but at a much lower yield (~3%). However the Adams reaction was carried out at 60°C using a Fe³⁺-montmorillonite in the presence of 1,4-dioxan, whereas Ballantine et al¹² used no solvent, and a reaction temperature of 200°C with Al³⁺-montmorillonite. Adams et al⁷ suggested that the low temperature coefficient of the ether forming reaction indicated the possible involvement of diffusion control in the reaction. However the

studies detailed in chapter 5 of this thesis show that the diffusion coefficients did not exhibit a temperature dependence. Since the alcohols can react within the temperature range of the sorption kinetics study (18°-105°C), it was decided to investigate the nature of the sorbed alcohols in the temperature range 18°-800°C.

This study was not restricted to alcohols alone as Adams et al^{6,31} have also established that cyclic ether type solvents give comparable yields of methyl-t-butyl-ether (MTBE) at temperatures 30°C lower than if hydrocarbon solvents are used. So the nature of the sorbed cyclic ethers in the temperature range 18°-800°C was also investigated. Table 6.1. indicates the efficiency of the process, which depends on the specific cyclic ether employed, is optimised if 1,4-dioxan is used as the solvent with Al³⁺-montmorillonite. However Cr³⁺- and Fe³⁺-montmorillonite also gave respectable yields with THF, and THP as the solvents.

Table 6.1 Solvent and cation dependence of yield of methyltert-
arybutyl ether

<u>Cation</u>	<u>Solvent (% yield of MTBE)</u>		
	<u>1,4-dioxan</u>	<u>THP</u>	<u>THF</u>
Al ³⁺	61	4	0
Fe ³⁺	65	35	32
Cr ³⁺	63	42	28

Adams et al³¹ suggested that 1,4-dioxan was the optimal solvent because all the molecules participating in the reaction were miscible in it, thereby facilitating the rapid distribution of all the reactants and products between the clay interlayer and the external solution. If Table 5.iv. of chapter 5 is considered it can be seen that the rate at which the three cyclic ethers were adsorbed by the cation-exchanged montmorillonite forms under discussion was of the

order THF > IHP >> 1,4-dioxan, with 1,4-dioxan being sorbed almost six times slower than IHP, and THF. However the diffusion coefficients for the cyclic ethers did not exhibit the increase with temperature expected of a thermally activated process nor did they conform to the $1/\sqrt{\text{mass}}$ dependence for limiting knudsen diffusion, as was found for the alcohol diffusion coefficients.

Consequently this investigation to ascertain whether the alcohols or cyclic ethers underwent any transformation in the temperature region (18°-105°C) of the diffusion experiments and was extended up to 800°C to conform with similar studies by Al-Oswais et al⁸⁴, on the nature of the intercalation of acetic acid on Al³⁺-montmorillonite, and Ballantine et al⁸⁵ on the interaction of nitrogen-containing bases such as cyclohexylamine.

6.2. Temperature Programmed Desorption and Infrared Spectroscopy Results.

6.2.1. The Temperature Programmed Desorption Results.

Using the experimental methods and techniques detailed in chapter 3, the following results were obtained. The basal spacing and percentage weight loss (18°-800°C) data for the alcohol saturated samples is listed in Table 6.11., and confirms that the desorption profiles reported below arise from intercalated and not surface species.

Fig 6.1.(i.-iv.) shows the desorption profiles for methanol, n-propanol, 1-propanol, and t-butanol from a range of cation-exchanged clays, (Na, Ca, Fe, Cr, and Al). The desorption of methanol from the trivalent cation exchanged and sodium-forms, (Fig 6.1.i.) was characterized by two peaks at 20°C and 110°C. In addition, the Al³⁺-form exhibited a weak broad desorption peak near 300°C, and the Ca²⁺-montmorillonite had a sharp peak at 140°C which partially masked

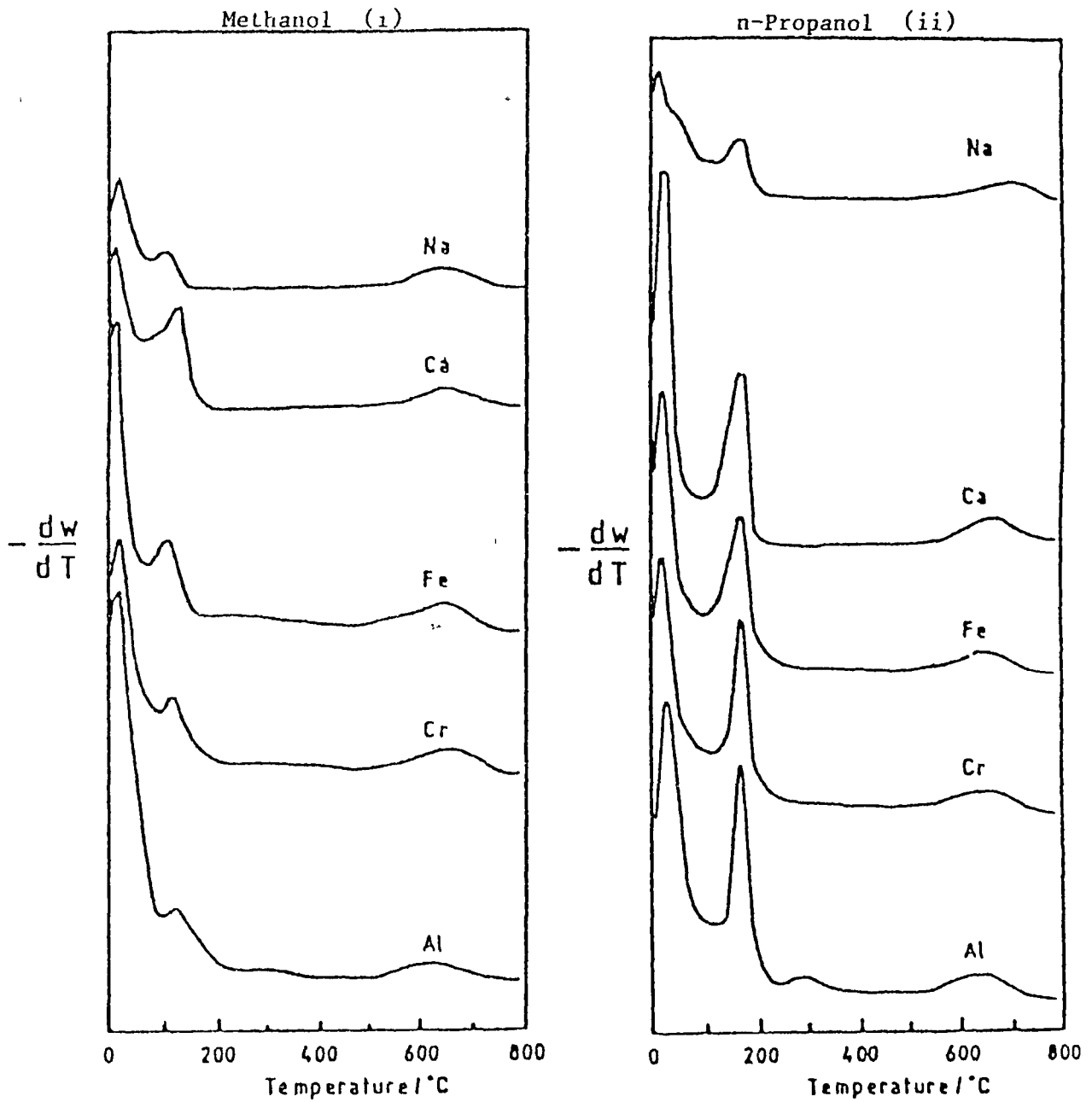


Fig 6.1.(1-11). Desorption profiles for methanol, and n-propanol from Na^+ , Ca^{2+} , Fe^{3+} , Cr^{3+} , and Al^{3+} -exchanged montmorillonite.

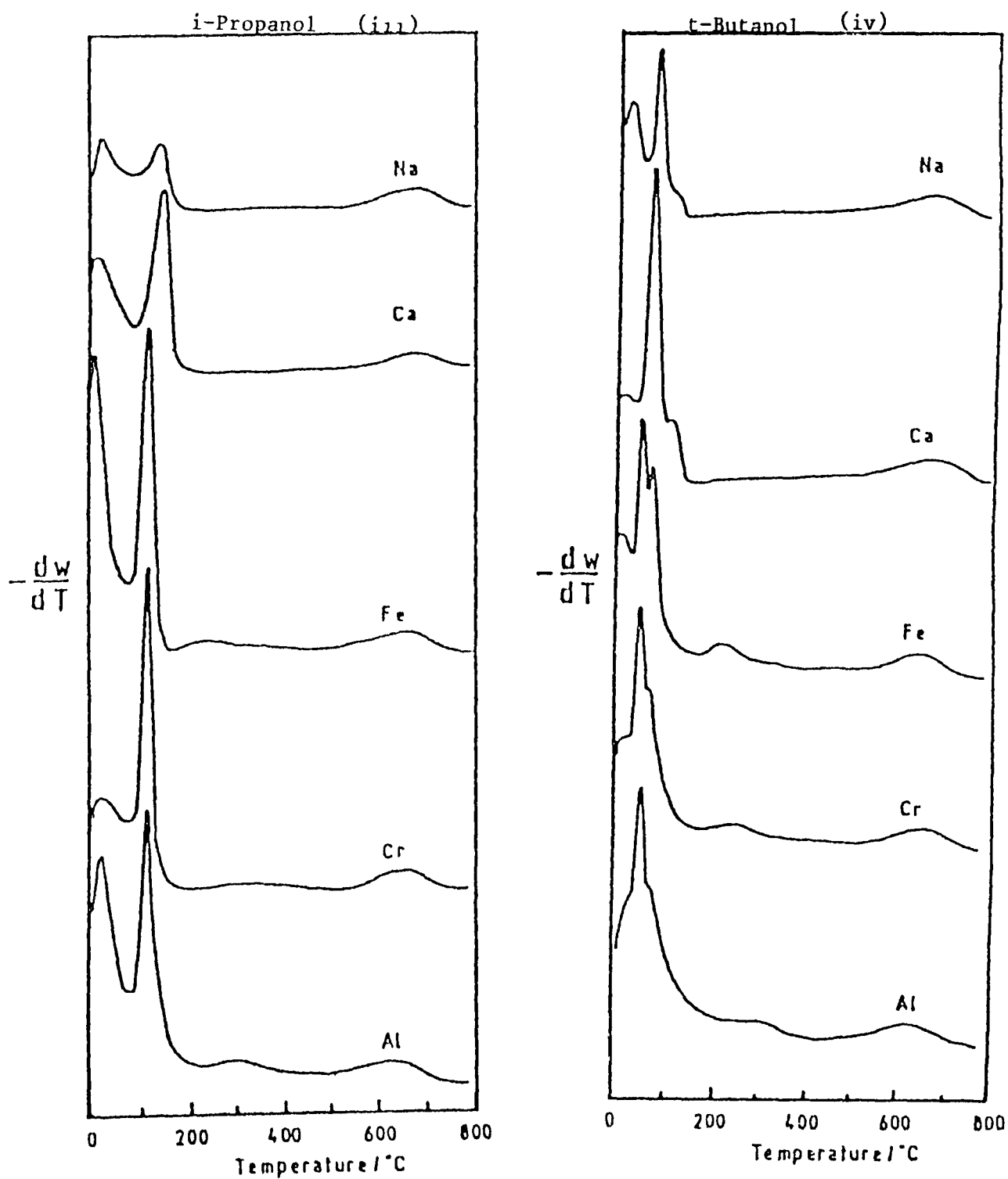


Fig 6.1.(iii-iv). Desorption profiles for i-propanol and t-butanol from Na⁺, Ca²⁺, Fe³⁺, Cr³⁺, and Al³⁺-exchanged montmorillonite.

that at 110°C. The temperature the maxima in the desorption profiles of n-propanol from all the cation-exchanged forms (Fig 6.1.ii.) were identical at 30° and 160°C. Only the Al³⁺-form exhibited a weak desorption peak near 290°C. The desorption profiles for 1-propanol from Na⁺ and Ca²⁺-montmorillonite showed two peaks near 20°C and 140°C, whilst the higher temperature desorption maximum in the trivalent cation-exchanged forms occurred at the lower temperature of 100°C (Fig 6.1.iii.). Furthermore all the trivalent cation-exchanged forms exhibited some deviation from baseline in the region 200-400°C and it was most noticeable for the Al³⁺-exchanged form. The desorption profiles for t-butanol (Fig 6.iv.) contained the lowest temperature desorption peaks in this study with three poorly resolved peaks occurring at or near 30, 50 and 70°C in the M³⁺-exchange forms and 30, 90 and 110°C in the Na⁺ and Ca²⁺-montmorillonite. Once again deviation from the background was observed in the region 200-400°C of the Al³⁺-, Cr³⁺-, and Fe³⁺-montmorillonite desorption profiles.

Table 6.11. Weight loss (%) by 800°C and basal spacings at 20°C for the cation-exchanged montmorillonite-alcohol systems.

<u>Cation</u>	<u>Solvent</u>	<u>Weight Loss (%)</u>	<u>Basal Spacing (Å)</u>
Al ³⁺	Methanol	36	14.0
	n-Propanol	26	----
	1-Propanol	27	14.3
	t-Butanol	23	15.3
Cr ³⁺	Methanol	26	15.0
	n-Propanol	24	----
	1-Propanol	24	13.8
	t-Butanol	21	17.4
Fe ³⁺	Methanol	25	15.5
	n-Propanol	27	----
	1-Propanol	25	16.0
	t-Butanol	24	17.7
Ca ²⁺	Methanol	17	----
	n-Propanol	22	----
	i-Propanol	19	----
	t-Butanol	16	----

Fig 6.2.(i.-iii) show the desorption profiles for THP, THF, and 1,4-dioxan, respectively, from a range of cation exchanged forms. In complete contrast to the desorption profiles for the alcohols, there was little uniformity in the position of the desorption maxima from the different cation-exchanged forms. Consequently the temperatures at which the major pre-dehydroxylation events occurred are presented in Table 6.111.

Table 6.111. The position of the peak maxima in Fig 6.2.(i.-iii.), ($^{\circ}\text{C}$).

Cation	1,4-Dioxan	Tetrahydropyran	Tetrahydrofuran
Al^{3+}	30, 150, 240	30, 130, 275	20, 120, 220
Cr^{3+}	30, 150, 270	30, 110, 300	20, 90, 180
Ca^{2+}	10, 45, ---	30, 120, ---	30, 145, ---
Na^{+}	10, 75, 115	30, 110, 160	30, 130, ---

Nonetheless some tentative trends were observed. Desorption from Ca^{2+} -montmorillonite always occurred in two distinct processes, the second of which was broad enough to encompass the two higher temperature maxima exhibited in the desorption profile of THP and 1,4-dioxan from Na^{+} -montmorillonite. Desorption from trivalent cation-exchanged forms always occurred in three steps, the second of which generally occurred at higher temperatures in the Al^{3+} -form, whereas the highest temperature desorption maxima were usually observed in the Cr^{3+} -form.

When interpreting the infrared spectra for both alcohols and the cyclic ethers it was noted that the trends were similar for all the cation-exchanged forms of the clay used. So the Cr^{3+} -montmorillonite spectra will be used to demonstrate the alcohol results as it is representative of all the M^{3+} -montmorillonites used.

6.2.ii. Infra-Red Spectroscopy Results.

Fig 6.3.(1-1v). shows the changes in the $1300\text{-}1800\text{cm}^{-1}$ region of the infra-red spectrum caused by outgassing the alcohol saturated

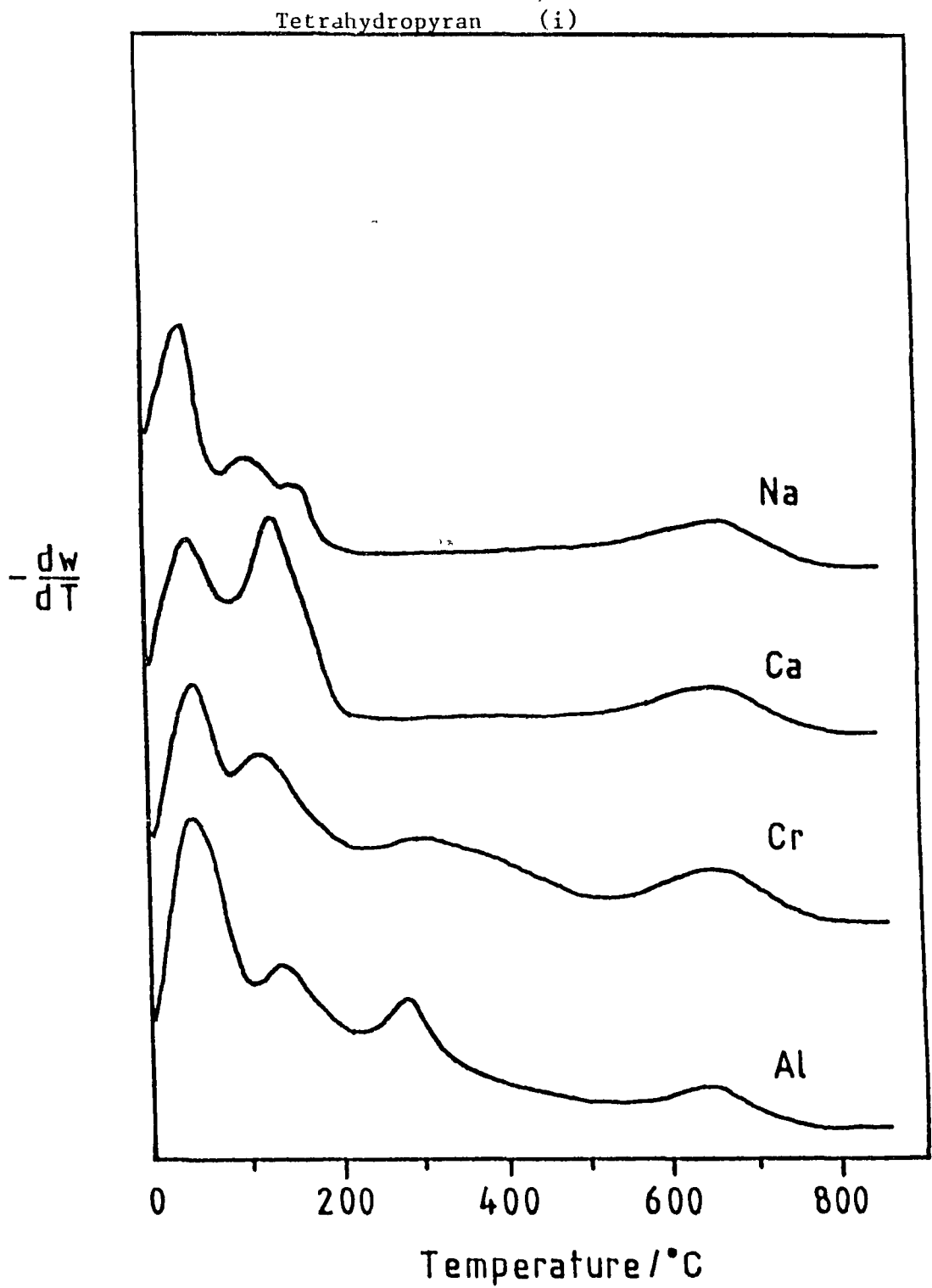


Fig 6.2.1. Desorption profiles for THP from Na^+ , Ca^{2+} , Cr^{3+} , and Al^{3+} -exchanged montmorillonite.

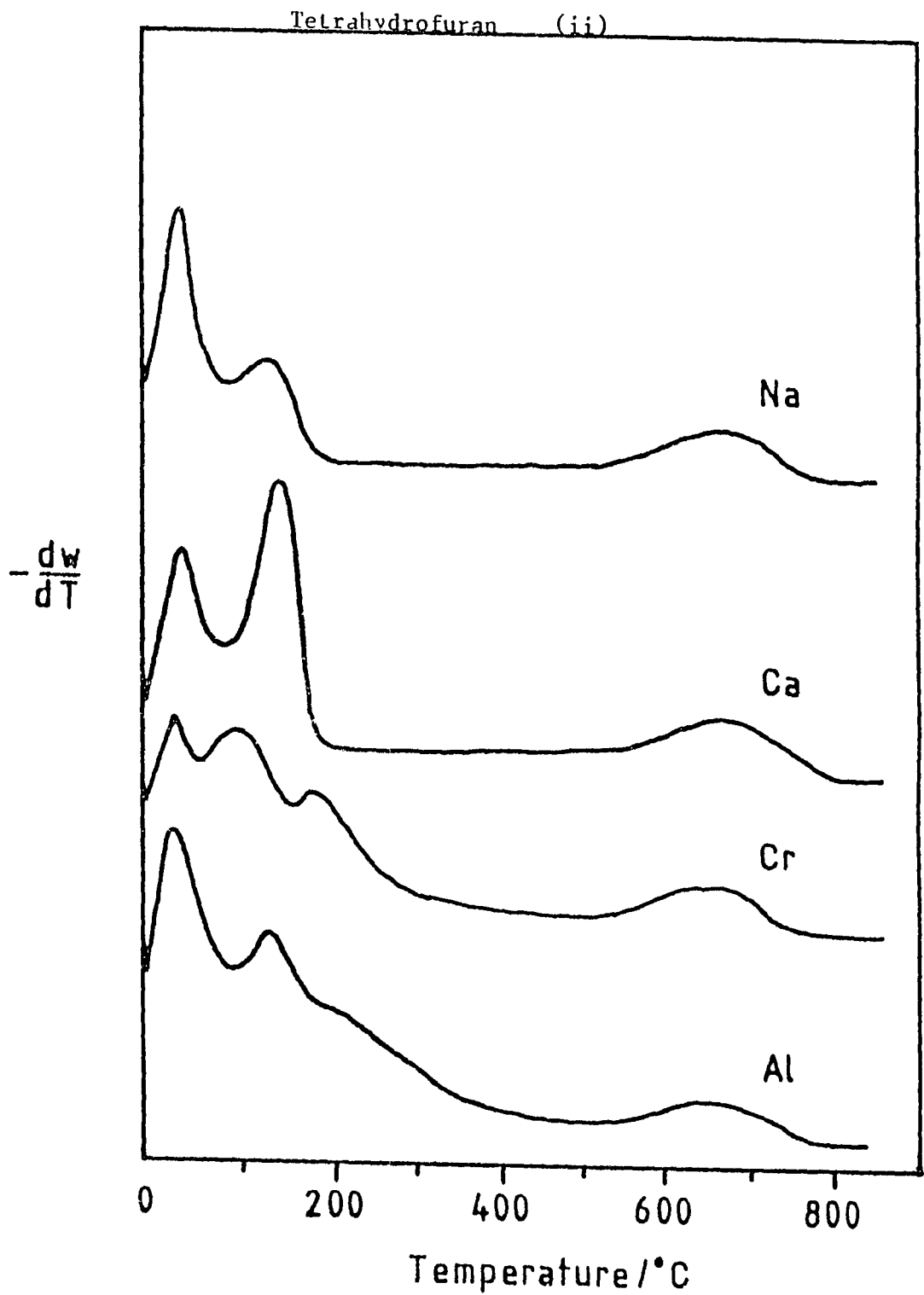


Fig 6.2.ii. Desorption profiles for THF from Na⁺, Ca²⁺, Cr³⁺, and Al³⁺-exchanged montmorillonite.

1,4-Dioxan (iii)

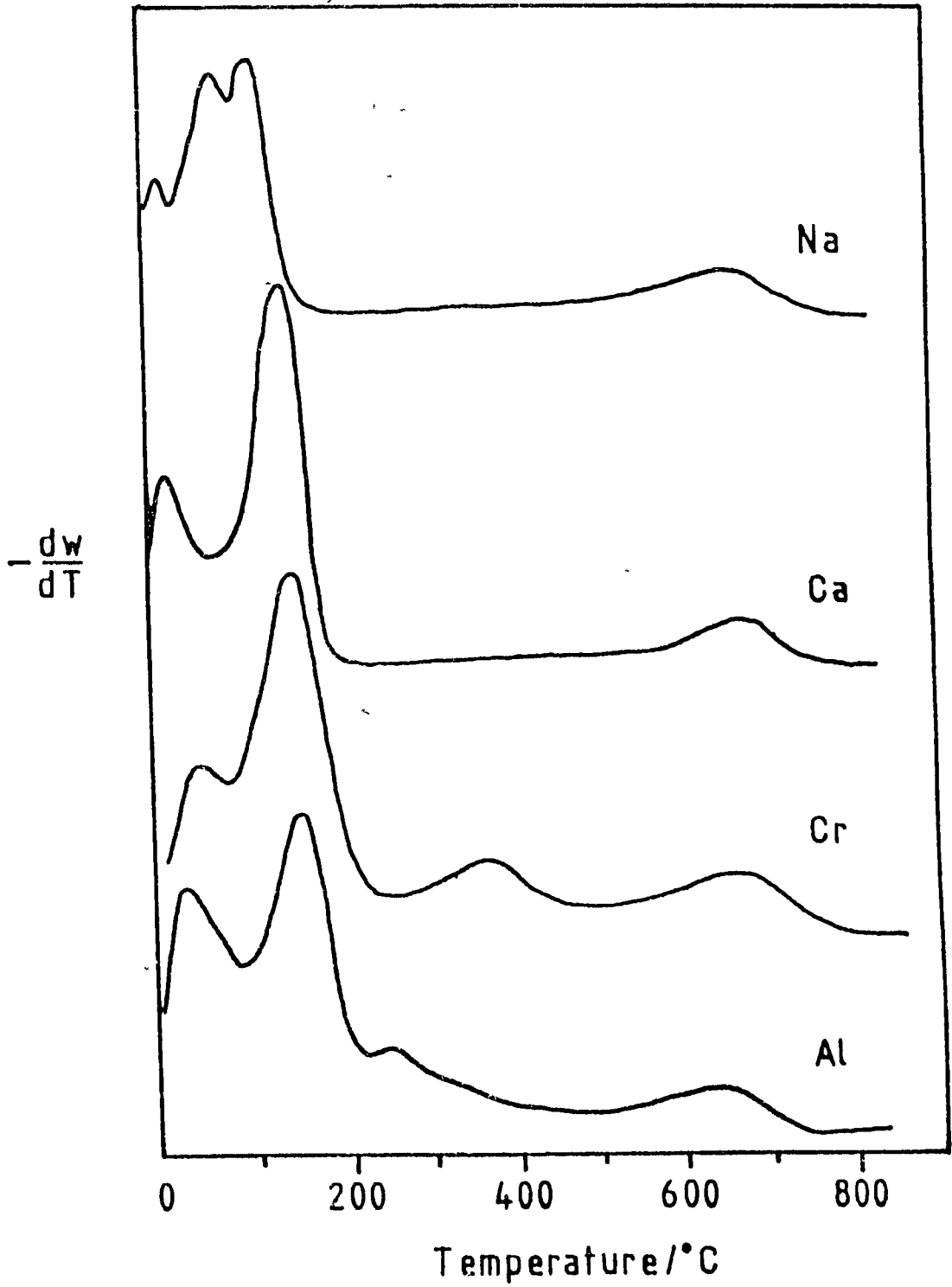


Fig 6.2.iii. Desorption profiles for 1,4-dioxan from Na⁺, Ca²⁺, Cr³⁺, and Al³⁺-exchanged montmorillonite.

Cr³⁺-montmorillonite at progressively higher temperatures 20°, 50°, 100° and 150°C. The infra-red spectrum of the Cr³⁺-montmorillonite/n-propanol intercalate (top spectra Fig 6.3.(i-iv)) changed little as the outgassing temperature was increased. The CH₃ deformation band at 1475cm⁻¹ was maintained up to 150°C, whilst the C-H band at 1397cm⁻¹ and the OH band at 1625cm⁻¹ became progressively weaker up to this temperature. In contrast the infra-red spectrum of Cr³⁺-montmorillonite/1-propanol system (middle spectrum Fig 6.3.(i.-iv.)) exhibited a marked change as the outgassing temperature was increased from 50°-100°C, (Fig 6.3.iii. and 6.3.iii.). The characteristic doublet at 1391 and 1377cm⁻¹ is lost and the bands at 1626 and 1457cm⁻¹ became the dominant feature of the spectrum. At 150°C (Fig 6.3.iv.), poorly resolved bands at 1435 and 1427cm⁻¹ were observed, together with a weak doublet at 1375 and 1363cm⁻¹. Increasing the outgassing temperature to only 50°C caused considerable changes in the spectra of the Cr³⁺-montmorillonite/t-butanol system (bottom spectra Fig 6.3.(i.-iv.)). The 1376cm⁻¹ band was considerably reduced in intensity and the bands at 1626, 1464, and 1363cm⁻¹ dominated the higher temperature spectra. Figs 6.4.(i.-iii.) illustrate the changes that occur in the C-H stretching region of the n-propanol, 1-propanol, and t-butanol saturated Cr³⁺-montmorillonite as the outgassing temperature is increased. The important feature to note is that the change in the characteristic absorption band profile occurs at progressively lower temperatures, 150°C for n-propanol (Fig 6.4.i.), 100°C for 1-propanol (Fig 6.4.ii), and 50°C for t-butanol (Fig 6.4.iii.). Thus reinforcing the changes observed in the 1300-1800cm⁻¹ region of the respective spectra.

Fig 6.5.(i-iii) shows the infrared spectra obtained from air-dried Al³⁺-montmorillonite exposed to THP, IHF, and 1,4-dioxan,

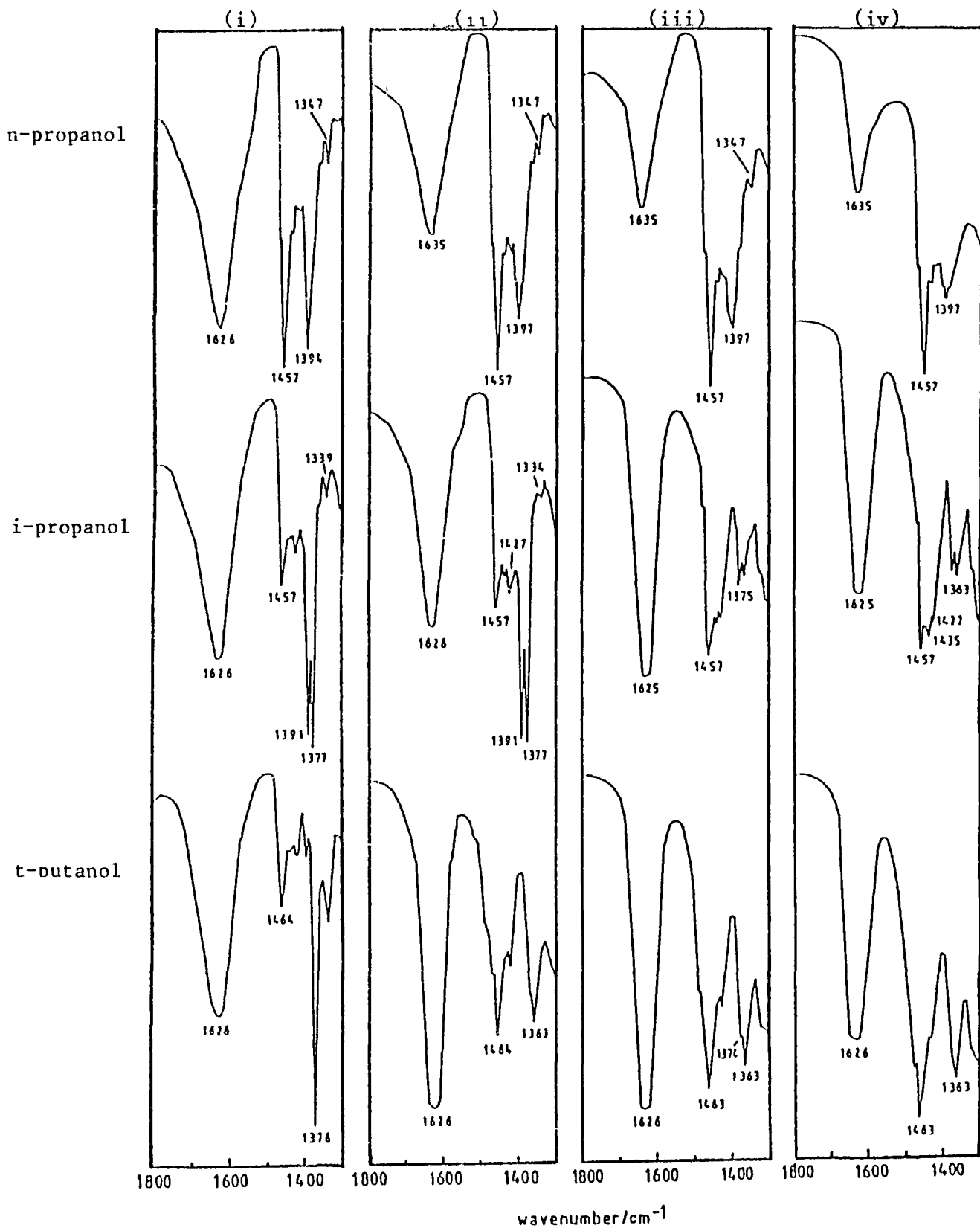


Fig 6.3.(i-iv). Effect of outgassing temperature on the IR spectra of Cr^{3+} -montmorillonite/alcohol intercalates (i) 20°C , (ii) 50°C , (iii) 100°C , and (iv) 150°C .

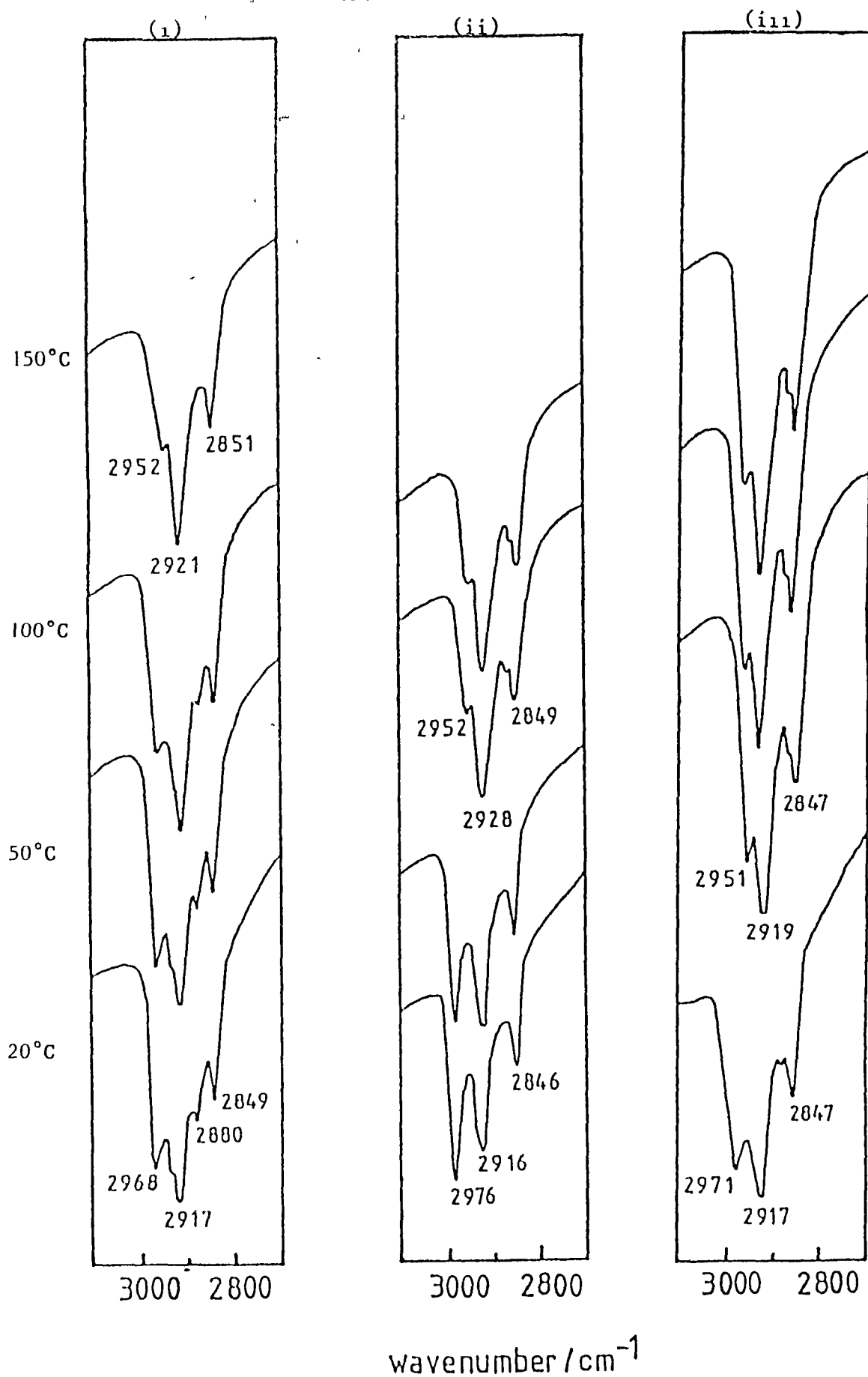


Fig 6.4.(i-iii). Effect of outgassing temperature on the C-H stretch region of the IR spectra of (i) n-propanol, (ii) i-propanol, and (iii) t-butanol.

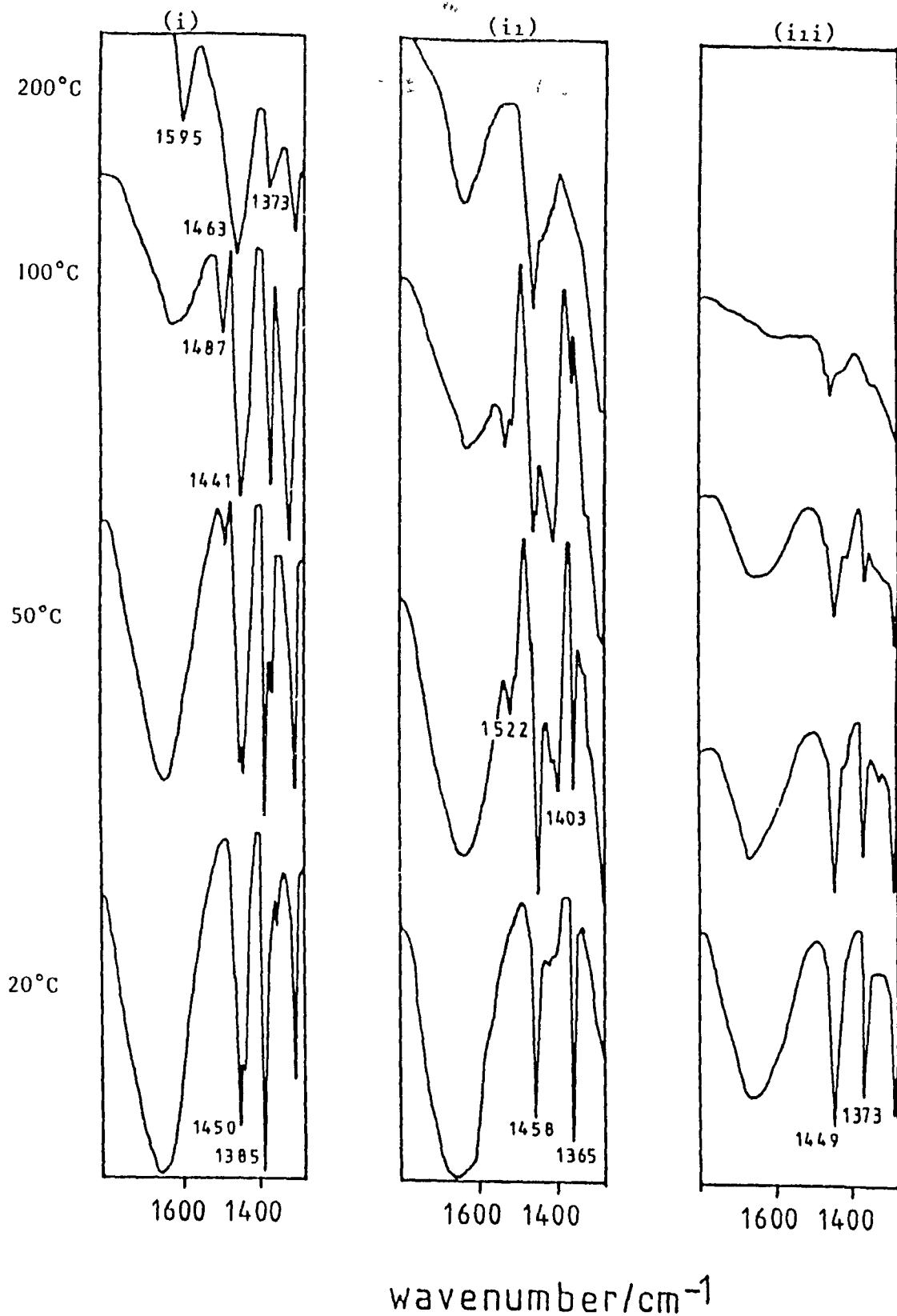


Fig 6.5.(i-iii). Effect of outgassing temperature on the IR spectrum of Al^{3+} -montmorillonite saturated with (i) THP, (ii) THF, and (iii) 1,4-dioxan.

respectively, and were representative of the desorption from the Cr^{3+} -form except that the desorption of THF occurred at lower temperatures in the latter. The bottom spectra Fig 6.5.i., obtained after degassing at room temperature, shows that the major absorption bands attributed to THF occurred at 1450, 1440, 1385, and 1303cm^{-1} , together with bands at 1275 and 1258cm^{-1} which are not illustrated. As the temperature was increased through 50° to 100°C the bands near 1440 and 1365cm^{-1} increased in intensity and then replaced the bands at 1450 and 1385cm^{-1} . Furthermore a band near 1487cm^{-1} appeared and grew in intensity but this disappeared upon heating to 150°C although the other bands were unaffected. The top spectrum Fig 6.5.1. shows the bands remaining at 200°C were centered near 1595, 1463, 1373, and 1309cm^{-1} . The bottom spectra in Fig 6.5.ii., obtained after degassing at room temperature, shows the two absorption bands for THF at 1458 and 1365cm^{-1} . Heating at 50°C for one hour resulted in the appearance of further bands at 1522, 1415, and 1403cm^{-1} . After one hour at 100°C the sharp, characteristic band near 1365cm^{-1} was much reduced in intensity whilst the bands at 1522 and 1404cm^{-1} were unaffected. The 1404cm^{-1} band was still in evidence after degassing at 150°C . But subsequent to heating at 200°C (top spectrum Fig 6.5.ii.) the predominant band was at 1456cm^{-1} . Interestingly, in contrast to the corresponding spectrum in Fig 6.5.1. the band at 1626cm^{-1} , normally attributed to water in these systems had survived.

The absorption spectrum of 1,4-dioxan adsorbed on Al^{3+} -montmorillonite subsequent to degassing at room temperature (bottom spectrum Fig 6.5.iii.) exhibited bands near 1449, 1373, and 1293cm^{-1} , together with a band at 1256cm^{-1} which is not illustrated. The position of these bands were unchanged as the temperature was increased up to 100°C . The 1373cm^{-1} band was removed on heating at 150°C and replaced

by a broad, unresolved absorption near 1350cm^{-1} and appears much the same as the top spectrum in Fig 6.5.111. obtained at 200°C .

6.3. Discussion of the Experimental Results.

6.3.1. The clay alcohol interactions.

The maxima at 20°C in the desorption profile of methanol from the various cation-exchanged forms Fig 6.1.(i-iv.) could be removed by passing dry nitrogen gas through the system and can thus be attributed to physisorbed alcohol, as can the peaks in the 20° - 30°C region for the desorption of n-propanol, i-propanol, and t-butanol, from the cation-exchange forms, (Fig 6.1.(i1-iv)). The maximum at 110°C in the desorption profile of methanol from the various cation-exchanged forms (Fig 6.1.1.) corresponds closely to the values of 117° - 140°C and 130°C reported for the desorption of methanol adsorbed, (i) on the surface hydroxyls of silica-magnesia mixed oxides⁴² and, (ii) in zeolite H-ZSM-5 reported by Ison and Gorte⁵⁷, respectively. However Ison and Gorte⁵⁷ observed a second desorption maximum near 180°C which they attributed to the desorption of a single methanol molecule from each cation site in H-ZSM-5, but there is no evidence of such an interaction in this study. Moreover, the exchange cation present in the interlayer space has no influence on the temperature of the desorption maximum at 110°C .

The higher temperature maximum at 160°C in the desorption profile for n-propanol from the various cation-exchanged forms (Fig 6.1.11.) similarly exhibits no cationic dependence. However, the corresponding maximum for i-propanol (Fig 6.1.iii.) occurs at 140°C in the Na^+ - and Ca^{2+} -forms but at 110°C in the trivalent cation-exchanged montmorillonite, and the reason is not immediately obvious. The results in Table 6.11. indicate that several processes can occur, which may be in competition.

Table 6.ii Product distribution (weight %) for reactions of alcohols with M^{3+} -montmorillonite.

Reactant	Reactant Recovered	Ethers	Alkenes
Methanol	- a , - b	- b , (2)	-
n-Propanol	22	63 c	3
1-Propanol	29	30 d, (3) d	40
t-Butanol	3	-	97 e, (8) f

Note: Figures in parantheses taken from Adams et al⁸⁷, using 1g Fe^{3+} -montmorillonite, 50mmol. of reactant alcohol, and 3cm³ of 1,4-dioxan at 60°C.

Other values are from Ballantine et al¹², using 0.5g of Al^{3+} -montmorillonite at 200°C for 4 hours.

a = Not reported by Adams et al⁸⁷.

b = Not reported by Ballantine et al¹².

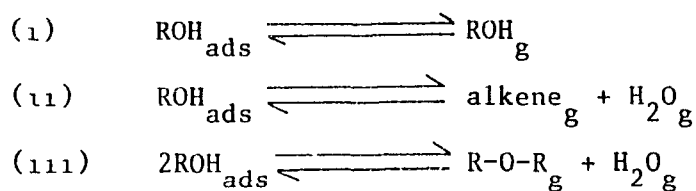
c = Yield of di-prop-1-ylether.

d = Yield of di-prop-2-ylether.

e = 18% alkene, 50% alkene dimer, and 29% alkene tetramer.

f = Alkene Dimer.

These reactions may be summarised as follows,



Where ads = an adsorbed molecule.

g = a vapour phase molecule.

The problem is further complicated in steps (11) and (111) because the products may not desorb at the same temperature that they are produced. However, if situation (1) pertains then the higher desorption temperature of 160°C for n-propanol compared to 110°C for 1-propanol could be attributed to the higher volatility and greater steric hinderance of 1-propanol. Moreover, primary amines are known to desorb at higher temperatures than secondary amines⁵⁸, but this approach does not

explain the higher desorption temperatures of 1-propanol from Na^+ - and Ca^{2+} -montmorillonite.

If equation (11) describes the desorption process then it is necessary to ascertain whether one or both products are desorbed upon formation. Noller and Ritter⁴² found that propene formed by the acid-catalysed dehydration of 1-propanol on silica-magnesia desorbed at least 65°C below that formed from n-propanol and that the alkene was desorbed upon formation.

Finally, if the reaction and desorption sequence follows scheme (111) then once again volatility and steric considerations suggest that di-prop-1-ylether would desorb at a higher temperature than di-prop-2-ylether.

Unfortunately, no single reaction sequence explains why the desorption of 1-propanol from the M^{3+} -exchange forms occurred at a lower temperature than that from Na^+ - and Ca^{2+} -montmorillonite, whilst the desorption of n-propanol exhibits no cationic dependence. The explanation lies in the lower desorption temperature of the species generated in the M^{3+} -montmorillonite/i-propanol system. The maximum at 110°C must be attributed to the desorption of propene from 1-propanol whereas, by analogy with methanol intercalates (Fig 6.1.1.), the peak at 140°C is due to the desorption of unchanged i-propanol. In contrast the desorption of n-propanol is governed by scheme (iii). In the M^{3+} -exchanged montmorillonite some or all of the n-propanol is converted to the corresponding di-prop-1-ylether and both the alcohol and the ether desorb at 160°C . Breen et al⁴⁷ have reported that amines such as n-butylamine and the corresponding di-but-1-ylamine desorb at the same temperature, although due to their greater basicity this desorption occurs at 410°C in M^{3+} -montmorillonite.

It is known that tertiary carbonium ions can be formed from

the protonation of species such as isobutene or the acid-catalysed dehydration of t-butanol at temperatures as low as 60°C³¹. Consequently if alkenes formed from alcohols do desorb at lower temperatures than the alcohol from which they are derived then the peaks in the desorption profile of t-butanol from the M³⁺-exchange forms should occur at lower temperatures than those from the Na⁺- and Ca²⁺-forms. This is clearly the case (Fig 6.1.iv.). Moreover, as Table 6.11. indicates, dimeric and tetrameric alkenes can be produced from t-butanol which may account for the complex nature of the desorption profiles. Furthermore, given the ease of dehydration of t-butanol and the relative stability of the tertiary butyl ion it is possible that the peak at 110°C in the desorption profile of t-butanol from the Na⁺- and Ca²⁺-exchange forms may be due to the desorption of alkene.

Corroborative evidence for the chosen interpretation of the temperature programmed desorption profiles can be inferred from Fig 6.3. and 6.4. Unfortunately, the main C-O stretching region (1000 - 1300cm⁻¹) is obscured by the alumino-silicate lattice absorption so definitive interpretations concerning the presence of alcohol versus ether are not available. However, Grady and Gorte⁵⁹ observed similar changes to those reported here, in the infrared spectrum of i-propanol adsorbed on H-ZSM-5 and attributed a marked change in the 2800 - 3000cm⁻¹ region, to the complete loss of the C-H band at 1380cm⁻¹ together with an increase in the intensity of the band at 1630cm⁻¹ (due to the elimination of water) to the formation of propene. Their interpretation was confirmed by mass spectroscopic determination of desorbed propene. Furthermore, there can be no question that the temperature at which the infra-red change in Figs 6.3. and 6.4. closely parallel the events in the temperature programmed desorption profiles and that the effect of temperature on these spectra indicate that i-propanol and t-butanol

undergo very similar changes to give peaks of similar intensities near 2950, 2925, 2848, 1626, 1460, and 1360 cm^{-1} .

The results of Ballantine et al¹² reported in Table 6.11. indicate that 1-propanol should form the di-prop-2-ylether in addition to the alkene. However, their study was conducted in a sealed vessel of 20 cm^3 capacity containing 0.5g of Al^{3+} -montmorillonite and 5g of 1-propanol. The results reported here suggest that the alcohol once converted to the alkene does not encounter an 1-propanol molecule with which to react. Consequently, an attempt was made to produce the di-prop-2-ylether in the experimental apparatus used for this study by subjecting the Al^{3+} -montmorillonite/i-propanol sample to a flow of 1-propanol saturated nitrogen gas whilst it underwent the normal temperature ramp used to obtain the desorption profile. The resulting differential thermogram is presented in Fig 6.6.111. together with the desorption profiles from i-propanol (Fig 6.6.i.) and n-propanol (Fig 6.6.11) saturated Al^{3+} -montmorillonite samples. In addition to the propene desorption peak at 110°C, there is an alcohol/ether desorption peak at 160°C and the maximum at 300°C is enhanced. Indicating that di-prop-2-ylether appears to be forming in the interlayer.

6.3 11 The clay-cyclic ether interactions.

Again all the maxima below 50°C in the desorption profiles in Fig 6.2.(1-111.) were removed by a prolonged flow of dry nitrogen proving that they arose from physisorbed species. The nature of the bonding or the transformation mechanism giving rise to the higher temperature desorption peaks is not easy to elucidate.

The infrared spectrum of THP-saturated Al^{3+} -montmorillonite Fig 6.5.(1-111). shows that after degassing at 100°C noticeable changes have taken place, in particular the appearance of the 1487 cm^{-1} band. Subsequent degassing to 200°C results in the appearance of bands at

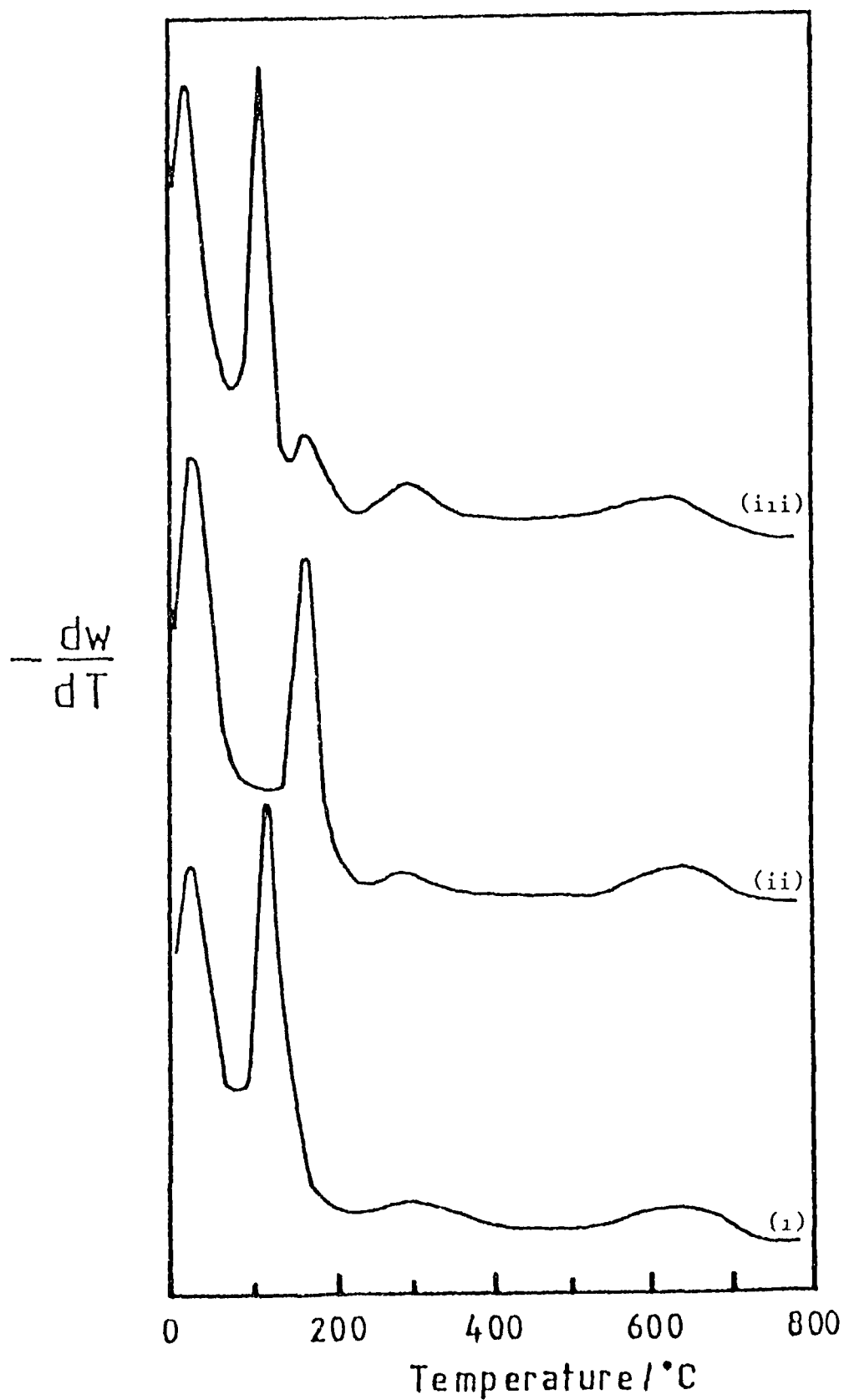
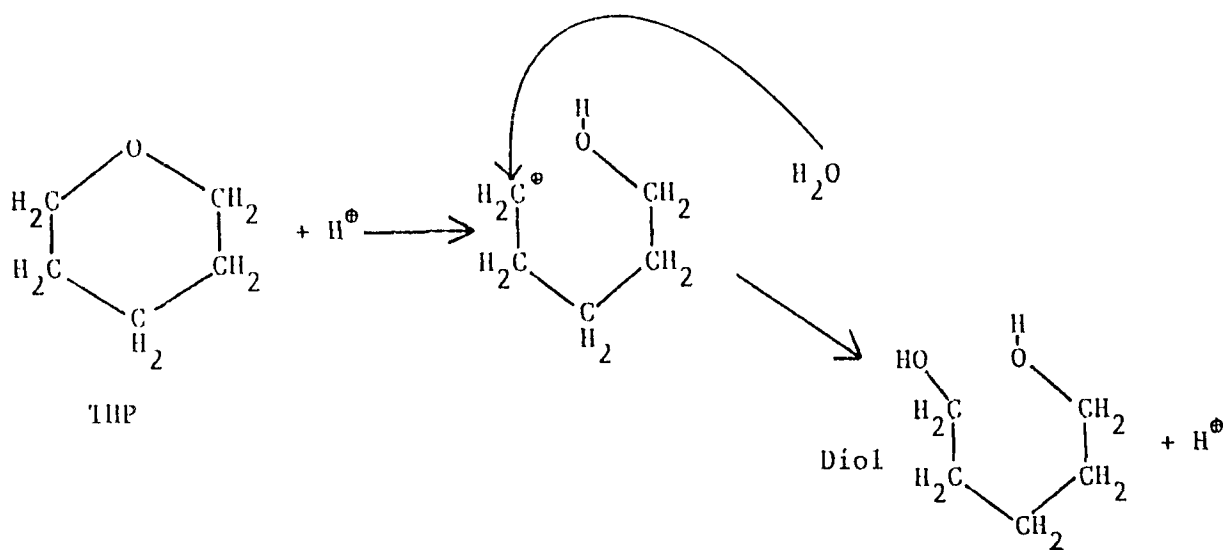


Fig 6.6.(i-iii). Comparison of the desorption profiles of (i) i-propanol and (ii) n-propanol sorbed on Al^{3+} -montmorillonite, (iii) Al^{3+} -montmorillonite/i-propanol subjected to nitrogen/i-propanol flow.

1595, 1463, and 1373cm^{-1} Datka⁸⁸ attributed bands near these frequencies to the formation of oligomeric moieties derived from the transformation of but-1-ene on dehydroxylated Y zeolite at room temperature. The formation of alkenes from THP is not unlikely insofar as the acid-catalysed ring opening of THP and THF over HY zeolites has been observed^{89,90}, and a similar mechanism has been suggested to explain the formation of 2-methyl-1,3-dioxalane from 1,4-dioxan⁹¹. The most likely product following acid-catalysed ring opening is the diol, which could then be dehydrated to yield alkenes. These alkenes could then oligomerise.



Correlation of the infrared and temperature programmed desorption results for the desorption of THP from the trivalent cation-exchanged forms suggests that the loss of THP in its unmodified form occurred at or before 200°C , thereby implying that the maxima near 300°C in the TPD profiles (Fig 6.2.i.) must be attributed to the desorption of the oligomeric species or a component thereof.

In the case of THF (Fig 6.2.11.) the changes in the infrared spectrum were not so drastic, although the interim formation of bands near 1520 and 1403cm^{-1} require consideration. Haber et al⁹² in an extensive study of the transformation of alcohols on HY and H-Z-79 zeolites attributed the band near 1520cm^{-1} to the formation of aromatic

surface structures. However Grady and Gorte⁵⁹ preferred, in the absence of aromatic compounds in the mass spectrum of the desorbed products, to assign it to a C-C double bond. If the latter interpretation pertains here then it would reinforce the proposed formation of alkenes following acid-catalysed ring opening. However, the infra-red evidence suggested that the transformation of THF to oligomeric species was not as extensive in the case of THP, since the OH absorption band at 1626cm^{-1} was still present at 200°C suggesting the presence of water or alcohol molecules. Nonetheless the possibility does exist that this absorption was of a C-C double bond although there was no evidence of the 1590cm^{-1} band which is indicative of the formation of oligomeric species⁸⁸.

The desorption thermogram of THF from Cr^{3+} -montmorillonite (Fig 6.2.111.) exhibited three desorption maxima at 20, 90, and 180°C , the latter two of which occurred at temperatures some 30° or 40°C below those in the desorption profile of THF from the Al^{3+} -form. This temperature difference agrees well with the infra-red observations and the tenacity of the band at 1626cm^{-1} , is similar to that in the desorption of alcohols discussed above, and may imply that the high temperature maximum was due to the desorption of an alcohol molecule.

The desorption of 1,4-dioxan from Al^{3+} -montmorillonite was quite uneventful by comparison. Neither shifts in the peak positions nor the appearance of new bands in the infra-red spectra were recorded suggesting that most of the 1,4-dioxan was desorbed without modification. This observation agrees with the temperature programmed desorption profiles in Fig 6.2.111. in that the major desorption of 1,4-dioxan occurred at 150°C for the Ca^{2+} , Cr^{3+} , and Al^{3+} -exchanged forms. The pre-dehydroxylation peaks above 200°C in the desorption profiles for 1,4-dioxan from Al^{3+} and Cr^{3+} -montmorillonite may be due to the desorption of oligomeric entities or strongly bound ether molecules

but there is little infrared evidence to support either suggestion.

It is interesting to once again find that 1,4-dioxan behaves in a different manner to the other two cyclic ethers. Adams et al³¹ reported that 1,4-dioxan was the optimum solvent for the formation of methyl t-butyl ether. Breen and Deane⁹³ in their studies on the sorption of methanol from binary solution with 1,4-dioxan, THF and THP, found that although the amount of 1,4-dioxan adsorbed exceeded that of THP and THF the ratio of 1,4-dioxan:methanol was lower than that of THP:methanol. The result of which is that the solvent 1,4-dioxan, allows more of the reactant, methanol, into the interlamellar space which contains the active, or acidic site. Finally it has been shown in chapter 5 that the rate of uptake of 1,4-dioxan onto Al^{3+} - and Cr^{3+} -montmorillonite, was considerably slower than that of the alcohols, (methanol, 1-propanol, and t-butanol), and that of the cyclic ethers, (THF and THP). Therefore, in both a dynamic and an equilibrium sense 1,4-dioxan allows more of a reactant molecule, such as an alcohol, to approach the active sites. Furthermore, the evidence in this study suggests that it is relatively stable towards acid attack in these systems.

CHAPTER 7Conclusions7.1. The Sorption Rate Studies.

The sorption rate was found to increase with decreasing sample and grain size, indicating that resistance to diffusion in the bed and to mass transfer between the various size particles which form the grain control the rate of uptake. The rate of uptake for the alcohols (methanol \gg i-propanol $>$ t-butanol) parallels the observed median size of particles which contribute to the grains. So implying that the measured rate reflects the tortuosity of the channel network within the grains.

Bed diffusion is the rate controlling stage for the alcohol sorption, and the sequence conforms to the $1/\sqrt{\text{mass}}$ required for knudsen diffusion as the major contributor to the mass transfer resistance. For the cyclic ethers the sorption rate decreases as THF $>$ THP \gg 1,4-dioxan, and this does not conform to the $1/\sqrt{\text{mass}}$ required for knudsen diffusion. This may be due to some concentration dependence as THF and THP have higher vapour pressures than 1,4-dioxan, or an alternative explanation may be that the 1,4-dioxan sorption rate is retarded due to bi-dentate coordination of the ether to Al^{3+} ions at the clay edges. Moreover, the sorption rate for the cyclic ethers shows no cationic dependence, whereas, the alcohols have a cationic dependence which increases as $\text{Fe}^{3+} < \text{Cr}^{3+} < \text{Al}^{3+}$. The integral diffusion coefficients for both the alcohols and the cyclic ethers are of the same order of magnitude which may reflect the fact that bed diffusion and not intracrystalline diffusion is the rate influencing factor.

The relatively low activation energy for the sorption process indicates that the sorption should have been almost instantaneous. However,

this was not the case. The time required to reach equilibrium loading probably reflects the fact that intercrystalline macropore diffusion resistance and the finite time required to dissipate the exothermic enthalpy of interaction of the vapour molecules retard the overall sorption rate. However, the contribution from the latter may be minimal since it was shown that the overall sorption process is virtually isothermal as little heat of adsorption is generated (in the clay-organic systems studied here) relative to the sorption temperature

The equilibrium loading found to decrease of the order methanol \gg THF $>$ 1-propanol $>$ t-butanol $>$ 1,4-dioxan and THP. This sequence may be explained by the fact that small molecules such as methanol have a more dense packing in the interlayer space (ie double-layer complex is formed⁶⁶), and so a higher equilibrium loading is obtained. This loading decreases as steric hinderance of the diffusing molecule increases. THF has a higher equilibrium loading than the other two cyclic ethers, and this may be attributed to its smaller size, which allows it to orientate or pack more densely into the interlayer space. The equilibrium loading decreases as the temperature increases because an increased temperature disfavours exothermic processes such as the adsorption processes occurring here.

The overall diffusion rates were of the order THF \gg THP $>$ methanol \gg 1-propanol $>$ t-butanol $>$ 1,4-dioxan. If the partial pressures of the vapours and the experimental imprecision are taken onto account, two groups each having about the same sorption rate (i) THP, THF, methanol, and 1-propanol, and (ii) t-butanol, and 1,4-dioxan, become apparent. The fact that no clear distinction between the sorption rates for the various compounds can be seen is probably due to the fact that the rate controlling influence is bed diffusion, so significant differences in the uptake rate due to steric hinderance

are less important.

7.2. Clay-Diffusivative Interaction Studies.

In the desorption profiles of the various compounds, low temperature peaks below 40°C are attributed to physisorbed species. n-Propanol was found to exhibit no cationic dependence in the desorption profiles and the i-propanol was found to desorb from the M^{3+} -exchange forms at a lower temperature than the Na^{+} - and Ca^{2+} -montmorillonite. These observations may be explained in terms of three possible processes occurring, (i) the alcohol is desorbed unchanged, (ii) the alcohol is transformed to an alkene and desorbed, and (iii) the alcohol is converted to a di-propyl ether and then desorbed. For the desorption of n-propanol on M^{3+} -montmorillonite some or all of the n-propanol is converted to the corresponding di-propyl ether and both ether and alcohol desorb at the same temperature. For t-butanol/ M^{3+} -montmorillonite the peaks occur at lower temperatures than for the Na^{+} - and Ca^{2+} -montmorillonite/t-butanol systems and based on the fact that alkenes formed from alcohols are known to desorb at lower temperatures than the alcohol³¹, and that t-butanol can form tetrameric alkenes as well as dimers, this would account for the more complex nature of the t-butanol/ M^{3+} -montmorillonite desorption profiles. The low temperature desorption peak in the i-propanol/ M^{3+} -montmorillonite system is also most likely to be due to the desorption of the corresponding alkene. These findings are corroborated by the infra-red studies. Finally to reinforce the conclusions reached here an i-propanol saturated Al^{3+} -montmorillonite underwent the normal temperature ramp used for the desorption profiles, while being exposed to a flow of i-propanol saturated nitrogen gas. This resulted in an additional peak in the desorption profile corresponding to an alcohol/ether desorption peak, indicating that di-propyl ethers may well be forming in the

interlayer on adsorption of alcohols, confirming the above conclusions.

For the cyclic ethers the bonding or transformation mechanism was not easy to elucidate. THP may undergo acid-catalysed ring opening to yield alkenes which could undergo oligomerisation prior to desorption. The infra-red and temperature programmed desorption results for THP from M^{3+} -montmorillonite suggests that THP desorbed in its unmodified form at or below 200°C, and is desorbed as an oligomeric species or a component thereof at 300°C. The THF infra-red results are not so drastic and acid-catalysed ring opening of the THF to an oligomeric species was not as extensive as for THP, although little evidence of the formation of oligomeric species from THF was found in the infra-red spectrum for THF/ M^{3+} -montmorillonite. The desorption of 1,4-dioxan is quite uneventful by comparison to the other two ethers. The infra-red spectrum suggests that most of the 1,4-dioxan was desorbed without modification, and this observation was confirmed by the temperature programmed desorption profiles as no evidence of the desorption of oligomeric entities or strongly bound ether molecules was found, except for a small maxima in the 200°-300°C region of the desorption profiles.

Once again the 1,4-dioxan is behaving differently to the other two cyclic ethers. Adams et al³¹ reported that 1,4-dioxan was the optimum solvent for the formation of MTBE, and Breen and Deane⁹³, in studies of the sorption of methanol from binary solution with 1,4-dioxan, THF and THP found that although the amount of 1,4-dioxan adsorbed exceeded that of THF and THP the ratio of 1,4-dioxan:methanol was lower than that of THP:methanol. The result of which is that the solvent 1,4-dioxan, allows more of the reactant methanol, into the interlamellar space which contains the active, acidic site. Finally it has been shown

that for the sorption of THF, THP, and 1,4-dioxan onto Al^{3+} - and Cr^{3+} -montmorillonite, the rate of uptake of 1,4-dioxan was considerably slower than that of the alcohols, methanol, i-propanol, and t-butanol, and the cyclic ethers THP, and THF. Therefore, in both a dynamic and an equilibrium sense 1,4-dioxan allows more of the reactant molecule, such as an alcohol, to approach the active sites. Furthermore, the evidence in this study suggests that it is relatively stable towards acid attack in these systems.

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