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Audrey Liu-Mei Huang

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DIFFUSION COEFFICIENTS OF D-GLUCOSE IN AQUEOUS CARBOXYMETHYLCELLULOSE AND CARBOXYPOLYMETHYLENE SOLUTIONS

BY

AUDREY LIU-MEI HUANG, 1942 -

A

THESIS

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Approved by

Robert M. Wellek (Advisor)   Frank H. Conrad

H. O. McDonald

ABSTRACT

A microinterferometric method was used to determine the concentration profiles in the infinite field unsteady state diffusion of D-Glucose in aqueous polymer solutions. Pseudo binary diffusion coefficients were determined as a function of reduced concentration both with and without the effect of liquid volume change during diffusion being considered. The systems studied were D-Glucose in aqueous Carboxymethylcellulose and D-Glucose in aqueous Carboxypolymethylene solutions. Solute concentration ranged from nearly zero to about 9% by weight D-Glucose in the aqueous polymer solutions.

ACKNOWLEDGEMENT

The author is greatly indebted to Dr. R. M. Wellek, Associate Professor of Chemical Engineering, who suggested this study and served as a research advisor. His help, guidance, kindness, and encouragement are sincerely appreciated.

The author wishes to dedicate this work to her loving parents, Dr. and Mrs. Chau-Lin Huang.

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PROLOGUE TO THESIS

The object of this investigation is to study the effect of solute concentration on the molecular diffusion coefficient in aqueous polymer solutions and also to determine the effect of polymer concentration on the diffusion coefficient. Besides these objectives, the importance of considering the effect of volume changes during the diffusion process is also investigated.

Information concerning molecular diffusion of solute-polymer pairs in concentrated solutions should be useful when considering many important polymer processing steps such as mixing, extraction, dissolution, and fiber formation by solution spinning.

The non-ionic, water-soluble polymers Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol) were used with D-Glucose as the solute. These particular polymer solutions were studied to aid in the prediction of molecular diffusivities for liquid extraction studies.

A microinterferometric technique was used to experimentally determine the diffusivities. Before 1967 the effect of volume changes during diffusion using the interferometric method was not considered. Previous measurements of the diffusivities by Desai(9) of the systems studied in this work were conducted before 1967. Therefore, Desai did not consider the effect of volume change on the diffusivity. In this study, the data of Desai were reanalyzed considering the effect of volume changes.

The microinterferometric method analyzes the concentration profiles in a free diffusion experiment. Free diffusion will occur when two phases having different concentrations are brought in direct contact with each other. The diffusion process occurs in a cell of effectively infinite length in which there are no concentration changes at the ends of the cell during the period of observation. The most general method of determining binary diffusion coefficients from free diffusion data is that developed by Boltzmann in 1894 (3). However, all of the numerical methods had been derived for the case in which no volume change occurs during the mixing of the diffusion species. As a result of this limitation, many experimenters have chosen to examine diffusion between two solutions of very nearly the same concentration in an attempt to minimize the effect of the volume change during diffusion. From the equation of change and equation of motion, Duda and Vrentas (10) derived an equation from which diffusion coefficients can be obtained from free diffusion experiments. Paul (18) modified the relation to a form which was easier to use. The equations considering both volume with and without change on mixing were used in this study.

Free diffusion by microinterferometric means is currently one of the most accurate methods of measuring molecular diffusion coefficients. Its major advantages in comparison with the normal interferometric method are, 1) the former equipment is less expensive; 2) the time required to obtain the data is much less; 3) only microgram amounts of solution are required in this method; and 4) since the microinterferometric diffusion cell is very thin, convection currents can be minimized; and hence temperature control is not as difficult to attain with the microinterferometry as it is with the macrointerferometry.

Diffusion Coefficients of D-Glucose in Aqueous Carboxymethylcellulose and Carboxypolymethylene Solutions

A. L. Huang, S. V. Desai, and R. M. Wellek
University of Missouri-Rolla, Rolla, Missouri

1. Introduction

Molecular diffusion coefficients of D-Glucose in aqueous Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol) solutions were measured in this work by a microinterferometric technique. Optical interference methods have been used previously by Kegeles and Gosting (9), Longsworth (10), Ambrose (1), Berg (2), Crank and Robinson (4), Robinson (15), Searle (16), Nishijima and Oster (11,12), and Secor (17). These workers assumed that there was no volume change on mixing during the diffusion process. However, Duda and Vrentas (6,7) derived a relation for calculating the molecular diffusivity which properly considers this effect. Paul (13) applied the relation of Duda and Vrentas for systems with linear density-concentration relations in a manner so that the calculations for diffusion coefficients using the interferometric technique is convenient.

In this investigation, one unsteady state solute concentration profile (observed at a certain time) was analyzed to study the effect of considering volume changes during mixing for the D-Glucose-CMC and D-Glucose-Carbopol systems. The ten systems studied are given in Table 1.

Table 1

Polymeric Systems Used

System	Polymer	Solvent	Polymer conc. wt. %	Solute	Initial solute conc. gm/100 cm^3 solution	Temperature Degrees C
1	CMC	Water	2.20	D-Glucose	10	23
2	CMC	Water	2.00	D-Glucose	10	23
3	CMC	Water	1.70	D-Glucose	10	23
4	CMC	Water	1.35	D-Glucose	10	23
5	CMC	Water	1.20	D-Glucose	10	23
6	Carbopol	Water	0.28	D-Glucose	10	23
7	Carbopol	Water	0.25	D-Glucose	10	21
8	Carbopol	Water	0.22	D-Glucose	10	21
9	Carbopol	Water	0.20	D-Glucose	10	23
10	Carbopol	Water	0.18	D-Glucose	10	23

2. Apparatus

The apparatus used in this work was basically the same as that used by Secor (16), except for the Carbopol systems for which platinum coated slides were used instead of aluminum coated slides to eliminate corrosion problems. In this study the range of the apparent viscosity of the polymer solutions used in the CMC system was from 635 centipoise to 9840 centipoise, and the range of viscosity used in the Carbopol system was from 819 centipoise to 17980 centipoise. For systems with viscosities significantly outside these ranges, the microinterferometric method could not be used; this effectively limited the range of polymer concentrations which could be studied.

3. Analysis of Data

Secor (16) used one concentration profile observed at a certain time and assumed no volume change on mixing during the diffusion process. The diffusion coefficient was calculated as a function of concentration using the following relation:

$$D_{AB}^{(3)} = - \frac{\int_{o}^{y} x dy}{2t \frac{dy}{dx}} \qquad (1)$$

Paul (13) observed that when the total fringe deflection was small and only a few fringes (10 or less) cross a line drawn parallel to the x axis, the errors involved in measuring the fringe deflection from a photograph as a function of x would considerably affect the evaluation of the integrals and make graphical differentiation of these data very unreliable. In view of this problem, Paul used several concentration profiles which were observed at various times in order to help reduce the random error of transposing the fringe contour on a photograph into digital data. The profiles were combined into a master plot by using the Boltzmann transformation. The diffusion coefficient which considers volume changes during diffusion was then calculated as a function of reduced concentration from the following relation:

$$D_{AB}^{(6)} = - \frac{2\Big[(1-AW_{A1}y^*)\int_0^{y^*} \eta\, dy^* + 2AW_{A1}\int_0^{y^*} \eta\, y^* dy^*}{(1+AW_{A1}y^*)(dy^*/d\eta)} \qquad (2)$$

where

$y^* = W_A/W_{A1}$ = reduced concentrations
W_A = weight fraction of the solute
$\rho = \rho_s(1+AW_A)$ = solution density
$\eta = x/2t^{\frac{1}{2}}$

The effect of volume changes during diffusion is considered through the variable solution density, ρ, for the different solute concentrations.

In this work, only one profile for each system was used -- both with and without the effects of volume changes during diffusion being considered in the calculations. The total fringe deflection in this work was not as small as Paul's; hence, the use of only one concentration profile probably does not contribute significantly to the possible errors mentioned by Paul. The time, t, which was a finite known value was separated from η in this work for calculational convenience. Thus, in the case of diffusion with volume change, the pseudo binary diffusivity was calculated from the following relation:

$$D_{AB}^{(1)} = - \frac{(1-AW_{A1}y^*) \int_0^{y^*} x dy^* + 2AW_{A1}\int_0^{y^*} xy^* dy^*}{2t\ (1 + AW_{A1}y^*)\ \frac{dy^*}{dx}} \qquad (3)$$

When the volume change was not considered, the above relation was simplified as follows:

$$D_{AB}^{(2)} = - \frac{\int_0^{y^*} x dy^*}{2t\ (dy^*/dx)} \qquad (4)$$

which is, except for the concentration variable, essentially equivalent to equation (1).

In order to find the position of the original interface (x=p) when it is assumed that no volume change during diffusion occurs, the original interface was located so that the amount of substance leaving one half-plane is equal to the amount of substance arriving at the second half-plane (4,8,17). That is

$$- \int_0^{yp} x dy^* = \int_{yp}^{1} x dy^* \qquad (5)$$

where yp is the value of y* corresponding to p. The relation for finding the original interface for volume changes during diffusion was presented by Paul (13) as follows:

$$-\int_{o}^{yp} xdy^* - 2AW_{Al}\int_{o}^{yp} xy^* = \int_{yp}^{1} xdy^* + 2AW_{Al}\int_{yp}^{1} xy^*dy^* \qquad (6)$$

The iterative procedure used to locate p is described in Appendix D.

In order to perform the integrations indicated in equations (1), (3), and (4), it is very useful to have an analytic relation between y* and x. The functional relation of the data is approximately represented by the following sigmoidal equation

$$y^* = ab^{c^{G(x)}} \qquad (7)$$

where

$G(x) = x/r - 1$

In this work, the scaling factor r was taken to be 0.005.

The method suggested by Davis (5) and used by Secor (17) required first that the data (y* versus x) be curve-fitted by passing a smooth curve through the data by "eye". From this smooth curve, values of y* at equal increments of x are obtained for use in the method of Davis to determine the constants a, b, and c. It was found in this work, however, that human bias in the smoothing of the data often resulted in significantly different final results of the curve-fit of equation (7).

Thus in this work, an iterative non-linear least squares method was used to determine the curve-fit of equation (7) (which is non-linear in the constants a, b, and c) directly from the original data--which in general were at unequal increments in x. The least squares procedure used in this work resulted in a closer fit of the data to equation (7) than the procedure of Davis (5). See Appendix D.

The integrals $\int_0^{y*} x\,dy*$ and $\int_0^{y*} xy*\,dy*$ were evaluated by Simpson's numerical method using equation (7). However, it was found convenient to first transform x to function of y*, i.e. x=f(y*), and then evaluate the integrals $\int_0^{y*} f(y*)\,dy*$ and $\int_0^{y*} f(y*)y*\,dy*$. The derivative dy*/dx was easily obtained by directly differentiating the Gompertz equation.

A detailed discussion of the analysis of the data is given in Appendix D.

4. Procedure and Results

The experimental procedure used here was basically the same as that used by Secor (17).

The refractive index-concentration relationships were obtained by making measurements of a series of polymer solutions with known solute concentration using an Abbe Spencer refractometer. The index of refraction using an Abbe Spencer refractometer could be determined to ± .0001. The resulting refractive index-concentration relationships were represented by the relation

$$n = R_o + R_1 y \qquad (8)$$

The constants R_o and R_1 are given in Table B.12 of Appendix B.

The densities were measured using a pycnometer using standard techniques (see Appendix G). The density and the concentration dependence of density are given in Table 2.

The molecular diffusion results are given in Figures 1 and 2 as the differential diffusion coefficient versus reduced concentration of the solute. Diffusion coefficient $D_{AB}^{(1)}$, presented in these figures were calculated using equation (3), which considers the density effect on mixing during molecular diffusion.

5. Discussion of Results

The diffusion coefficients were calculated for two cases: $D_{AB}^{(1)}$ using equation (3) and $D_{AB}^{(2)}$ using equation (4). For each system, each value of diffusivity, $D_{AB}^{(2)}$, which does not consider the volume change is always slightly smaller than the diffusivity, $D_{AB}^{(1)}$ which does consider volume changes. The absolute percentage deviation of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$ decreases as the reduced concentration increases. For all ten systems, the maximum percentage deviations ranged from -4.49% to -0.62%, depending on the system. Though the deviation is not large, the small changes in volume on mixing have been properly considered. See Appendix F for further analysis of the various differential diffusivities.

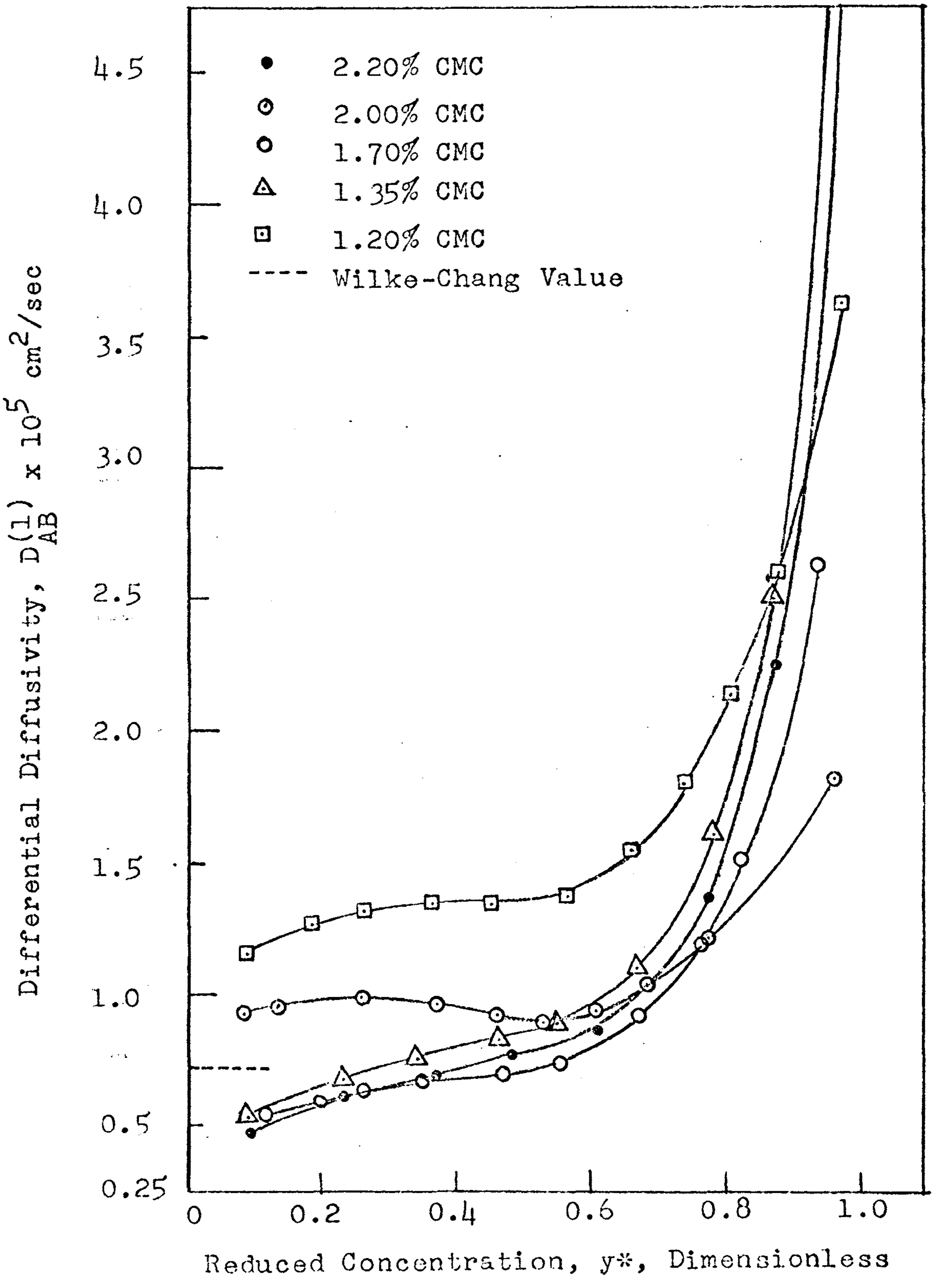

Figure 1. Differential Diffusivity vs. Solute Reduced Concentration for CMC-Water System

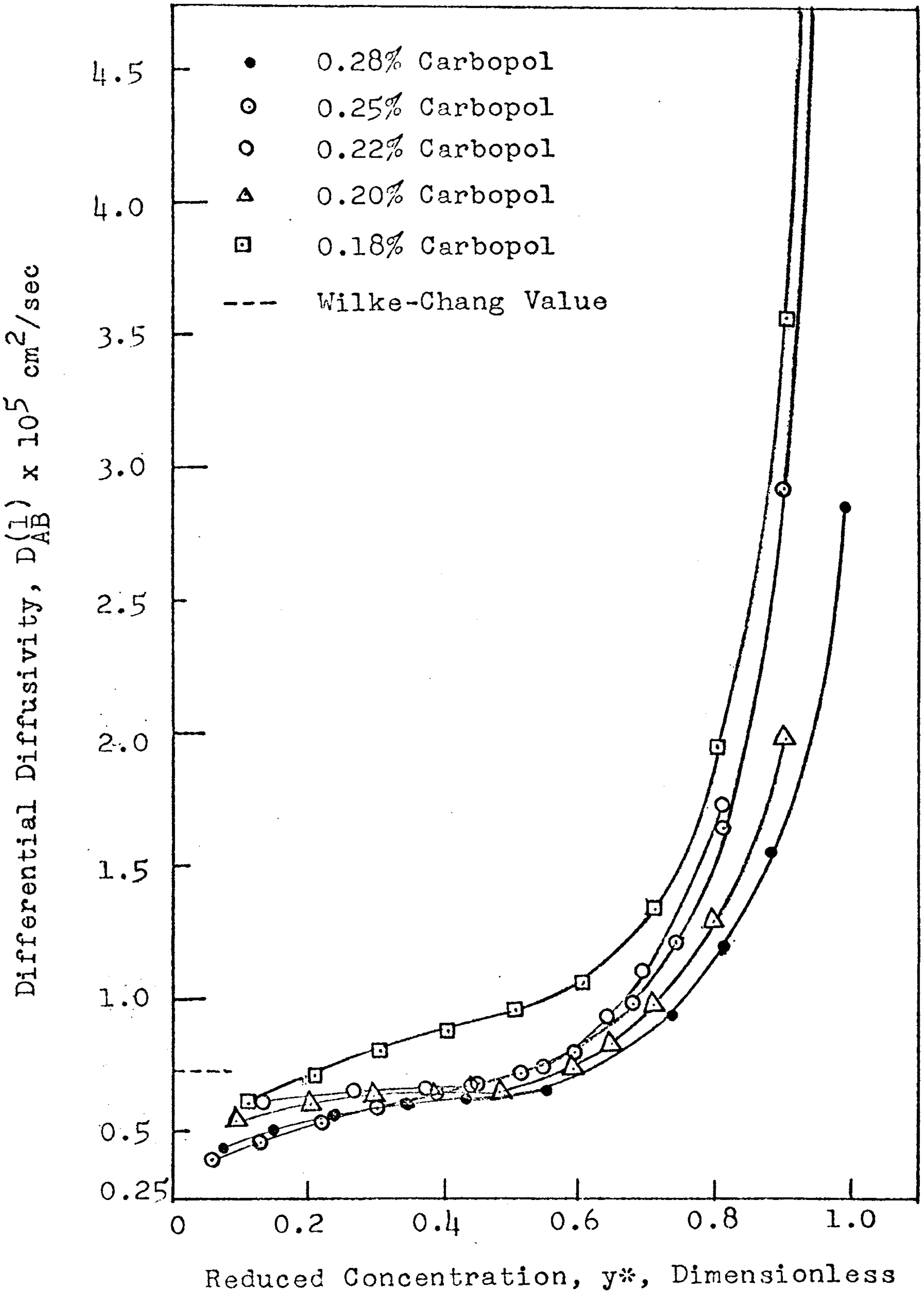

Figure 2. Differential Diffusivity vs. Solute Reduced Concentration for Carbopol-Water System

Table 2

Density of Pure Solvent and the Concentration Dependence of the Solution Density

System Number	ρ_s	A	°C	W_{A1}
1	1.0089	0.3387	23	0.0902
2	1.0070	0.3507	23	0.0903
3	1.0048	0.3328	23	0.0905
4	1.0041	0.3132	23	0.0906
5	1.0029	0.2630	23	0.0907
6	0.9987	0.3790	23	0.0910
7	0.9999	0.3552	21	0.0909
8	0.9991	0.3750	21	0.0910
9	0.9990	0.3573	23	0.0910
10	0.9989	0.3558	23	0.0910

Table 3

Values of the Integrated Average Diffusivity, $\overline{D}_{AB}^{(1)}$ for the System Studied

System Number	Polymer	Solvent	Solute 10 gm/100 cm^3 Solution	$\overline{D}_{AB}^{(1)}$ cm^2/sec$(10)^5$
1	CMC 2.20%	Water	D-Glucose	1.140
2	CMC 2.00%	Water	D-Glucose	1.121
3	CMC 1.70%	Water	D-Glucose	0.969
4	CMC 1.35%	Water	D-Glucose	1.292
5	CMC 1.20%	Water	D-Glucose	1.717
6	Carbopol 0.28%	Water	D-Glucose	0.874
7	Carbopol 0.25%	Water	D-Glucose	1.120
8	Carbopol 0.22%	Water	D-Glucose	0.878
9	Carbopol 0.20%	Water	D-Glucose	0.861
10	Carbopol 0.18%	Water	D-Glucose	1.415

The integral average diffusivities, $\overline{D}$, for the two polymers were given in Table 3. Though the data are somewhat scattered, the integral diffusivities of both D-Glucose-CMC and D-Glucose-Carbopol appear to increase with decreases of polymer concentration.

The diffusion coefficient of D-Glucose in pure water at 23°C calculated using the Wilke-Chang (18) equation (for dilute Newtonian solutions) was found to be $0.71(10)^{-5}$ cm^2/sec, while at 21°C it was $0.67(10)^{-5} cm^2/sec$. These predictions may be compared with the experimental values (at the lowest value solute concentration for each system). The percentage deviation of the Wilke-Chang prediction from the experimental value ranged from -39.2% to 52.2% (the respective experimental diffusivities were $1.18(10)^{-5}$ cm^2/sec and $0.439(10)^{-5} cm^2/sec$). For very low solute concentrations and low polymer concentrations, the Wilke-Chang equation may be used for only approximate estimations of the diffusivity.

Clough _et al_ (3) have suggested a semi-theoretical equation for predicting the diffusivity of a solute in non-Newtonian solutions.

$$D_{NN}/D = X_{cp} (\xi/\xi_{cp})(\mu/\mu_{cp}) \tag{9}$$

Ree and Eyring (14) show that the average of ξ is about 6.0 in non-polar, organic fluids, and the best available average value of ξ is 15.5 in aqueous systems. Therefore, ξ / ξ_{cp} equal to 15.5/6.0 was used in this work for comparisons with experimental data. Though the ratio μ/μ_{cp} in the work of Clough et al may be established by means of direct rheological measurements, the rheological measurements for these ten systems were not performed in this study. Clough et al studied β-napthol diffusing through a 1% aqueous solution of sodium carboxymethylcellulose. None of ten systems in this work was exactly the same as those studied by Clough. However, system 5 (D-Glucose diffusing through a 1.2% aqueous solution of CMC) is relatively similar to the 1% CMC system used by Clough et al. Therefore, as an approximation Clough's value of $\mu_{cp}=3.0$ centipoise for a 1.0% CMC system was used here. If one assumes solvation to triple the effective volume of a CMC molecule in solution (3), X_{cp} would be equal to 0.97. The Wilke-Chang (18) value of the diffusivity (in pure water) was calculated to be $0.71(10)^{-5}cm^2/sec$ and was used as the diffusivity of Newtonian fluid, D. Then D_{NN} for system 5 using equation (9) is predicted to be $0.547(10)^{-5}cm^2/sec$. The lowest experimental value of the diffusivity for this system (at the solute concentration of 0.84 gm/100 cc solution) is $1.18(10)^{-5}cm^2/sec$. The percentage deviation of the Clough et al predicted value from this experimental value is -53.7%. The percentage deviation of the Wilke-Chang predicted value from this experimental value is

-39.8%. Thus, for this one particular system, the Wilke-Chang relation seemed to be slightly more accurate than the relation of Clough *et al* (3).

6. Nomenclature

A = concentration dependence of the solution density
a, b, c = constants in Gompertz equation
D = molecular diffusion coefficient of a solute, cm^2/sec
G = coordinate, corresponds to distance after the changing of the scale
p = original interface at x axis, cm
t = time measured from the beginning of the experiment, seconds
x = coordinate, corresponds to distance cm
Y = concentration of solute, $gm/100\ cm^3$
y = concentration of solute, gm/cm^3
y^* = reduced concentration W_A/W_{A1}
yp = reduced concentration y^* corresponds to p
W = weight fraction of solute, $Y/(Y + \text{wt. of Polymer solution})$
X = the volume fraction of the continuous phase
n = refractive index
$\bar{D}$ = integral (average) diffusion coefficient of a solute, cm^2/sec

Subscripts

A = solute A
B = solvent B
$A1$ = initial weight fraction of solute
AO = solute free weight fraction

NN = diffusivity of a non-Newtonian fluid

cp = properties or parameters of the continuous phase portion of the non-Newtonian fluid

Greek Letters

μ = viscosity of the fluid

ξ = number of neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter

η = Boltzmann transformation, $x/2t^{\frac{1}{2}}$, cm/sec$^{\frac{1}{2}}$

ρ = total mass density (solution density) gm/cm^3

ρ_s = solute-free density, gm/cm^3

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Appendix A

Computer Programs

Program No. 1

Calculation of Reduced Concentration from Concentration of Solute

```
C   A   =WT. OF D-GLUCOSE DURING DIFFUSION
C   B   =WT. OF POLYMER AS SOLVENT
C   AB  =WT. OF SOLUTION DURING DIFFUSION
C   C   =WT. OF D-GLUCOSE AT THE BEGINNING
C   BC  =WT. OF SOLUTION AT THE BEGINNING
C   AAB=WT. FRACTION DURING DIFFUSION
C   CCB=WT. FRACTION AT THE BEGINNING
C   DHO=DENSITY OF WATER
C   WHO=WT. OF WATER 25ML
C   WPO=WT. OF POLYMER 25ML
      DIMENSION A(30),AB(30),AAB(30),RC(30),X(30),Z(30)
      READ(1,100)KK
      DO 10 IK=1,KK
      WRITE(3,1001)
      WRITE(3,1000)IK
      READ(1,200)C,K
      READ(1,300)DHO,WHO,WPO
      READ(1,400)(A(I),I=1,K)
      READ(I,400)(X(I),I=1,K)
         BO=DHO*WPO/WHO
         B=100.0*DHO*WPO/WHO
         BC=B+C
         CCB=C/BC
      WRITE(3,3001)BO
      WRITE(3,2000)
      WRITE(3,3000)CCB
      DO 20 I=1,K
         AB(I)=A(I)+B
         AAB(I)=A(I)/AB(I)
         RC(I)=AAB(I)/CCB
      WRITE(3,4000)AAB(I),RC(I),X(I)
   20 CONTINUE
   10 CONTINUE
      STOP
```

Continued on next page

```
  100 FORMAT(I5)
  200 FORMAT(F14.4,I10)
  300 FORMAT(3F15.5)
  400 FORMAT(5E14.4)
 1001 FORMAT(1H1)
 1000 FORMAT(4X'SYSTEM NO.',I3)
 2000 FORMAT(/2X'WT. FRACTION OF WA1',4X'WT. FRACTION OF WA',4X'REDUCED
     CCONCENTRATION',8X'X(I)')
 3001 FORMAT(//4X'DENSITY OF THE POLYMER ='F10.4//)
 3000 FORMAT(F18.8)
 4000 FORMAT(/20XF18.8,10XF10.3,14XF10.3)
      END
/DATA
```

kk = number of total systems

k = number of total data points (input) for each system

x = distance from original data.

Program No. 2

Calculation of the Concentration Dependence of Density A

```
C   VS=WT. OF PURE POLYMER
C   WS=WT. OF WATER
C   V =WT. OF POLYMER DURING MIXING
         DIMENSION D(20),A(20),W(20),V(20)
         READ(1,100)KK
         DO 10 IK=1,KK
         READ(1,200)N,VS,WS
         READ(1,300)(V(I),W(I),I=1,N)
         WRITE(3,1000)IK
            DS  =VS/WS
         WRITE(3,2000)DS
         WRITE(3,3000)
            SUM=0.0
         DO 20 I=1,N
            D(I)=V(I)/WS
            A(I)=(D(I)-DS)/(DS*W(I))
         WRITE(3,4000)D(I),W(I),A(I)
            SUM=SUM+A(I)
      20 CONTINUE
            AA=SUM/N
         WRITE(3,5000)AA
            SUM1=0.0
            SUM2=0.0
         DO 30 I=1,N
            DF=(AA-A(I))*100.0
            DV=DF/AA
            SUM1=SUM1+(ABS(DF))
            SUM2=SUM2+(ABS(DV))
         WRITE(3,6000)DF,DV
      30 CONTINUE
            DEV1=SUM1/N
            DEV2=SUM2/N
         WRITE(3,6000)DEV1,DEV2
      10 CONTINUE
         STOP
```

Continued on next page

```
  100 FORMAT(I5)
  200 FORMAT(I5,2F18.8)
  300 FORMAT(2E18.8)
 1000 FORMAT(1H1,2X'SYSTEM NO.='I3)
 2000 FORMAT(//10X'SP. WT. OF PURE SOLVENT ='F18.8)
 3000 FORMAT(4X'SP. WT.',10X'WT. FT.',10X'A(I)')
 4000 FORMAT(3E18.8)
 5000 FORMAT(/4X'AVERAGE CONSTANT A ='E18.8)
 6000 FORMAT(/2E18.8)
      END
/DATA
```

kk = number of total systems

A = the concentration dependence of density

W = weight fraction

Program No. 3

Least-Square Curve Fit of Gompertz Equations, for Equal Intervals of the Independent Variable (Method of Davis)

```
      DIMENSION X(30),Y(30),S(3),G(30),YC(30)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)N
      READ(1,109)(X(I),Y(I),I=1,N)
         S(1)=0.0
         S(2)=0.0
         S(3)=0.0
      DO 1 I=1,N
    1    G(I)=X(I)/0.005-1.0
         SUM=0.0
         K=N/3
         L=1
         K1=K
      DO 10 J=1,3
      DO 11 I=L,K
   11    S(J)=S(J)+ALOG(Y(I))
         L=K+1
   10    K=K+K1
         P=N/3
         P=1./P
         CN=(S(2)-S(3))/(S(1)-S(2))
         C=CN**P
         AL=(S(1)-((S(1)-S(2))/(1.-CN)))*P
         AL=EXP(AL)
         BL=(S(1)-S(2))*(1.-C)/((1.-CN)**2)
         BL=EXP(BL)
         SR=0.0
      WRITE(3,103)AL,BL,C
      WRITE(3,105)
      WRITE(3,104)
      DO 12 I=1,N
```

Continued on next page

```
            YC(I)=AL*(BL**(C**G(I)))
            D=YC(I)-Y(I)
            DV=(D/Y(I))*100.0
            SUM=SUM+(ABS(DV))
            SR=SR+(D**2)
         WRITE(3,107)X(I),Y(I),YC(I),D,DV
      12 CONTINUE
         WRITE(3,105)
         WRITE(3,106)SR
            E=N
            DEV=SUM/E
         WRITE(3,105)
         WRITE(3,108)DEV
     900 CONTINUE
         STOP
     101 FORMAT(I5)
     102 FORMAT(4F18.8)
     103 FORMAT(4X,2HA=,F18.8,4X2HB=,E18.8,4X2HC=,E18.8)
     104 FORMAT(9X4HX(I),14X4HY(I),12X8HY(I)CALC,12X4HDIFF,12X8HPER DEVI)
     105 FORMAT(///)
     106 FORMAT(25H SUM OF RESIDUAL SQUARE =,E18.8)
     107 FORMAT(5F18.8)
     108 FORMAT(25H ABS. AVE. PERCENT DEVI.=,E18.8)
     109 FORMAT(2F18.8)
     901 FORMAT(1H1)
     902 FORMAT(1X10HSYSTEM NO.,I3)
     903 FORMAT(//)
     904 FORMAT(/)
     905 FORMAT(I5)
         END
   /DATA
```

kk = number of total system
N = number of total data points for each system
X = distance in cm
Y = reduced concentration

AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c

Program No. 4

Non-Linear, Iterative Least Squares Curve Fit to the Data of Gompertz Equations

```
C   N = 3
C   N9= NUMBER OF DATA POINTS
C   N = NUMBER OF PARAMETERS
        DIMENSION A(30,30),D(30,30),E(30),C(1,30),X(30),Y(30),YHEAD(30)
        DIMENSION AA(30,30),G(30),P(30),PP(30),PD(30)
        READ(1,102)KK
        DO 999 NKI=1,KK
        WRITE(3,2000)
        READ(1,100)N9,N
            M=N+1
        WRITE(3,202)NKI
        READ(1,103)A1,A2,A3
        READ(1,101)(G(I),Y(I),I=1,N9)
        WRITE(3,201)A1,A2,A3
            ABC=1
        DO 31 I=1,N9
   31       X(I)=G(I)/0.005-1.0
        GO TO 226
   99   DO 90 I=1,N
        DO 90 J=1,M
   90       A(I,J)=0
        DO 10 I=1,N9
        DO 10 K=1,N
        DO 10 J=1,M
            X(I)=G(I)/0.005-1.0
            P(I)=A1*A2**A3**X(I)
            AA(1,I)=P(I)/A1
            AA(2,I)=((A3**X(I))*P(I))/A2
            AA(3,I)=(X(I)*A3**(X(I)-1.0))*P(I)*ALOG(A2)
            AA(4,I)=Y(I)-P(I)
            A (K,J)=A(K,J)+AA(J,I)*AA(K,I)
   10   CONTINUE
        WRITE(3,1000)((A(I,J),J=1,M),I=1,N)
        DO 11 I=1,N
        DO 11 J=1,M
   11       D(I,J)=A(I,J)
```

continued on next page

```
      DO 60 I=1,N
         K1=I
      IF(I-N)52,39,39
 52      N2=0
         NK=N-K1+1
         TEST=0
      DO 12 I1=K1,N
      IF(D(I1,I))13,14,13
 13      TEST=TEST-ABS(D(I1,I))
      IF(TEST)15,12,12
 15      TEST=ABS(D(I1,I))
         IPR=I1
      GO TO 12
 14      N2=N2+1
      IF(N2-NK)12,16,16
 16   WRITE(3,200)
      GO TO 999
 12   CONTINUE
      DO 51 K2=K1,M
         C(1,K2)=D(IPR,K2)
         D(IPR,K2)=D(I,K2)
 51      D(I,K2)=C(1,K2)
 39      DII=D(I,I)
      DO 40 K3=K1,M
 40      D(I,K3)=D(I,K3)/DII
      DO 60 J1=1,N
         DJ1I=D(J1,I)
      IF(J1-I)30,60,30
 30   DO 62 K4=K1,M
 62      D(J1,K4)=D(J1,K4)-DJ1I*D(I,K4)
 60   CONTINUE
      DO 19 I=1,N
         SUM=0
      DO 20 J=1,N
 20      SUM=SUM+A(I,J)*D(J,M)
 19      E(I)=A(I,M)-SUM
      WRITE(3,207)
      WRITE(3,208)(E(I),I=1,N)
         A1=A1+D(1,M)
         A2=A2+D(2,M)
         A3=A3+D(3,M)
      WRITE(3,201)A1,A2,A3
         ABC=2
         DEVI=DEV
```

continued on next page

```
  226     SUM=0
          SR=0.0
       DO 66 I=1,N9
          YHEAD(I)=A1*A2**A3**X(I)
          PP(I)=(YHEAD(I)-Y(I))/Y(I)
          PD(I)=(YHEAD(I)-Y(I))/Y(I)*100.
          SR=SR+(PP(I)**2)
   66     SUM=SUM+ABS(PD(I))
       WRITE(3,205)SR
          DEV=SUM/N9
       WRITE(3,206)DEV
       IF(ABC-1)990,99,990
  990     DDEV=DEV-DEVI
       IF(ABS(DDEV/DEV)-5.E-3)98,98,99
   98  WRITE(3,203)
       WRITE(3,204)(YHEAD(I),Y(I),PD(I),I=1,N9)
  999  CONTINUE
       STOP
  100  FORMAT(2I10)
  101  FORMAT(2E18.8)
  102  FORMAT(I5)
  103  FORMAT(3F18.8)
  200  FORMAT(//15X,'SINGULAR MATRIX')
  201  FORMAT(//4X'A1='F18.8,4X'A2='F18.8,4X'A3='F18.8)
  202  FORMAT(/9X,'SYSTEM NO.',I3)
  203  FORMAT(///9X,'CALCULATED VALUES OF Y(I)',15X,'Y(I)',18X,'PD(I)')
  204  FORMAT(10XE18.8,15XE18.8,8XE18.8)
  205  FORMAT(///4X'SUM OF RESIDUAL SQUARE =',E18.8)
  206  FORMAT(///4X'ABS. AVE. PERCENT DEVI.=',E18.8)
  207  FORMAT(4X'E(I)')
  208  FORMAT(4XF18.8)
 1000  FORMAT(/4E18.8)
 2000  FORMAT(1H1)
       END

  /DATA
```

kk = number of total systems
A1 = constant of Gompertz equation a
A2 = constant of Gompertz equation b
A3 = constant of Gompertz equation c
G = distance in cm (original data)
Y = reduced concentration

Program No. 5

Reduced Concentration Gradient as a Function of Distance

```
C     DV=DY/DX
      DIMENSION X(15),DV(15),Y(15),G(15)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,102)K
      READ (1,101)AL,BL,CL
      WRITE(3,101)AL,BL,CL
      READ(1,109)(G(I),Y(I),I=1,K)
      DO 10 I=1,K
         X(I)=G(I)/0.005-1.0
         DV(I)=1./0.005*(AL*BL**CL**X(I)*ALOG(BL)*CL**X(I)*ALOG(CL))
      WRITE(3,200)G(I),DV(I)
   10 CONTINUE
  900 CONTINUE
      STOP
  101 FORMAT(3E18.8)
  102 FORMAT(I10)
  109 FORMAT(2E18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
  200 FORMAT(2E18.8)
      END

/DATA
```

kk = number of total systems
k = number of total data points for each system
AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c
G = distance in cm
Y = reduced concentration

Program No. 6a

Locating the Original Interface Considering Volume Changes

```
   DIMENSION YA(50),YB(50),XA(50),XB(50),GGA(50),GGB(50),GA(50),GB(50
  0)
   READ(1,905)KK
   DO 900 IJK=1,KK
   WRITE(3,901)
   WRITE(3,902)IJK
   WRITE(3,903)
   WRITE(3,904)
   READ(1,100)A,B,P,N
   WRITE(3,100)A,B,P,N
   READ(1,101)AL,BL,CL
   WRITE(3.101)AL,BL.CL
   READ(1,106)AO,WO
   WRITE(3,106)AO,WO
   WRITE(3,102)
        DP=0.00005
        BY=AL*(BL**(CL**(B/0.005-1.0)))
        BBY=BY*P
        F=N-1
        M=F/2.0+1.0
        DA=(B-A)/F
        DAY=(BY-A)/F
        X=A
        Y=A
        YA(1)=A
        GA(1)=BBY
   DO 10 I=2,N
        X=X+DA
        Y=Y+DAY
        YA(I)=AL*(BL**(CL**(X/0.005-1.0)))
        XA(I)=(ALOG((ALOG(Y)-ALOG(AL))/ALOG(BL)))/ALOG(CL)
        GGA(I)=0.005*(XA(I)+1.0)
        GA(I)=BBY-GGA(I)*Y
10 CONTINUE
        S1=0.0
        S2=0.0
        S1Y=0.0
```

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```
        S2Y=0.0
        MA=N-1
     DO 20 I=2,MA,2
        S1=S1+YA(I)
        S1Y=S1Y+GA(I)
  20 CONTINUE
        MB=N-2
     DO 21 I=3,MB,2
        S2=S2+YA(I)
        S2Y=S2Y+GA(I)
  21 CONTINUE
        SIM=(YA(1)+YA(N)+4.0*S1+2.0*S2)*DA/3.0
        SIMY=(GA(1)+GA(N)+4.0*S1Y+2.0*S2Y)*DAY/3.0
        A1=SIM+SIMY*2.0*A0*W0
  15    DP=(P-A)/(F/2.0)
        PY=A1*(BL**(CL**(P/0.005-1.0)))
        DPY=(PY-A)/(F/2.0)
        PPY=PY*P
        X=A
        Y=A
        YB(1)=A
        GB(1)=PPY
     DO 11 I=2,M
        X=X+DP
        Y=Y+DPY
        YB(I)=AL*(BL**(CL**(X/0.005-1.0)))
        YB(I)=(ALOG((ALOG(Y)-ALOG(AL))/ALOG(BL)))/ALOG(CL)
        GGB(I)=0.005*(YB(I)+1.0)
        GB(I)=PPY-GGB(I)*Y
   11 CONTINUE
        S1=0.0
        S2=0.0
        S1Y=0.0
        S2Y=0.0
        MA=M-1
     DO 22 I=2,MA,2
        S1=S1+YB(I)
        S1Y=S1Y+GB(I)
   22 CONTINUE
        MB=M-2
     DO 23 I=3,MB,2
        S2=S2+YB(I)
        S2Y=S2Y+GB(I)
   23 CONTINUE
        SIM=(YB(1)+YB(M)+4.0*S1+2.0*S2)*DB/3.0
```

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```
          SIMY=(GP(1)+GP(M)+4.0*S1Y+2.0*S2Y)*DBY/3.0
          A2=SIM+SIMY*2.0*AO*WO
          A3=(R-P)*YA(N)+(RBY-DBY)*2.0*AO*WO*YA(N)-(A1-A2)
          D=A2-A3
          DV=(A2-A3)/A2
          PD=DV*100.0
      WRITE(3,103)A1,A2,A3,D,PD,P
      IF(ABS(DV)-8.0E-03)6,6,7
    7 IF(A2-A3)12,6,14
   12     P=P+DP
      WRITE(3,105)P
      GO TO 15
   14     P=P-DP
      WRITE(3,105)P
      GO TO 15
    6 WRITE(3,104)
      WRITE(3,102)
      WRITE(3,103)A1,A2,A3,D,PD,P
          YP=AL*BL**CL**(P/0.005-1.0)
      WRITE(3,107)YP
  900 CONTINUE
      STOP
  100 FORMAT(3F18.8,I18)
  101 FORMAT(4F18.8)
  102 FORMAT(11X,2HA1,15X,2HA2,15X,2HA3,13X,5HA2-A3,11X,5HP.DEV,16X,1HP)
  103 FORMAT(6F17.8)
  104 FORMAT(///)
  105 FORMAT(5X,2HP=,F18.8)
  106 FORMAT(2F18.8)
  107 FORMAT(/4X'YP='F18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END

/DATA
```

kk = number of total systems
A = lower bound of distance
B = upper bound of distance
P = estimated interface from distance-reduced concentration plot
N = any odd number
AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c
AO = concentration dependence of density
WO = initial weight fraction W_{A1}

Problem No. 6b

Locating the Original Interface Neglecting Volume Changes

```
      DIMENSION YA(50),YB(50)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,100)A,B,P,N
      WRITE(3,100)A,B,P,N
      READ(1,101)AL,BL,CL
      WRITE(3,101)AL,BL,CL
      WRITE(3,102)
           DP=0.00005
           F=N-1
           M=F/2.0+1.0
           DA=(B-A)/F
           X=A
      DO 10 I=1,N
           YA(I)=AL*(BL**(CL**(X/0.005-1.0)))
           X=X+DA
   10 CONTINUE
           S1=0.0
           S2=0.0
           MA=N-1
      DO 20 I=2,MA,2
           S1=S1+YA(I)
   20 CONTINUE
           MB=N-2
      DO 21 I=3,MB,2
           S2=S2+YA(I)
   21 CONTINUE
           SIM=(YA(1)+YA(N)+4.0*S1+2.0*S2)*DA/3.0
           A1=SIM
   15      DB=(P-A)/(F/2.0)
           X=A
      DO 11 I=1,M
           YB(I)=AL*(BL**(CL**(X/0.005-1.0)))
```

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```
      X=X+DB
   11 CONTINUE
      S1=0.0
      S2=0.0
      MA=M-1
   DO 22 I=2,MA,2
      S1=S1+YB(I)
   22 CONTINUE
      MB=M-2
   DO 23 I=3,MB,2
      S2=S2+YB(I)
   23 CONTINUE
      SIM=(YB(1)+YB(M)+4.0*S1+2.0*S2)*DB/3.0
      A2=SIM
      A3=(B-P)*YA(N)-(A1-A2)
      D=A2-A3
      DV=(A2-A3)/A2
      PD=DV*100.0
   WRITE(3,103)A1,A2,A3,D,PD,P
   IF(ABS(DV)-8.0E-03)6,6,7
 7 IF(A2-A3)12,6,14
12    P=P+DP
   WRITE(3,105)P
   GO TO 15
14    P=P-DP
   WRITE(3,105)P
   GO TO 15
 6 WRITE(3,104)
   WRITE(3,102)
   WRITE(3,103)A1,A2,A3,D,PD,P
      YP=AL*BL**CL**(P/0.005-1.0)
   WRITE(3,106)YP
900 CONTINUE
    STOP
100 FORMAT(2F18.8,I18)
101 FORMAT(3F18.8)
102 FORMAT(11X,2HA1,15X,2HA2,15X,2HA3,13X,5HA2-A3,11X,5HP.DEV,16X,1HP)
103 FORMAT(6F17.8)
104 FORMAT(///)
105 FORMAT(5X,2HP=,F18.8)
106 FORMAT(/4X'YP='F18.8)
```

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```
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END

/DATA
```

kk = number of total systems
A = lower bound of distance
B = upper bound of distance
P = estimated interface from distance-reduced concentration plot
N = any odd number
AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c

Problem No. 7a

Evaluation of Integral: $\int f(y^*)dy^*$

```
      DIMENSION X(700),Y(700),GD(70),YD(70),G(700),GG(700)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)A1,A2,A3
      READ(1,101)A,B,P
      READ(1,103)N,K,L,NT
         F=N
      READ(1,104)(GD(I).YD(I),I=1,NT)
         JJ=1
         YP=A1*A2**A3**(P/0.005-1.0)
      DO 10 I=1.K
      GO TO (30,31),JJ
30       M=I*N
      GO TO 32
31       M=(I*N)+1
         JJ=JJ-2
      GO TO 32
32       G(1)=P-A
         MA=M-1
         MB=M-2
         AM=MA
         Y(M)=YD(I)
         Y(1)=P
         DY=(Y(M)-Y(1))/(AM)
         S1=0.0
         S2=0.0
      DO 11 J=1.MA
         Y(J+1)=Y(J)+DY
         X(J+1)=(ALOG((ALOG(Y(J+1))-ALOG(A1))/ALOG(A2)))/ALOG(A3)
         GG(J+1)=0.005*(X(J+1)+1.0)
         G(J+1)=P-0.005*(X(J+1)+1.0)
 11   CONTINUE
      DO 12 J=2.MA,2
```

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```
          S1=S1+G(J)
   12 CONTINUE
      DO  13  J=3,MB,2
          S2=S2+G(J)
   13 CONTINUE
          SIM=(G(1)+G(M)+4.0*S1+2.0*S2)*DY/3.0
      WRITE(3,102)GG(M),Y(M),SIM,I
          JJ=JJ+1
   10 CONTINUE
          AA2=SIM
          JJ=1
      DO  20  I=1,L
      GO  TO  (40,41),JJ
   40     M=I*N
      GO  TO  42
   41     M=(I*N)+1
          JJ=JJ-2
   42     G(1)=P-P
          MA=M-1
          MB=M-2
          AM=MA
          KJ=K+I
      IF(KJ-NT)24,24,900
   24     Y(M)=YD(KJ)
          Y(1)=YP
          DY=(Y(M)-Y(1))/(AM)
          S1=0.0
          S2=0.0
      DO  21  J=1,MA
          Y(J+1)=Y(J)+DY
          X(J+1)=(ALOG((ALOG(Y(J+1))-ALOG(A1))/ALOG(A2)))/ALOG(A3)
          GG(J+1)=0.005*(X(J+1)+1.0)
          G(J+1)=0.005*(X(J+1)+1.0)-P
   21 CONTINUE
      DO  22  J=2,MA,2
          S1=S1+G(J)
   22 CONTINUE
      DO  23  J=3,MB,2
          S2=S2+G(J)
   23 CONTINUE
          SIM=(G(1)+G(M)+4.0*S1+2.0*S2)*DY/3.0
```

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```
          SIM=SIM+AA2
      WRITE(3,102)GG(M),Y(M),SIM,I
          JJ=JJ+1
   20 CONTINUE
  900 CONTINUE
      STOP
  101 FORMAT(3F18.8)
  102 FORMAT(3F18.8,I18)
  103 FORMAT(4I10)
  104 FORMAT(2F18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END

/DATA
```

kk = number of total systems
A1 = constant of Gompertz equation a
A2 = constant of Gompertz equation b
A3 = constant of Gompertz equation c
A = lower bound of distance
B = lower bound of reduced concentration
P = original interface
N = any odd number
K = number of data points before P add 1
L = number of data points after P
NT = K + L
GD = distance in cm
YD = reduced concentration

Program No. 7b

Evaluation of Integral: $\int f(y^*)y^*dy^*$

```
      DIMENSION X(700),Y(700),GD(70),YD(70),G(700),GY(700)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)A1,A2,A3
      READ(1,101)A,B,P
      READ(1,103)N,K,L,NT
         F=N
      READ(1,104)(GD(I),YD(I),I=1,NT)
         JJ=1
         YP=A1*A2**A3**(P/0.005-1.0)
      DO 10 I=1,K
      GO TO (30,31),JJ
30       M=I*N
      GO TO 32
31       M=(I*N)+1
         JJ=JJ-2
      GO TO 32
32       G(1)=A
         Y(1)=B
         GY(1)=P*YP-G(1)*Y(1)
         MA=M-1
         MP=M-2
         AM=MA
         Y(M)=YD(I)
         DY=(Y(M)-Y(1))/(AM)
         S1=0.0
         S2=0.0
      DO 11 J=1,MA
         Y(J+1)=Y(J)+DY
         X(J+1)=(ALOG((ALOG(Y(J+1))-ALOG(A1))/ALOG(A2)))/ALOG(A3)
         G(J+1)= 0.005*(X(J+1)+1.0)
         GY(J+1)=P*YP-G(J+1)*Y(J+1)
```

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```
 11  CONTINUE
     DO 12 J=2,MA,2
         S1=S1+GY(J)
 12  CONTINUE
     DO 13 J=3,MB,2
         S2=S2+GY(J)
 13  CONTINUE
         SIM=((GY(1)+GY(M)+4.0*S1+2.0*S2)*DY)/3.0
     WRITE(3,102)GY(M),Y(M),SIM,I
         JJ=JJ+1
 10  CONTINUE
         AA2=SIM
         JJ=1
     DO 20 I=1,L
     GO TO (40,41),JJ
 40      M=I*N
     GO TO 42
 41      M=(I*N)+1
         JJ=JJ-2
 42      G(1)=P
         Y(1)=YP
         GY(1)=G(1)*Y(1)-P*YP
         MA=M-1
         MB=M-2
         AM=MA
         KJ=K+I
      IF(KJ-NT)24,24,900
 24      Y(M)=YD(KJ)
         DY=(Y(M)-Y(1))/(AM)
         S1=0.0
         S2=0.0
     DO 21 J=1,MA
         Y(J+1)=Y(J)+DY
         X(J+1)=(ALOG((ALOG(Y(J+1))-ALOG(A1))/ALOG(A2)))/ALOG(A3)
         G(J+1)= 0.005*(X(J+1)+1.0)
         GY(J+1)=G(J+1)*Y(J+1)-P*YP
 21  CONTINUE
     DO 22 J=2,MA,2
         S1=S1+GY(J)
```

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```
   22 CONTINUE
      DO 23 J=3,M3,2
         S2=S2+GY(J)
   23 CONTINUE
         SIM=(GY(1)+GY(M)+4.0*S1+2.0*S2)*DY/3.0
         SIM=SIM+AA2
      WRITE(3,102)GY(M),Y(M),SIM,I
         JJ=JJ+1
   20 CONTINUE
  900 CONTINUE
      STOP
  101 FORMAT(3F18.8)
  102 FORMAT(3F18.8,I10)
  103 FORMAT(4I10)
  104 FORMAT(2F18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END

 /DATA
```

kk = number of total systems
A1 = constant of Gomperta equation a
A2 = constant of Gompertz equation b
A3 = constant of Gompertz equation c
A = lower bound of distance
B = lower bound of reduced concentration
P = original interface
N = any odd number
K = number of data points before P add 1
L = number of data points after P
NT = K + L
GD = distance in cm
YD = reduced concentration

Program No. 7c

Evaluation of Integral: $\int xdy$*

```
      DIMENSION X(700),C(700),XD(70),YD(70)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)AL,BL,CL
      READ(1,101)A,B,R
      READ(1,103)N,K,L,NT
        E=N
      READ(1,104)(XD(I),YD(I),I=1,NT)
        JJ=1
      DO 10 I=1,K
      GO TO (30,31),JJ
 30     M=I*N
      GO TO 32
 31     M=(I*N)+1
        JJ=JJ-2
      GO TO 32
 32     X(1)=A
        C(1)=AL*(BL**(CL**(X(1)/0.005-1.0)))
        MA=M-1
        MB=M-2
        AM=MA
        X(M)=YD(I)
        DX=(X(M)-X(1))/(AM)
        S1=0.0
        S2=0.0
      DO 11 J=1,MA
        X(J+1)=X(J)+DX
        C(J+1)=AL*(BL**(CL**(X(J+1)/0.005-1.0)))
 11   CONTINUE
      DO 12 J=2,MA,2
```

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```
          S1=S1+C(J)
   12  CONTINUE
       DO 13 J=3,MB,2
          S2=S2+C(J)
   13  CONTINUE
          SIM=(C(1)+C(M)+4.0*S1+2.0*S2)*DX/3.0
          SIM=SIM+C(M)*(P-X(M))
       WRITE(3,102)X(M),C(M),SIM,I
          JJ=JJ+1
   10  CONTINUE
          A2=SIM
          JJ=1
       DO 20 I=1,L
       GO TO (40,41),JJ
   40     M=I*N
       GO TO 42
   41     M=(I*N)+1
          JJ=JJ-2
   42     X(1)=P
          C(1)=AL*(BL**(CL**(X(1)/0.005-1.0)))
          MA=M-1
          MB=M-2
          AM=MA
          KJ=K+I
       IF(KJ-NT)24,24,900
   24     X(M)=XD(KJ)
          DX=(X(M)-X(1))/(AM)
          S1=0.0
          S2=0.0
       DO 21 J=1,MA
          X(J+1)=X(J)+DX
          C(J+1)=AL*(BL**(CL**(X(J+1)/0.005-1.0)))
   21  CONTINUE
       DO 22 J=2,MA,2
          S1=S1+C(J)
   22  CONTINUE
       DO 23 J=3,MB,2
          S2=S2+C(J)
   23  CONTINUE
          SIM=(C(1)+C(M)+4.0*S1+2.0*S2)*DX/3.0
          SIM=C(M)*(X(M)-P)-SIM
          SIM=SIM+A2
       WRITE(3,102)X(M),C(M),SIM,I
```

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```
          JJ=JJ+1
   20  CONTINUE
  900  CONTINUE
       STOP
  101  FORMAT(3F18.8)
  102  FORMAT(3F18.8,I18)
  103  FORMAT(4I10)
  104  FORMAT(2F18.8)
  901  FORMAT(1H1)
  902  FORMAT(1X10HSYSTEM NO.,I3)
  903  FORMAT(//)
  904  FORMAT(/)
  905  FORMAT(I5)
       END
```

```
/DATA
```

kk = number of total systems
AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c
A = lower bound of distance
B = upper bound of distance
P = original interface
N = any odd number
K = number of data points before P add 1
L = number of data points after P
NT = K + L
XD = distance in cm
YD = reduced concentration (or concentration)
AL = constant of Gompertz equation a
BL = constant of Gompertz equation b
CL = constant of Gompertz equation c

Program No. 8a

Calculation of the Diffusivity as a Function of Reduced Concentration for Systems with Volume Change

```
C        A= CONCENTRATION DEPENDENCE OF DENSITY
C        W= WEIGHT FRACTION
C        C= REDUCED CONCENTRATION
C        T= TIME IN SEC.
C        FI= INTERGAL OF XDC
C        TI= INTERGAL OF XCDC
C        DT= DC/DX
C        NN= NUMBER OF DATA POINT
C        WF= WEIGHT FRACTION
C        Y = CONCENTRATION GM/100CC SOLUTION
      DIMENSION FI(20),TI(20),DT(20),C(20),X(20),CT2(20),RA(20),RB(20)
      DIMENSION RC(200),D(20),WF(20),Y(20)
      READ(1,100)KK
      DO 10 IJK=1,KK
      WRITE(3,1000)IJK
      READ(1,200)NN
      READ(1,300)A,W,T
      READ(1,400)(X(K),C(K),K=1,NN)
      READ(1,400)(FI(K),TI(K),K=1,NN)
      READ(1,500)(DT(K),K=1,NN)
      READ(1,600)(WF(K),K=1,NN)
      READ(1,600)(Y(K),K=1,NN)
      WRITE(3,3000)T
        CT1=A*W
      DO 20 K=1,NN
        CT2(K)=CT1*C(K)
        RA(K)=(1-CT2(K))*FI(K)
        RB(K)=2*CT1*TI(K)
        RC(K)=2*T*(1+CT2(K))*DT(K)
        D(K)=(RA(K)+RB(K))/RC(K)
        D(K)=D(K)*10.**5
      WRITE(3,2000)X(K),Y(K),WF(K),C(K),FI(K),TI(K),DT(K),D(K)
   20 CONTINUE
```

Continued on next page

```
   10 CONTINUE
      STOP
  100 FORMAT(I5)
  200 FORMAT(I10)
  300 FORMAT(3F18.8)
  400 FORMAT(2F18.8)
  500 FORMAT(F18.8)
  600 FORMAT(4F18.8)
 1000 FORMAT(1H1,4X,'SYSTEM NO.'I5)
 2000 FORMAT(///4X,4F7.3,2F8.4,2F7.3)
 3000 FORMAT(/4X,'TIME  T ='F5.1)
      END

/DATA
```

kk = number of total systems
NN = number of total data points for each system
X = distance in cm
C = reduced concentration
W = initial weight fraction W_{Al}
WF = weight fraction during diffusion
D = diffusivity

Program No. 8b

Calculation of the Diffusivity as a Function of Reduced Concentration for Systems without Volume Change

```
      DIMENSION X(30),C(30),EN(30),ED(30),DC(30),R(30)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      READ(1,100)N,T
      WRITE(3,200)T
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)(X(I),C(I),I=1,N)
      READ(1,102)(EN(I),I=1,N)
      READ(1,102)(ED(I),I=1,N)
      DO 10 I=1,N
         DC(I)=(EN(I)/(2.0*T*ED(I)))
         ED(I)=ED(I)/100.0
         DC(I)=DC(I)*(10.0**5)
      WRITE(3,203)X(I),C(I),EN(I),ED(I),DC(I)
      WRITE(3,904)
   10 CONTINUE
  900 CONTINUE
      STOP
  100 FORMAT(I10,F10.1)
  101 FORMAT(2F18.8)
  102 FORMAT(F18.8)
  200 FORMAT(5X8HTIME T =,F5.1)
  203 FORMAT(5X,F10.3,F11.3,F9.3,2F10.3)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
/DATA
```

kk = number of total systems
T = time in seconds
N = number of total data points for each system
X = distance in cm
C = reduced concentration (or concentration)
EN = integral of $\int x dy^*$ or $\int f(y^*) dy^*$ (or $\int x dy$)
ED = derivative dy^*/dx (or dy/dx)
DC = diffusivity

Appendix B

Data and Results

Table B.1

Polymeric Systems Used for the Study

System Number	Polymer	Solvent	Polymer Concent. Wt.%	Solute	Initial Solute Conc. gm/100 cc Soln.
1	CMC	Water	2.20%	D-Glucose	10.0
2	CMC	Water	2.00%	D-Glucose	10.0
3	CMC	Water	1.70%	D-Glucose	10.0
4	CMC	Water	1.35%	D-Glucose	10.0
5	CMC	Water	1.20%	D-Glucose	10.0
6	Carbopol	Water	0.28%	D-Glucose	10.0
7	Carbopol	Water	0.25%	D-Glucose	10.0
8	Carbopol	Water	0.22%	D-Glucose	10.0
9	Carbopol	Water	0.20%	D-Glucose	10.0
10	Carbopol	Water	0.18%	D-Glucose	10.0

Table B.2

Data and Results for System 1

X cm	Y $\frac{\text{gm solute}}{100\text{cm}^3\text{sol.}}$	W_A	y*	$\int_0^{y^*} f(y^*)\,dy^*$	$\int_0^{y^*} f(y^*)\,y^*\,dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} \times 10^5$ cm^2/sec
0.008	0.947	0.009	0.099	0.0020	0.0012	17.070	0.512
0.014	2.067	0.020	0.230	0.0038	0.0027	25.716	0.627
0.019	3.482	0.033	0.368	0.0048	0.0037	28.803	0.719
0.023	4.664	0.044	0.483	0.0052	0.0042	28.422	0.784
0.028	5.861	0.055	0.619	0.0054	0.0044	25.465	0.902
0.035	7.674	0.071	0.776	0.0065	0.0059	19.374	1.415
0.041	8.606	0.079	0.877	0.0079	0.0077	14.255	2.317
0.052	9.923	0.090	0.992	0.0104	0.0112	7.353	5.902

Time t=12.0 seconds; T=23°C; W_{A1}=0.0902

Concentration dependence of density A=0.3387

Table B.3

Data and Results for System 2

X cm	Y $\frac{\text{gm solute}}{100\text{cm}^3\text{sol.}}$	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)}\times10^5$ cm^2/sec
0.026	0.775	0.008	0.084	0.0045	0.0025	4.887	0.953
0.035	1.233	0.012	0.136	0.0065	0.0039	6.673	0.997
0.050	2.415	0.023	0.258	0.0095	0.0065	9.532	1.020
0.061	3.524	0.034	0.372	0.0108	0.0080	11.163	0.993
0.069	4.395	0.042	0.465	0.0111	0.0083	11.980	0.943
0.074	5.028	0.048	0.526	0.0113	0.0086	12.318	0.934
0.080	5.760	0.054	0.600	0.0120	0.0096	12.552	0.970
0.087	6.667	0.062	0.689	0.0134	0.0117	12.603	1.078
0.094	7.638	0.071	0.776	0.0154	0.0148	12.439	1.255
0.109	9.522	0.086	0.957	0.0215	0.0252	11.529	1.892

Time t=50.0 seconds; T=23°C; W_{A1}=0.0903

Concentration dependence of density A=0.3507

Table B.4

Data and Results for System 3

X cm	Y gm solute / 100cm^{3}sol.	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} \times 10^5$ cm^2/sec
0.017	1.018	0.010	0.112	0.0029	0.0018	12.884	0.572
0.022	1.726	0.017	0.187	0.0041	0.0029	16.800	0.628
0.026	2.423	0.024	0.259	0.0050	0.0037	19.169	0.667
0.030	3.207	0.031	0.339	0.0056	0.0044	20.644	0.698
0.036	4.378	0.042	0.465	0.0060	0.0048	21.159	0.725
0.040	5.271	0.050	0.549	0.0062	0.0050	20.544	0.763
0.046	6.428	0.060	0.667	0.0070	0.0061	18.636	0.947
0.051	7.410	0.069	0.755	0.0081	0.0077	16.538	1.232
0.055	8.026	0.074	0.818	0.0091	0.0092	14.739	1.563
0.064	9.255	0.084	0.932	0.0118	0.0132	10.844	2.742

Time t=20.0 seconds; T=23°C; W_{A1}=0.0905

Concentration dependence of density A=0.3328

Table B.5

Data and Results for System 4

X cm	Y gm solute / $100 cm^3$ sol.	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} x 10^5$ cm^2/sec
0.008	0.825	0.008	0.085	0.0023	0.0013	11.838	0.558
0.017	2.085	0.020	0.229	0.0048	0.0032	19.467	0.704
0.022	3.107	0.030	0.332	0.0059	0.0043	21.501	0.782
0.028	4.381	0.042	0.462	0.0066	0.0050	21.585	0.865
0.032	5.263	0.050	0.547	0.0067	0.0051	20.520	0.919
0.038	6.396	0.060	0.663	0.0072	0.0057	17.921	1.131
0.045	7.599	0.070	0.776	0.0085	0.0073	14.316	1.656
0.052	8.528	0.078	0.864	0.0101	0.0095	10.878	2.585
0.065	9.667	0.088	0.971	0.0130	0.0135	6.017	6.043

Time t=18.0 seconds; T=23°C; W_{A1}=0.0906

Concentration dependence of density A=0.3132

Table B.6

Data and Results for System 5

X cm	Y gm solute / 100cm^{3}sol.	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)}$x10^5 cm^2/sec
0.016	0.840	0.008	0.091	0.0035	0.0019	7.551	1.181
0.026	1.730	0.017	0.186	0.0059	0.0037	11.459	1.306
0.032	2.438	0.024	0.261	0.0071	0.0048	13.404	1.357
0.039	3.340	0.032	0.361	0.0082	0.0059	15.004	1.387
0.045	4.363	0.042	0.453	0.0086	0.0063	15.727	1.380
0.052	5.339	0.051	0.564	0.0089	0.0067	15.845	1.410
0.058	6.352	0.060	0.658	0.0097	0.0078	15.421	1.582
0.063	7.187	0.067	0.734	0.0108	0.0093	14.782	1.835
0.068	7.931	0.073	0.806	0.0122	0.0114	13.955	2.194
0.073	8.636	0.079	0.873	0.0138	0.0139	13.003	2.673
0.081	9.647	0.088	0.971	0.0168	0.0137	11.352	3.729

Time 5=20.0 seconds; T=23°C; W_{A1}=0.0907

Concentration dependence of density A=0.2631

Table B.7

Data and Results for System 6

X cm	Y gm solute / $100 cm^3$ sol.	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} x 10^5$ cm^2/sec
0.011	0.715	0.007	0.077	0.0025	0.0015	9.258	0.468
0.017	1.335	0.013	0.146	0.0041	0.0027	13.410	0.528
0.023	2.198	0.022	0.237	0.0057	0.0040	16.804	0.593
0.029	3.282	0.032	0.345	0.0069	0.0053	18.834	0.631
0.034	4.125	0.040	0.440	0.0075	0.0059	19.377	0.661
0.040	5.268	0.050	0.556	0.0077	0.0061	18.835	0.692
0.047	6.580	0.062	0.682	0.0084	0.0071	17.049	0.834
0.051	7.365	0.069	0.747	0.0092	0.0082	15.707	0.984
0.056	8.092	0.075	0.821	0.0104	0.0099	13.892	1.254
0.061	8.740	0.080	0.886	0.0117	0.0119	12.062	1.633
0.072	9.962	0.091	0.998	0.0149	0.0167	8.424	2.976

Time t=30.0 seconds; T=23°C; W_{A1}=0.0910

Concentration dependence of density A=0.3790

Table B.8

Data and Results for System 7

X cm	Y gm solute / $100 cm^3$ sol.	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} x10^5$ cm^2/sec
0.010	0.734	0.007	0.078	0.0023	0.0014	11.197	0.439
0.015	1.355	0.013	0.146	0.0038	0.0026	15.936	0.508
0.020	2.140	0.021	0.235	0.0052	0.0039	19.516	0.579
0.024	2.994	0.029	0.317	0.0063	0.0049	21.107	0.636
0.028	3.741	0.036	0.403	0.0070	0.0057	21.528	0.691
0.031	4.455	0.043	0.467	0.0073	0.0060	21.173	0.732
0.034	5.111	0.049	0.529	0.0074	0.0062	20.362	0.770
0.038	5.882	0.056	0.608	0.0075	0.0063	18.775	0.847
0.043	6.727	0.063	0.696	0.0081	0.0070	16.338	1.039
0.047	7.367	0.069	0.757	0.0087	0.0079	14.275	1.284
0.052	8.070	0.075	0.822	0.0097	0.0093	11.785	1.728
0.061	9.013	0.083	0.910	0.0116	0.0119	7.967	3.063
0.076	9.970	0.091	0.995	0.0145	0.0159	3.828	7.922

Time t=24.0 seconds; T=21°C; W_{A1}=0.0909

Concentration dependence of density A=0.3552

Table B.9

Data and Results for System 8

X cm	Y gm solute / 100cm^{3}sol	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)}$x10^5 cm^2/sec
0.012	1.217	0.012	0.132	0.0017	0.0010	22.747	0.640
0.017	2.501	0.024	0.269	0.0025	0.0017	31.528	0.687
0.020	3.382	0.033	0.368	0.0027	0.0019	34.151	0.685
0.022	4.290	0.041	0.437	0.0028	0.0020	34.708	0.681
0.025	5.144	0.049	0.541	0.0031	0.0023	33.988	0.765
0.028	6.148	0.058	0.640	0.0036	0.0031	31.844	0.967
0.030	6.786	0.064	0.702	0.0042	0.0038	29.890	1.175
0.034	8.007	0.074	0.812	0.0054	0.0055	25.354	1.801

Time t=6.0 seconds; T=21°C; W_{A1}=0.0910

Concentration dependence of density A=0.3749

Table B.10

Data and Results for System 9

X cm	Y gm solute / $100cm^3$/sol	W_A	y*	$\int_0^{y^*} f(y^*)\,dy^*$	$\int_0^{y^*} f(y^*)\,y^*\,dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)} \times 10^5$ cm^2/sec
0.014	0.870	0.009	0.092	0.0024	0.0013	11.194	0.545
0.022	1.855	0.018	0.207	0.0042	0.0027	17.331	0.618
0.027	2.809	0.027	0.301	0.0050	0.0036	19.909	0.648
0.031	3.717	0.036	0.383	0.0054	0.0040	21.013	0.660
0.036	4.622	0.044	0.489	0.0056	0.0041	21.232	0.666
0.041	5.627	0.053	0.593	0.0060	0.0047	20.384	0.751
0.044	6.273	0.059	0.653	0.0066	0.0054	19.498	0.851
0.047	6.982	0.065	0.710	0.0072	0.0063	18.417	0.992
0.052	7.840	0.073	0.797	0.0086	0.0083	16.356	1.326
0.059	8.905	0.082	0.901	0.0108	0.0116	13.318	2.054

Time t=20.0 seconds; T=23 °C; W_{A1}=0.0910

Concentration dependence of density A=0.3573

Table B.11

Data and Results for System 10

X cm	Y $\frac{\text{gm solute}}{100\text{cm}^3\text{sol}}$	W_A	y*	$\int_0^{y^*} f(y^*)dy^*$	$\int_0^{y^*} f(y^*)y^*dy^*$	dy*/dx cm^{-1}	$D_{AB}^{(1)}\times10^5$ cm^2/sec
0.013	0.970	0.010	0.108	0.0030	0.0020	13.282	0.591
0.019	1.940	0.019	0.203	0.0049	0.0035	18.068	0.695
0.024	2.727	0.027	0.300	0.0062	0.0048	20.408	0.783
0.029	3.883	0.037	0.404	0.0071	0.0058	21.029	0.869
0.034	4.812	0.046	0.508	0.0075	0.0063	20.200	0.950
0.039	5.816	0.055	0.605	0.0077	0.0065	18.390	1.058
0.045	6.863	0.064	0.707	0.0083	0.0074	15.578	1.353
0.052	7.892	0.073	0.804	0.0096	0.0091	12.169	1.990
0.062	8.948	0.082	0.904	0.0117	0.0120	8.000	3.693
0.078	9.931	0.090	0.994	0.0148	0.0162	3.728	9.963

Time t=20.0 seconds; T=23°C; W_{A1}=0.0910

Concentration dependence of density A=0.3558

Table B.12

Values of R_o and R_1 in Equation (8)

System Number	R_o	R_1
1	1.3385	0.00120
2	1.3380	0.00127
3	1.3380	0.00118
4	1.3378	0.00117
5	1.3370	0.00123
6	1.3360	0.00130
7	1.3360	0.00122
8	1.3360	0.00123
9	1.3360	0.00130
10	1.3362	0.00118

Appendix C

Theoretical Equation of Diffusion

Duda and Vrentas (10) based their work on the assumptions of 1) free diffusion, 2) in an isothermal system of N components which do not react with each other, 3) the components involved are neither viscoelastic materials nor the polar materials, 4) $W_I = \rho_I / \rho$, 5) liquid system, 6) one directional motion with all variables changing only in that direction and derived from the equation of continuity and equation of motion the following:

$$v^i_{;i} = (1/\rho^2) \sum_{I=1}^{N-1} (\partial \rho / \partial W_I)_{W_j} (j^i_I)_{,i} \qquad (C.1)$$

where

v^i = ith component of mass average velocity

j^i_I = ith component of mass diffusion flux of component I relative to mass average velocity

W_I = mass fraction of component I.

For binary free diffusion relative to rectangular cartesian coordinate axis, it became

$$(\partial v / \partial x) = -(1/\rho^2)(d\rho / dW_A) \frac{\partial}{\partial x} \left(\rho D \frac{\partial W_A}{\partial x} \right) \qquad (C.2)$$

Equation (C.1), with the boundary conditions for one-dimensional free diffusion,

$$W_A\ (0,\ x) = W_{A0} \qquad x < 0 \qquad (C.3)$$

$$W_A\ (0,\ x) = W_{A1} \qquad x > 0 \qquad (C.4)$$

$$W_A\ (t,\ -\infty) = W_{A0} \qquad (C.5)$$

$$W_A\ (t,\ +\infty) = W_{A1} \qquad (C.6)$$

By applying the famous Boltzmann transformation $\eta = x/2t^{\frac{1}{2}}$ and constraining one of the infinite boundaries to set the velocity there equal to zero, equation (C.2) can be simplified to the form:

$$\rho D(dW_A/d\eta) = -\int_{W_{AO}}^{W_A} 2\rho\eta\, dW_A + \int_{W_{AO}}^{W_A}\int_{\rho_0}^{\rho} 2\eta\, d\rho\, dW_A \qquad (C.7)$$

If W_A is determined as a function of x and t, integration by parts of the double integral transforms equation (C.7) into

$$D = -2(d\eta/dW_A)\Big[\frac{1}{\rho}\int_{W_{AO}}^{W_A}\eta\rho\, dW_A + \frac{1}{\rho}\int_{\rho_0}^{\rho}\eta W_A\, d\rho - (W_A/\rho)\int_{\rho_0}^{\rho}\eta\, d\rho\Big] \qquad (C.8)$$

In the case when there is no volume change during diffusion, equation (C.8) will reduce to the familiar result (10).

$$D = -2\,(d\eta/dW_A)\int_{W_{AO}}^{W_A}\eta\, dW_A \qquad (C.9)$$

Paul (18) pointed out that when the solution density is linear in the weight fraction of the solute

$$\rho = \rho_s(1 + AW_A) \qquad (C.10)$$

$$y^* = W_A/W_{A1} \qquad (C.11)$$

Equation (C.8) will transform to

$$D = -2\,\frac{\Big[(1 - AW_{A1}y^*)\int_0^{y^*}\eta\, dy^* + 2AW_{A1}\int_0^{y^*}\eta\, y^* dy^*\Big]}{(1 + AW_{A1}y^*)(dy^*/d\eta)} \qquad (C.12)$$

Appendix D

Diffusivity Computation Techniques

The reduced concentration, y^*, was defined by Paul (18) as

$$y^* = W_A/W_{A1} \tag{D.1}$$

where

W_A = weight fraction during diffusion

W_{A1} = weight fraction of initial solution on the solute rich side

From data given by Desai (9) in the concentration units (gm solute/100 cm^3 solution), the weight fraction can be obtained as

$$W = \frac{\text{gm solute/100 cm}^3\text{ solution}}{\text{gm solute/100 cm}^3\text{ solution} + (100)(\text{density of polymer solution})}$$

The concentration dependence of density A was calculated from equation (C.10)

$$\rho = \rho_s\,(1 + AW_A)$$

From each known polymer solution density and the corresponding weight fraction, the value A can be obtained. For each system three different pairs -- weight fraction and solution density -- were used to calculate the arithmetic average A.

The curve of reduced concentration vs. distance (i.e., y^* vs. x) is sigmoid (see Figure D.1). The curve is characterized by a very small initial slope followed

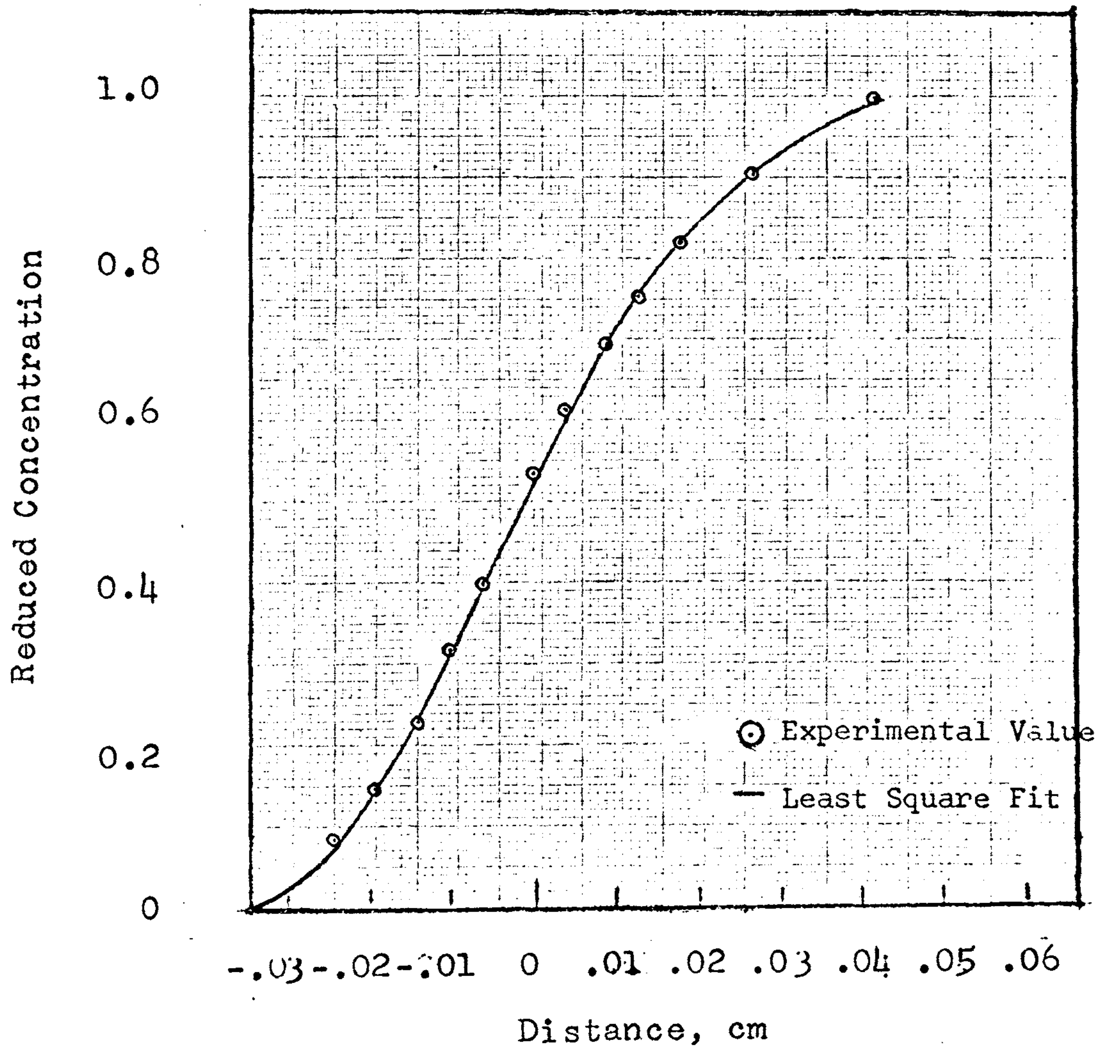


Figure D.1. Experimental Reduced Concentration Profile for 0.25 wt.% Carbopol System.

by a period of rapidly increasing slope which gives way to an interval of nearly constant slope succeeded by a period when the rapidly decreasing slope approaches zero. The Gompertz equation

$$y^* = ab^{c^G} \tag{D.2}$$

where

G is a linear function of x used in order to scale the x variables,

has been found to satisfactorily represent such data (8). Davis' method of determining the constants, a, b, and c, in the Gompertz equation requires that the independent variable be in equal intervals. (The independent variable may be time or distance for instance, and the data may appear as the dates 1890, 1900, 1910, and 1920, or the distance 0.005, 0.010, 0.015, and 0.020 to which are assigned values of G of 0, 1, 2, and 3. See Davis (8).)

In this work, the data were not in equal intervals. From the y* vs. x plot, the equal interval 0.005 cm of x were picked up through the use of a curve which was fitted by "eye". Therefore, following linear relationship between G and x was used:

$$G = (x/0.005) - 1$$

Whenever y* is calculated, the x scale must be changed to the G scale, i.e.

$$y^* = ab^{c^G} \qquad \text{or} \qquad y^* = ab^{c^{(x/0.005 - 1)}}$$

The data are divided into three parts of n entries each. S_1, S_2, and S_3 represent the sums of the three groups of values of log y, starting with the lowest values. The constants a, b, and c can then be evaluated from the equations

$$c = \left[(S_2 - S_3)/(S_1 - S_2)\right]^{1/n} \qquad (D.3)$$

$$\log a = (1/n)(S_1 - \frac{S_1 - S_2}{1 - c^n})$$

and

$$\log b = (S_1 - S_2)(1-c)/(1-c^n)^2 \qquad (D.5)$$

where n equals one-third of the total data points used.

It was found that using the same data, when curves were passed through the data points by "eye", several slightly different curves would be obtained.

In order to eliminate human bias when passing a curve through the y* vs. x data (as is possible in the previous method of Davis), a non-linear least squares method was used. The Gompertz equation is non-linear in the constants a, b, and c. Therefore the Gompertz equation was linearized in terms of the constants, a, b, and c, before the least squares technique was applied. The resulting least square "normal" equations were:

$$\Delta a \sum_{i=1}^{N} (Pi/a_o)^2 + \Delta b \sum_{i=1}^{N} (c_o^{G_i} p_i^2/a_o b_o)$$

$$+ \Delta c \sum_{i=1}^{N} (G_i c_o^{(G_i-1)} p_i^2 \ln(b_o)/a_o = \sum_{i=1}^{N}\left[(P_i/a_o)y^*_i - (P_i^2/a_o)\right]$$

$$\Delta a \sum_{i=1}^{N} (P_i^2 \, C_o^{G_i}/a_o b_o) + \Delta b \sum_{i=1}^{N} (p_i c_o^{G_i}/b_o)^2$$

$$+ \Delta c \sum_{i=1}^{N} (p_i^2 G_i c_o^{G_i} C_o^{(G_i-1)} \ln(b_o)/b_o)$$

$$= \sum_{i=1}^{N} (p_i c_o^{G_i} y_i^*/b_o) - p_i^2 c_o^{G_i}/b_o) \qquad (D.7)$$

$$\Delta a \sum_{i=1}^{N} (p_i^2 G_i c_o^{(G_i-1)} \ln(b_o)/a_o)$$

$$+ \Delta b \sum_{i=1}^{N} (p_i^2 G_i c_o^{(G_i-1)} c_o^{G_i} \ln(b_o)/b_o)$$

$$+ \Delta c \sum_{i=1}^{N} (p_i G_i c_i^{(G_i-1)} \ln(b_o))^2$$

$$= \sum_{i=1}^{N} (p_i G_i c_o^{(G_i-1)} \ln(b_o) y_i^* - p_i^2 G_i c_o^{(G_i-1)} \ln(b_o)) \qquad (D.8)$$

where

$$p_i = a_o b_o^{c_o^{G_i}}$$

$$\Delta a = a - a_o$$

$$\Delta b = b - b_o$$

$$\Delta c = c - c_o$$

a_c, b_o, and c_o (obtained from Davis' method) represent initial estimates of a, b, and c, for Δ a, Δ b, and Δ c. This 3 by 4 matrix was solved by an iterative process to obtain the best values of a. b, and c. The iterative process was terminated when DDEV/DEV $\leqslant$ 5x10^{-3}.

where

$$\mathrm{DEV} = \sum \left| (\hat{y}_i - y_i)/y_i \times 100 \right| / \text{number of data points}$$

and

$$\mathrm{DDEV} = (\mathrm{DEV})_j - (\mathrm{DEV})_{j-1}$$

and j is iteration index.

Dalal (7) and Desai (9) used a modified Gompertz equation $y = \alpha + ab^{c^G}$ instead of $y^* = ab^{c^G}$, where α is intercept of y^*. In these systems, α is nearly zero for all loces. In Desai's analysis, all αs were zero. When the modified Gompertz equation is used, there are four paratmeters α, a, b, and c instead of three a, b, and c. Some αs from the least squares method were negative; but the limits of y^* in this study were from 0 to 1. Therefore, the unmodified Gompertz equation was used here.

In Desai's program No. 2-A: "Experimental Concentration Gradient as a Function of Distance", Desai treated the derivative as

$$dy/dx = (ab^{c^G})(\ln b)\, c^G(\ln c).$$

Actually, it is

$$dy/dx = (dy/dG)(dG/dx) = (1/0.005)(ab^{c^G})$$
$$(\ln b)\, c^G(\ln c)$$

where x is the experimental scale, and G is the changing scale for y value. The unit for dy/dx in this program is gm/100 cm^3/cm. Even using the a, b, and c which Desai obtained from Gompertz equation to calculate dy/dx by his program 2-A, the results are different from the

Table D-1

Constants of Gompertz Equation from Non-Linear Least Squares Method and the Initial Values a_o, b_o, c_o

System Number	a_o	b_o	c_o	$AAPD_o$	a	b	c	AAPD
1	1.1305	0.0509	0.7106	1.4829	1.1006	0.0508	0.6996	1.4741
2	1.5335	0.0083	0.8966	2.5353	1.8039	0.0103	0.9094	0.4613
3	1.1788	0.0162	0.7958	1.1963	1.1840	0.0146	0.7839	0.4899
4	1.0983	0.0482	0.7641	1.6161	1.0878	0.0498	0.7612	0.9621
5	1.3496	0.0195	0.8515	1.7370	1.4295	0.0214	0.8598	0.7094
6	1.1839	0.0263	0.7994	1.5904	1.2122	0.0282	0.8047	0.6252
7	1.0615	0.0314	0.7590	1.1034	1.0677	0.0321	0.7602	0.8460
8	1.8502	0.0214	0.7563	3.5711	1.2137	0.0218	0.6779	1.0257
9	1.2215	0.0185	0.7887	1.5168	1.2353	0.0191	0.7912	1.3758
10	1.0569	0.0279	0.7600	1.1031	1.0658	0.0298	0.7647	1.0266

values he presented in his thesis. The values of dy/dx for comparison for system 9 are given below:

From Desai's Thesis gm/cm^3/cm	Using Desai's Constants & His prog. 2-A gm/100 cm^3/cm	After prog. 2-A Corrected gm/100 cm^3/cm
1.077	0.518	103.155
1.640	0.830	163.596
1.939	0.969	191.410
2.079	1.034	205.186
2.115	1.057	211.437
2.057	1.024	206.989
1.975	0.984	200.274
1.849	0.934	191.302
1.652	0.834	172.989
1.346	0.684	144.250

The results in columns one and three are quite close; but column two differs greatly from columns one and three. Thus it appears that the program 2-A in Desai's thesis is an incorrect earlier version from his work which he included in the thesis instead of the correct program which leads to the results indicated in column one.

Dalal (7) used Davis' method to calculate the derivative dy/dx. Desai (9) also presented this method for comparison (prog. no. 2-B in Desai's thesis).

$$\phi = (x-x_1)/(a+bx) \qquad \text{(D.9)}$$

where x_1 corresponds to $y=-.1$

$$\phi = \log\left[(20y)/\log\,(100-y)\right] \qquad \text{(D.10)}$$

$$dy/dx = (a+bx_1)/(a+bx)^2 S \qquad \text{(D.11)}$$

where

$$S = 0.434\left[(1/y) + 0.4343/((100-y)\log(100-y))\right]$$

The constants, a and b are not the same as from Gompertz equation. For instance consider system 9.

	Davis' method	From Gompertz equation
a	0.0076	16.0439
b	0.3593	0.0142

The derivatives were also different.

Davis' method	This work
107.3252	103.1551
154.9678	163.5955
177.0873	191.4097
190.5045	205.1862
202.4429	211.4372
209.8411	206.9893
212.4551	200.2737
213.9209	191.3021
214.2631	172.9885
211.3698	144.2495

Therefore Davis' method for evaluating the derivative was not considered here.

After the Gompertz equation was obtained from the least squares method, the location of the original interface, i.e., the locus of $x=0$, was obtained. Simpson's numerical method was used to evaluate the areas A_1 and A_2 at a distance $x=p$ as shown in Figure D.2 and Figure D.3. Area A_3 was then evaluated and compared with A_2. If these were unequal, then another value of p was specified, $(p_j=p_{j-1}\pm Dp)$ depending on which area is large or small. This trial and error procedure was followed until the percentage deviation is defined as follows:

$$\text{percentage deviation} = ((A_2-A_3)/A_2)(100)$$

In other words, the absolute value of $(A_2-A_3)/A_2$ should be less than $8(10)^{-3}$ for all the systems at a final value of p. This very closely satisfied the requirement that

$$-\int_0^{y^*} x\,dy^* = \int_{y^*}^{1} x\,dy^* \quad (\text{i.e. } \int_0^{1} x\,dy^* = 0) \qquad (D.12)$$

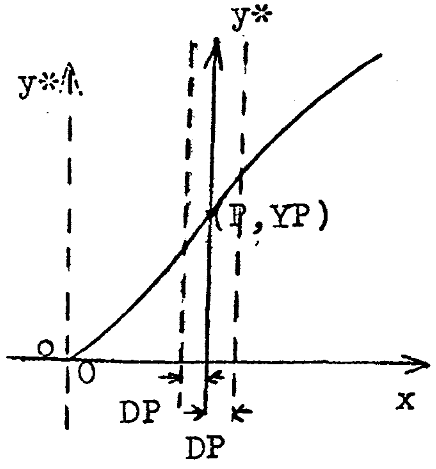
for neglecting volume change during diffusion; and

$$-\int_0^{y^*} x\,dy^* - 2AW_{A1}\int_0^{y^*} xy^*dy^* = \int_{y^*}^{1} x\,dy^* + 2AW_{A1}\int_{y^*}^{1} xy^*dy^*$$

$$(\text{i.e. } \int_0^{1} x\,dy^* + 2AW_{A1}\int_0^{1} xy^*dy^* = 0) \qquad (D.13)$$

for volume change during diffusion. Thus the location of the original interface was obtained.

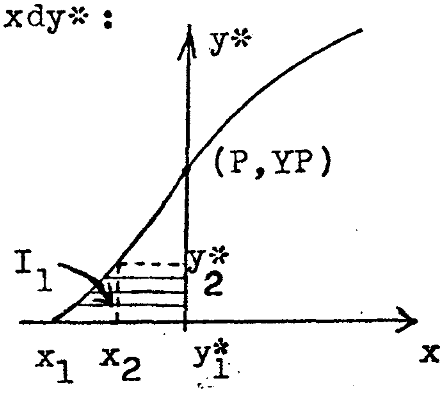
Consider program number 6 for locating the original interface. In this program, N is any odd number, DP is the increment of the iteration. If these two numbers were not suitably used, the satisfactory value of $|(A_2-A_3)/A_2|$, i.e. $|(A_2-A_3)/A_2| \leqslant 8(10)^{-3}$, would not be obtained. In Desai's analysis, DP=0.0002 was small enough; but in this work, only DP=0.00005 satisfied all the systems.



There are two ways to evaluate the integral of $\int x\,dy^*$:

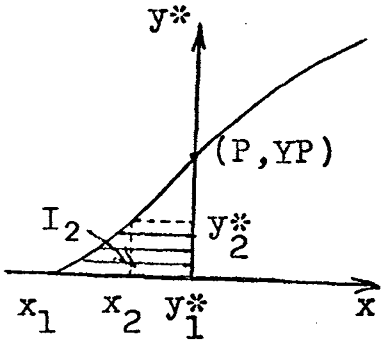
1.

$$I_1 = \int_{y_1^*}^{y_2^*} x\,dy^* = \int_{x_1}^{x_2} x\,dy^* + (p-x_2)(y_2^*-y_1^*)$$



2. x was first changed to a function of y*.

$$x=f(y^*)=0.005\left(\frac{\ln((\ln(y^*)-\ln(a))/\ln(b))}{\ln(c)}+1.0\right) \qquad (D.12)$$



$$I_2=\int_{y_1^*}^{y_2^*} x\,dy^* = \int_{y_1^*}^{y_2^*} f(y^*)\,dy^*$$

The results of system 9 by these two ways are given below:

I_1	I_2
0.00235	0.00235
0.00412	0.00411
0.00496	0.00496
0.00534	0.00533
0.00547	0.00547
0.00598	0.00598
0.00651	0.00651
0.00719	0.00719
0.00857	0.00857
0.01083	0.01083

They are almost the same, as they should be. For evaluating $\int xy^*dy^*$, the I_1 method is not valid. Therefore, for consistency, I_2 method was used to calculate $\int xdy^*$ and $\int xy^*dy^*$ for the final results present in this work.

In Appendix F, five different values of diffusion coefficient are presented. $D_{AB}^{(1)}$ is calculated considering volume change during diffusion with the integration technique of I_2. $D_{AB}^{(2)}$ is calculated for no volume change during diffusion with the integration technique of I_2. $D_{AB}^{(3)}$ is calculated in the same manner as Secor, i.e. the

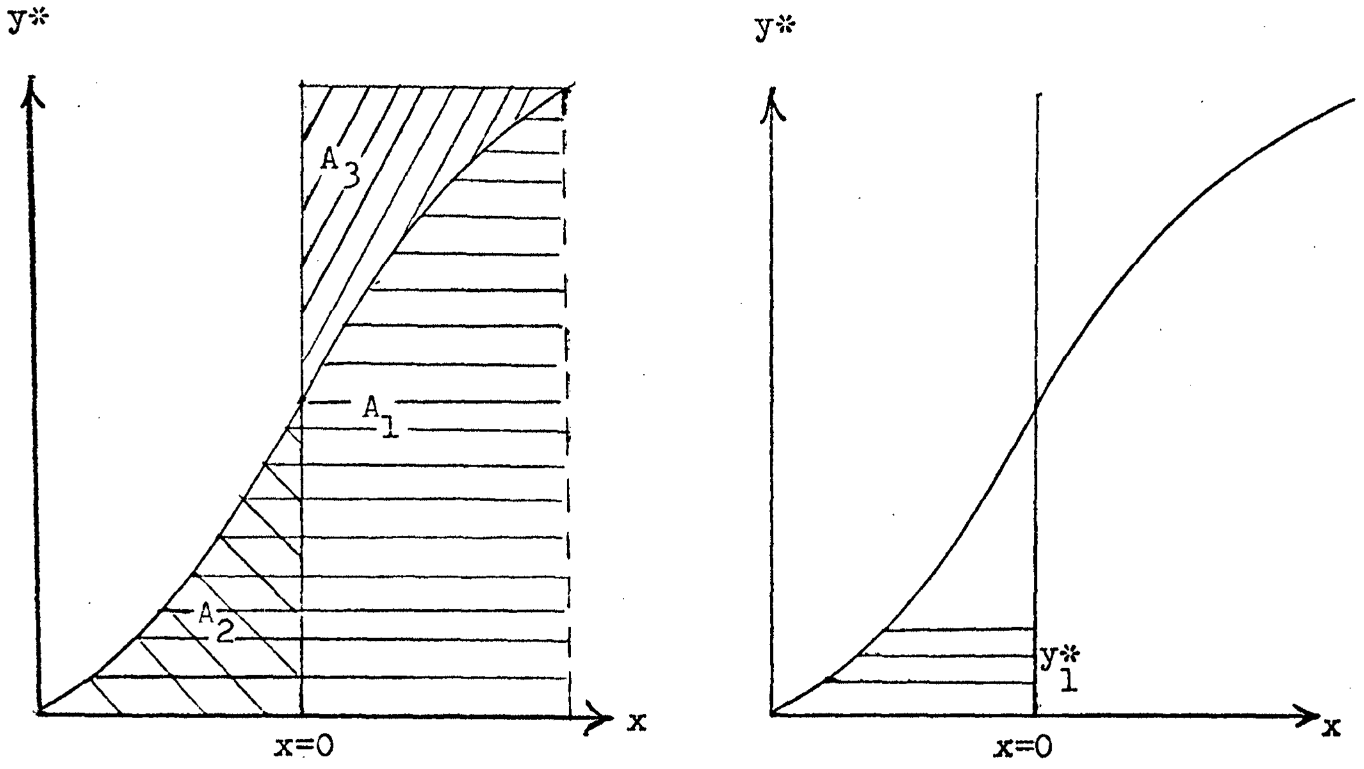
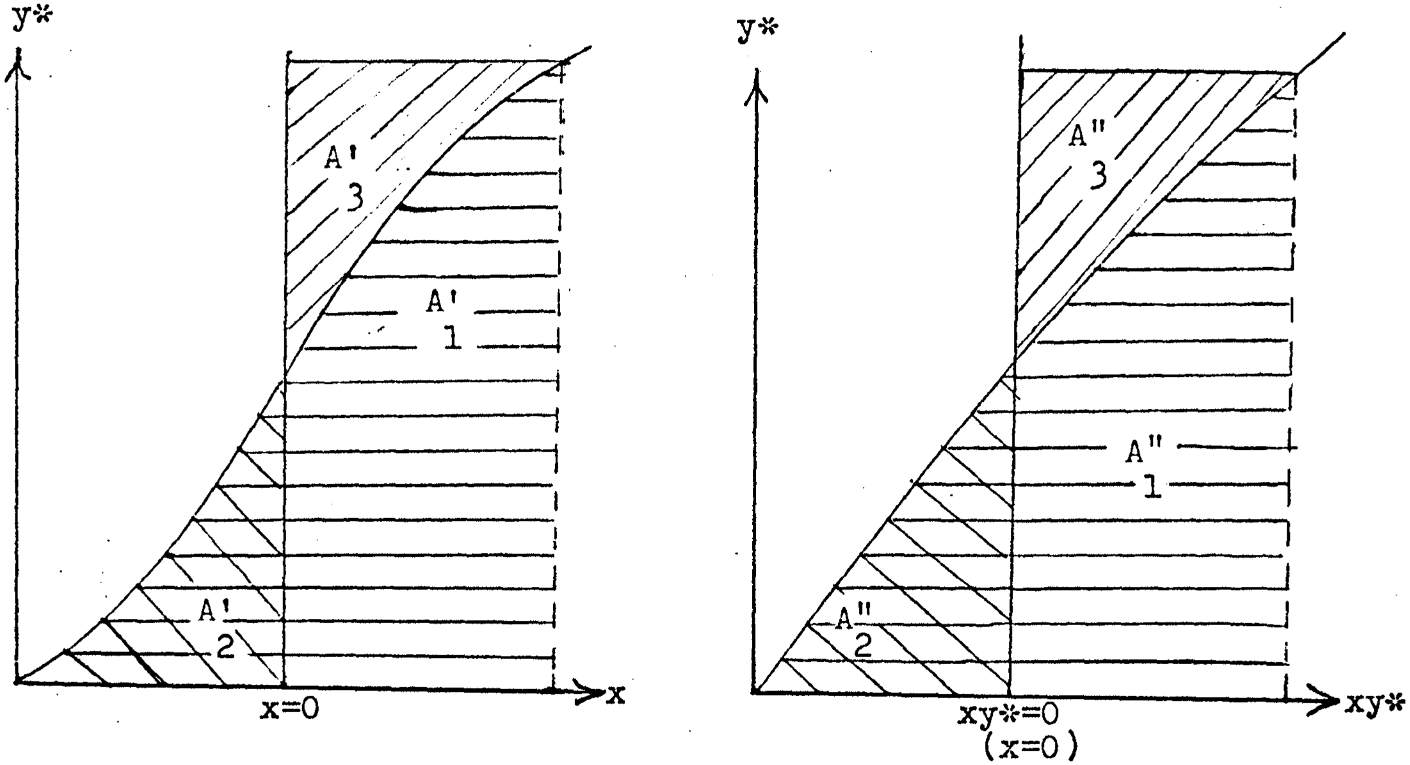


Figure D-2. Evaluation of $\int_0^{y^*} x dy^*$ for $\int_0^1 x dy^* = 0$



(A) (B)

Figure D-3. Evaluation of $\int_0^{y*} x\,dy*$ and $\int_0^{y*} xy*dy*$ for $\int_0^1 x\,dy* + 2AW_{A1}\int_0^1 xy*dy* = 0$; $A_1 = A'_1 + 2AW_{A1}A''_2$, $A_2 = A'_2 + 2AW_{A1}A''_2$, $A_3 = A'_3 + 2AW_{A1}A''_3$

diffusivity is function of the concentration without volume change during diffusion. $D_{AB}^{(4)}$ is calculated for no volume change during diffusion with the integration technique of I_1. $D_{AB}^{(5)}$ considers volume changes during diffusion with the integration technique I_1 for $\int xdy*$ and I_2 for $\int xy*dy*$. The five different values are given in Appendix F.

Appendix E

Figures of Diffusivity (cm^2/sec) Versus Reduced Concentration

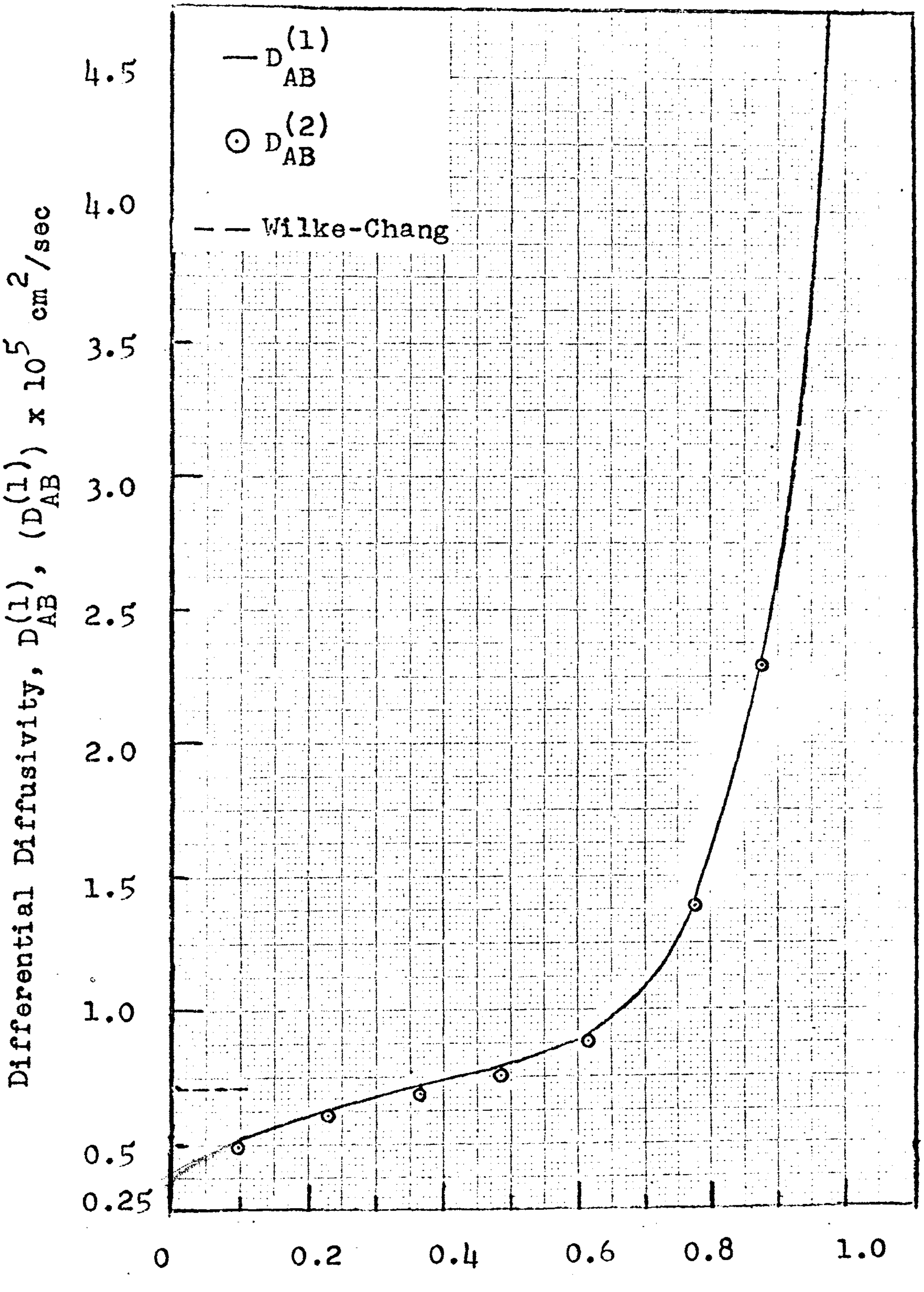


Figure E.1. Differential Diffusivity vs. Reduced Concentration for 2.2 wt.% CMC in Water with D-Glucose as Solute, at 23°C, with t=12 seconds.

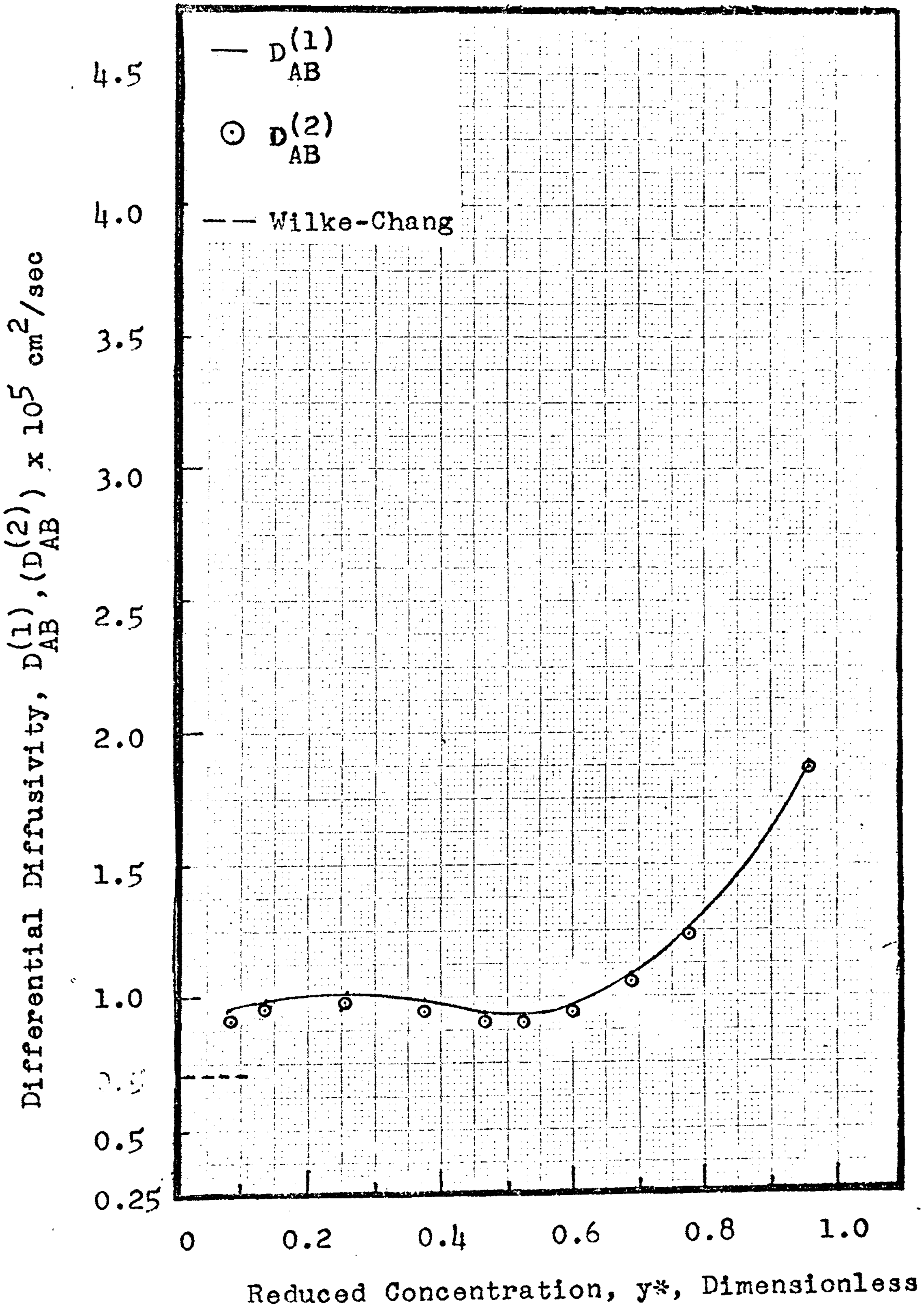


Figure E.2. Differential Diffusivity vs. Reduced Concentration for 2.0 wt.% CMC in Water with D-Glucose as Solute at 23°C, with t=50 seconds.

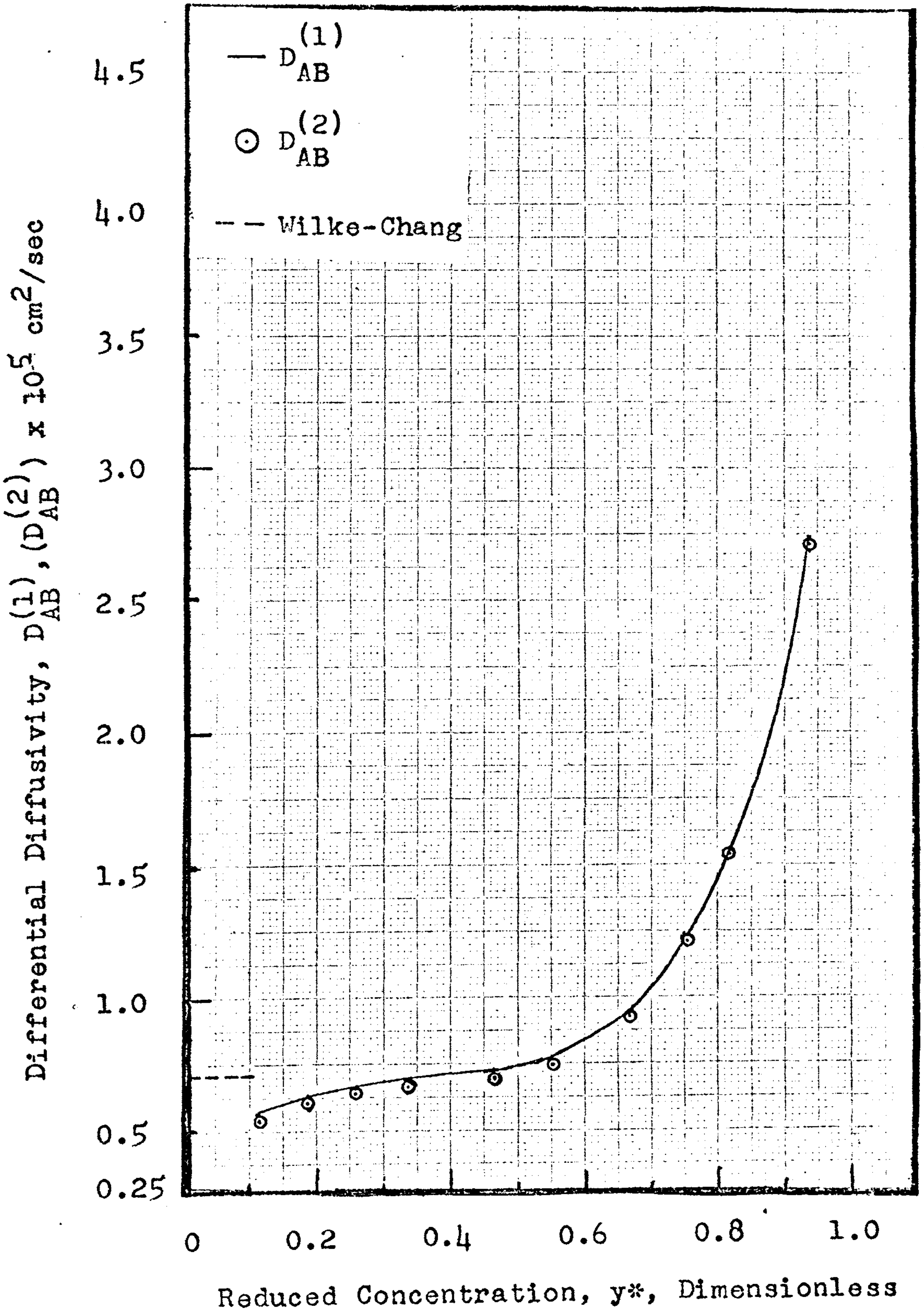


Figure E.3. Differential Diffusivity vs. Reduced Concentration for 1.7 wt.% CMC in Water with D-Glucose as Solute, at 23°C, with t=20 seconds

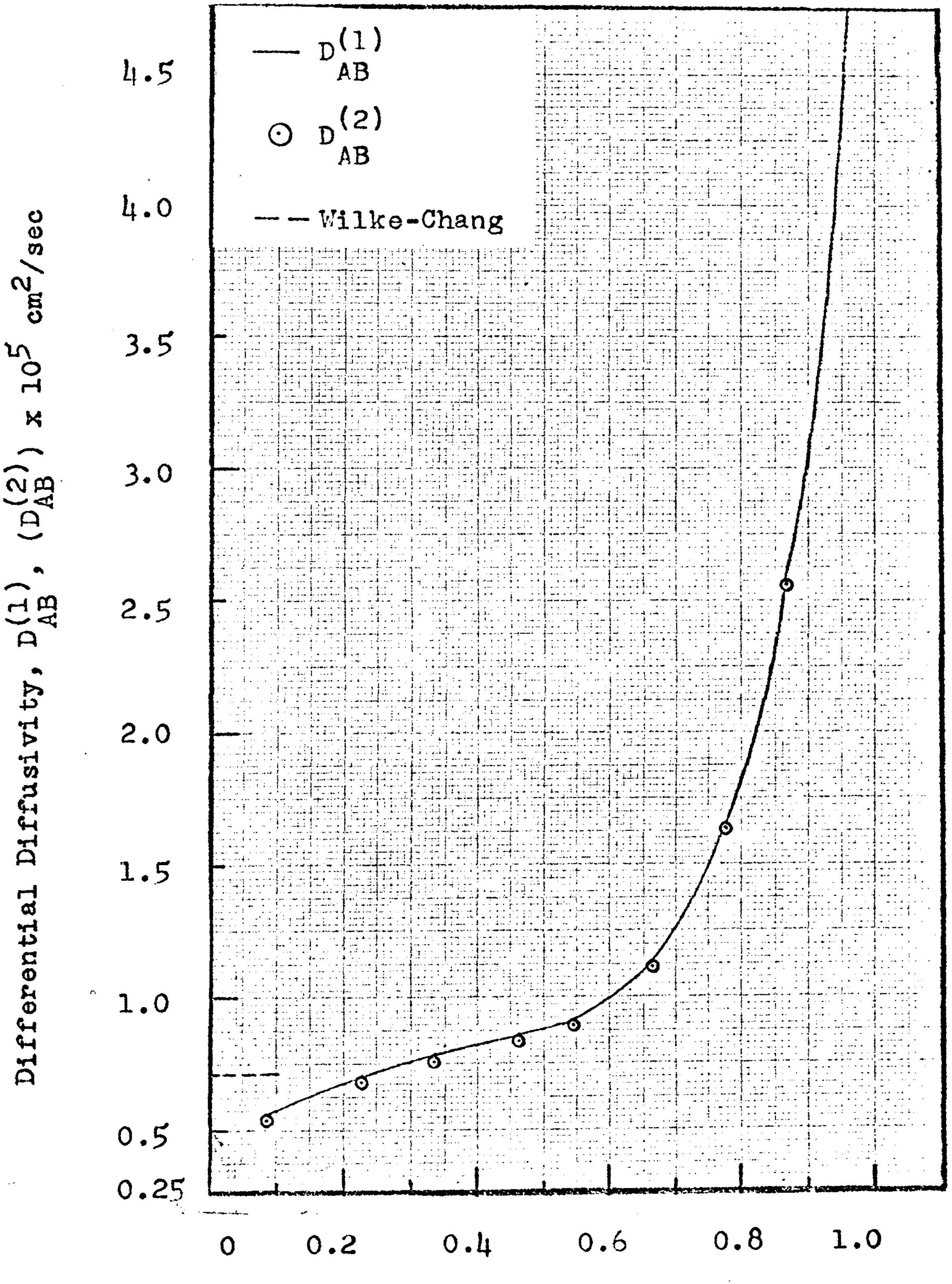


Figure E.4. Differential Diffusivity vs. Reduced Concentration for 1.35 wt.% CMC in Water with D-Glucose as Solute, at 23°C, with t=18 seconds

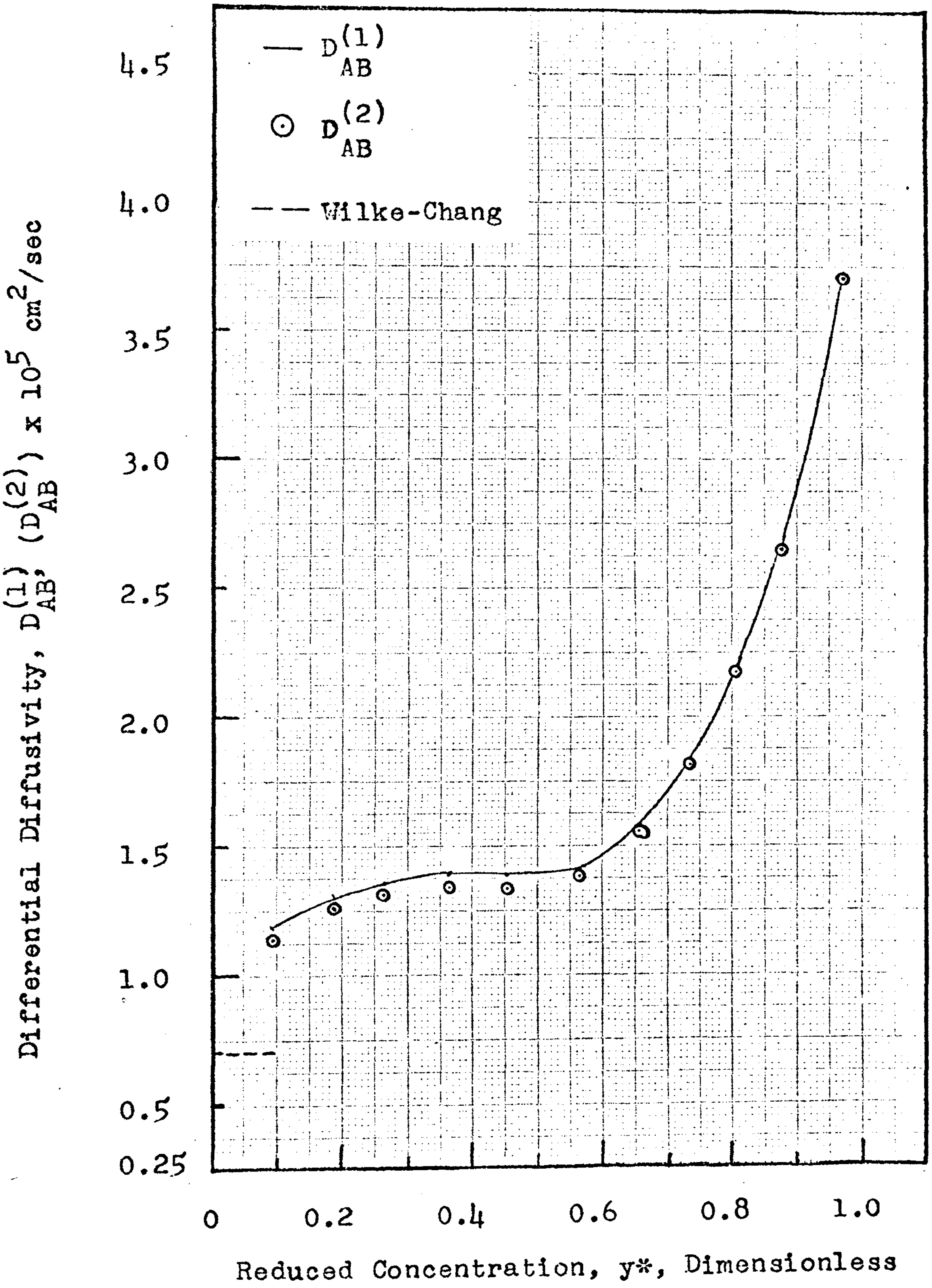


Figure E.5. Differential Diffusivity vs. Reduced Concentration for 1.20 wt.% CMC in Water with D-Glucose as Solute, at 23°C, with t=20 seconds

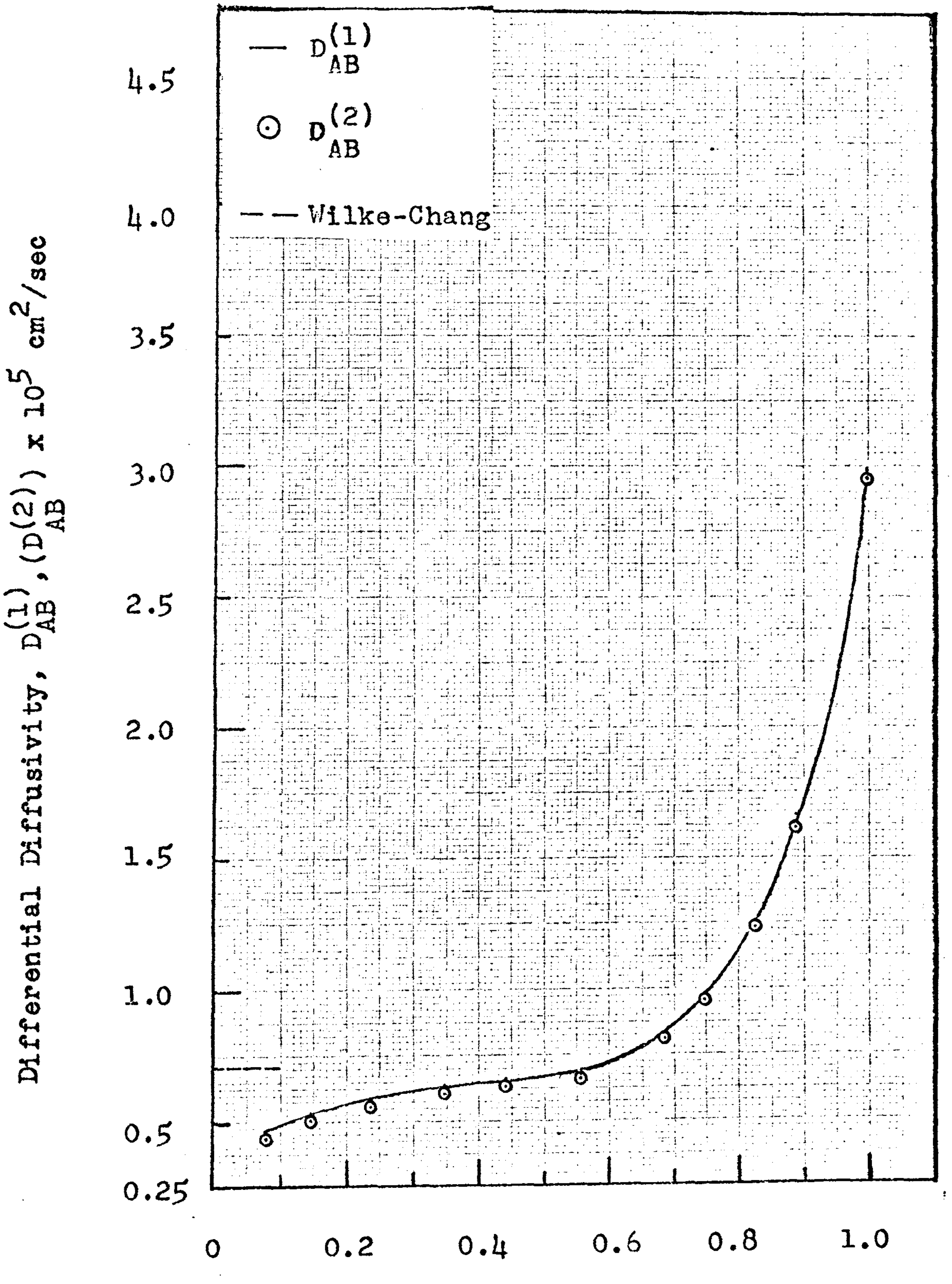


Figure E.6. Differential Diffusivity vs. Reduced Concentration for 0.28 wt.% Carbopol in Water with D-Glucose as Solute, at 23°C, with t=30 seconds

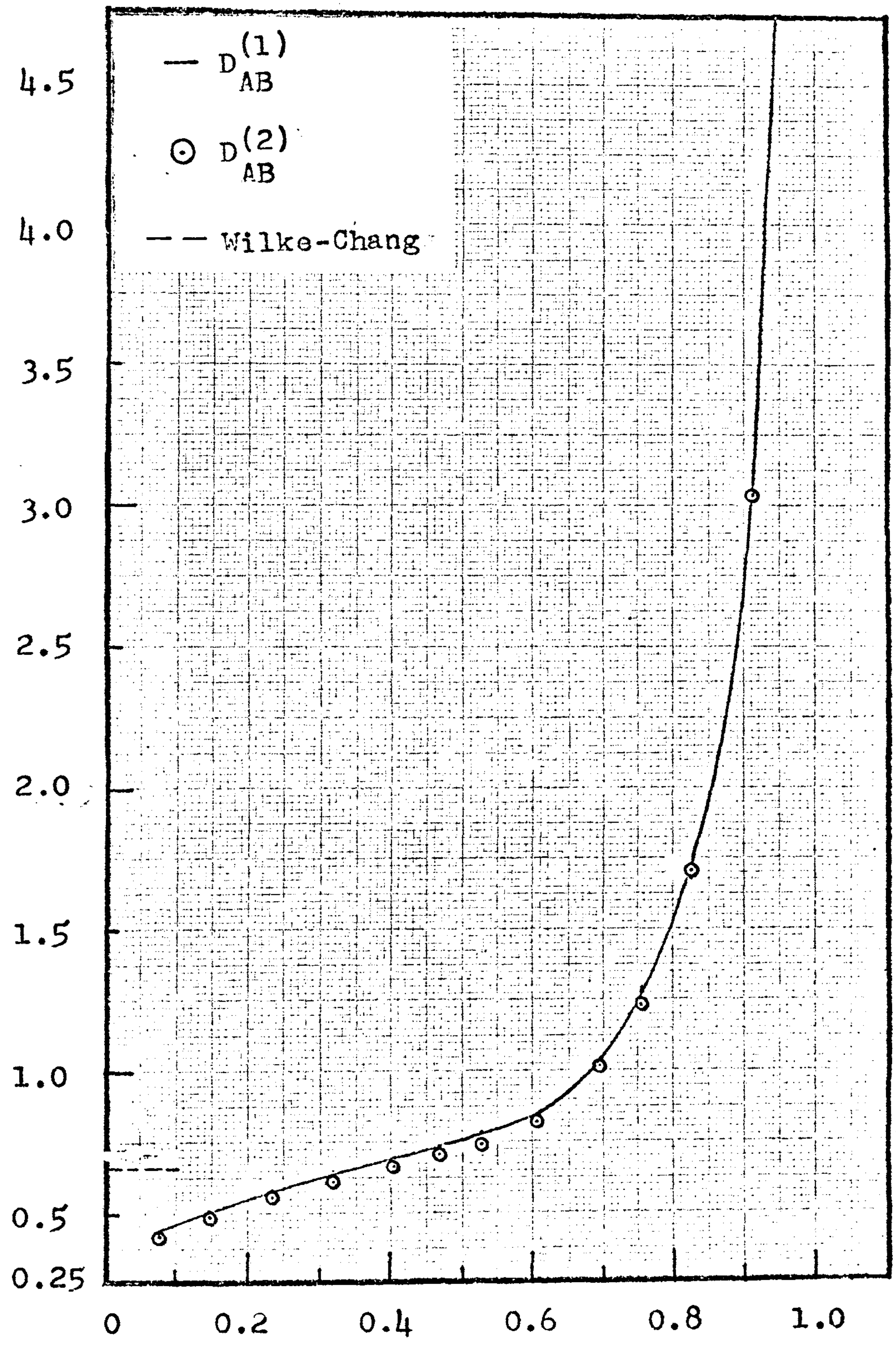


Figure E.7. Differential Diffusivity vs. Reduced Concentration for 0.25 wt.% Carbopol in Water with D-Glucose as Solute, at 21 °C, with t=24 seconds

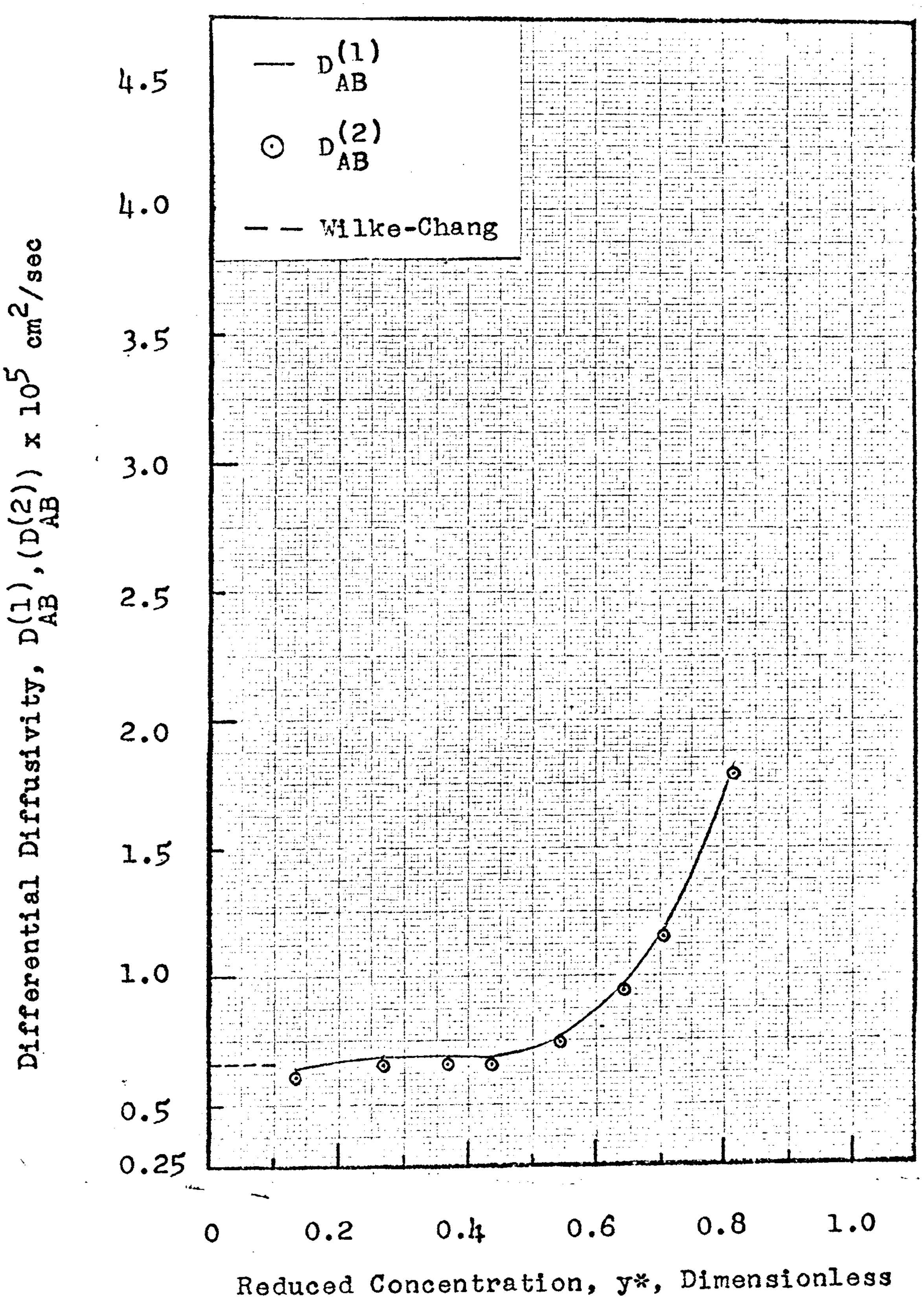


Figure E.8. Differential Diffusivity vs. Reduced Concentration for 0.22 wt.% Carbopol in Water with D-Glucose as Solute, at 21°C, with t=6 seconds

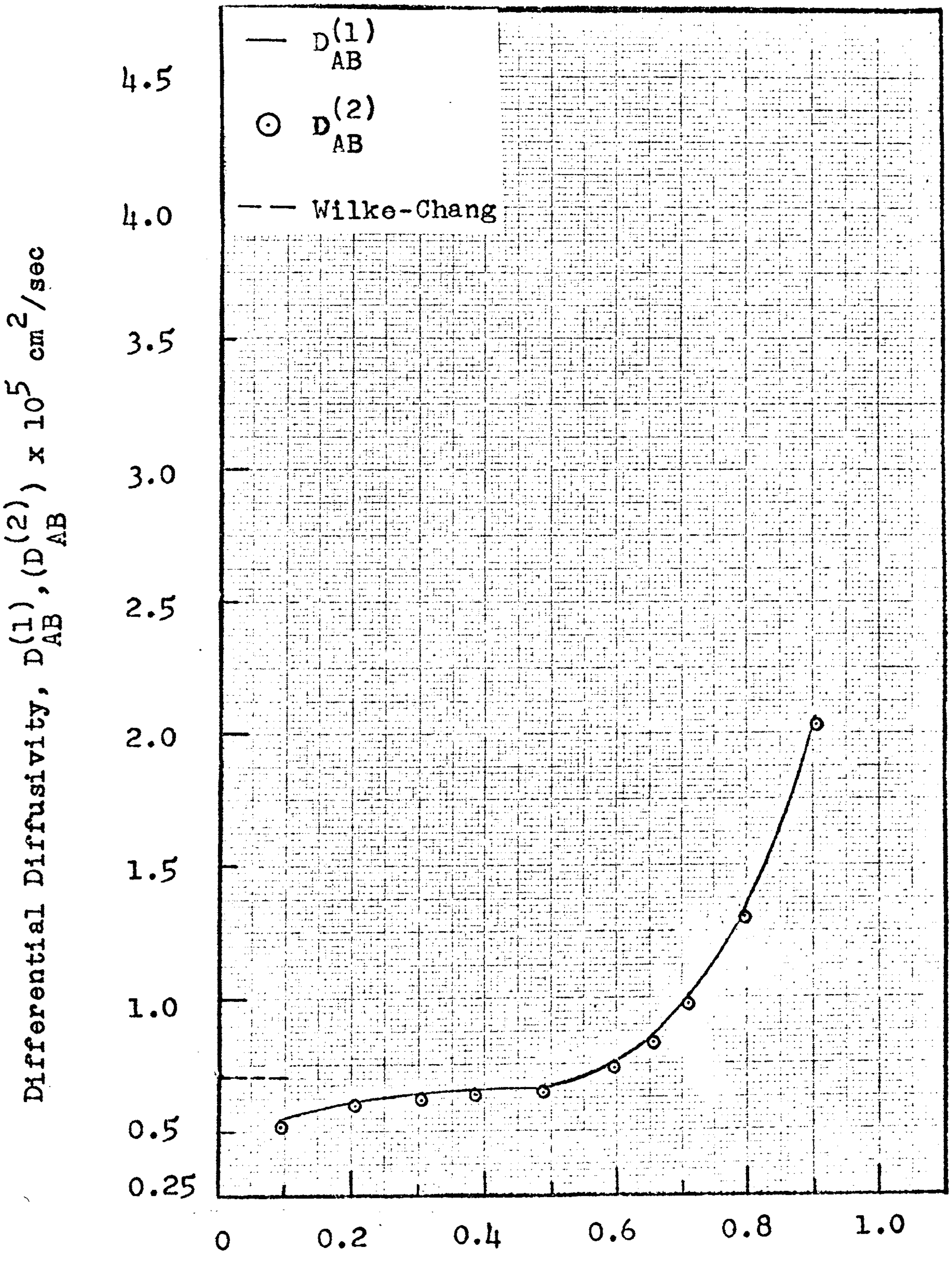


Figure E.9. Differential Diffusivity vs. Reduced Concentration for 0.20 wt.% Carbopol in Water with D-Glucose as Solute, at 23 °C, with t=20 seconds

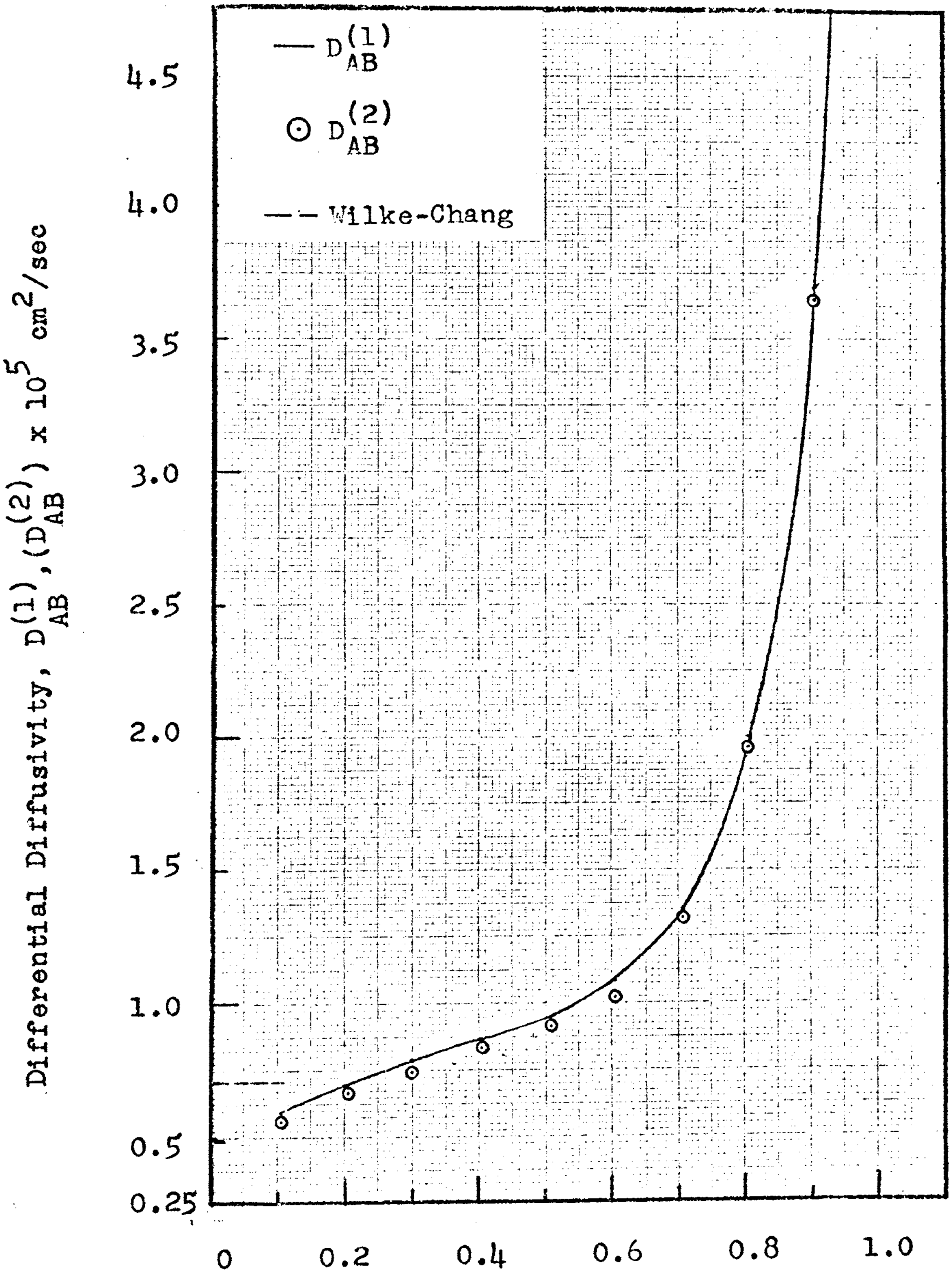


Figure E.10. Differential Diffusivity vs. Reduced Concentration for 0.18 wt.% Carbopol in Water with D-Glucose as Solute, at 23°C, with t=20 seconds

Appendix F

Comparison for Five Different Methods of Calculating the Diffusivity

$$D_{AB}^{(1)} = \frac{(1 - AW_{A1}y^*)\int_0^{y^*} f'(y^*)dy^* + 2AW_{A1}\int_0^{y^*} f(y^*)y^*dy^*}{2t(1 + AW_{A1}y^*)(dy^*/dx)} \qquad (F.1)$$

$$D_{AB}^{(2)} = \frac{\int_0^{y^*} f'(y^*)dy^*}{2t(dy^*/dx)} \qquad (F.2)$$

$$D_{AB}^{(3)} = \frac{\int_0^{y} xdy}{2t(dy/dx)} \qquad (F.3)$$

$$D_{AB}^{(4)} = \frac{\int_0^{y^*} xdy^*}{2t(dy^*/dx)} \qquad (F.4)$$

$$D_{AB}^{(5)} = \frac{(1 - AW_{A1}y^*)\int_0^{y^*} xdy^* + 2AW_{A1}\int_0^{y^*} f(y^*)y^*dy^*}{2t(1 + AW_{A1}y^*)(dy^*/dx)} \qquad (F.5)$$

Table F.1

List of Five Values of Diffusivity for System 1

y*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.099	0.512	0.491	0.501	0.490	0.510
0.230	0.627	0.602	0.610	0.601	0.626
0.368	0.719	0.691	0.697	0.690	0.718
0.483	0.784	0.755	0.758	0.755	0.783
0.619	0.902	0.878	0.855	0.876	0.916
0.776	1.415	1.394	1.304	1.392	1.413
0.877	2.317	2.294	2.107	2.291	2.315
0.992	5.902	5.865	5.285	5.860	5.897

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -4.10 to -0.63

where % DEV $=\left(\left(D_{AB}^{(2)} - D_{AB}^{(1)}\right)/D_{AB}^{(1)}\right)(100)$

Table F.2

List of Five Values of Diffusivity for System 2

y*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.084	0.953	0.915	0.941	0.913	0.952
0.136	0.997	0.956	0.973	0.951	0.993
0.258	1.020	0.976	0.985	0.974	1.019
0.372	0.993	0.949	0.951	0.948	0.992
0.465	0.942	0.904	0.896	0.903	0.942
0.526	0.934	0.901	0.877	0.900	0.933
0.600	0.970	0.944	0.900	0.943	0.969
0.689	1.078	1.056	0.987	1.054	1.077
0.776	1.255	1.235	1.139	1.234	1.254
0.957	1.892	1.872	1.697	1.879	1.891

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -3.98 to -1.06

Table F.3

List of Five Values of Diffusivity for System 3

y^*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.112	0.572	0.549	0.561	0.551	0.574
0.187	0.628	0.602	0.611	0.603	0.629
0.259	0.667	0.640	0.646	0.640	0.668
0.339	0.698	0.670	0.673	0.671	0.699
0.465	0.725	0.697	0.696	0.698	0.726
0.549	0.763	0.739	0.721	0.740	0.763
0.667	0.947	0.926	0.876	0.927	0.948
0.755	1.232	1.211	1.127	1.212	1.233
0.818	1.563	1.540	1.420	1.541	1.563
0.932	2.742	2.711	2.469	2.713	2.743

Range of % DEV or $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -4.19 to -1.14

Table F.4

List of Five Values of Diffusivity for System 4

y^*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.085	0.558	0.539	0.541	0.531	0.551
0.229	0.704	0.679	0.682	0.675	0.701
0.332	0.782	0.755	0.756	0.752	0.779
0.462	0.865	0.837	0.834	0.833	0.862
0.547	0.919	0.892	0.879	0.888	0.915
0.663	1.131	1.109	1.058	1.105	1.126
0.776	1.656	1.637	1.523	1.631	1.651
0.864	2.585	2.564	2.354	2.557	2.578
0.971	6.043	6.016	5.442	6.002	6.030

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -3.41 to -0.45

Table F.5

List of Five Values of Diffusivity for System 5

y*	$D_{AB}^{(1)}$ cm^2/sec(10^5)	$D_{AB}^{(2)}$ cm^2/sec(10^5)	$D_{AB}^{(3)}$ cm^2/sec(10^5)	$D_{AB}^{(4)}$ cm^2/sec(10^5)	$D_{AB}^{(5)}$ cm^2/sec(10^5)
0.091	1.181	1.149	1.164	1.141	1.174
0.186	1.306	1.268	1.275	1.262	1.299
0.261	1.357	1.319	1.319	1.313	1.351
0.361	1.387	1.349	1.341	1.344	1.382
0.453	1.380	1.343	1.327	1.338	1.375
0.564	1.410	1.383	1.329	1.377	1.404
0.658	1.582	1.560	1.466	1.554	1.576
0.734	1.835	1.815	1.682	1.808	1.828
0.806	2.194	2.175	1.997	2.168	2.188
0.873	2.673	2.653	2.420	2.646	2.666
0.971	3.729	3.706	3.356	3.697	3.721

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -2.71 to -0.62

Table F.6

List of Five Values of Diffusivity for System 6

y^*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.077	0.468	0.447	0.454	0.444	0.465
0.146	0.528	0.505	0.510	0.502	0.526
0.237	0.583	0.557	0.561	0.555	0.581
0.345	0.631	0.603	0.604	0.601	0.629
0.440	0.661	0.633	0.631	0.631	0.660
0.556	0.692	0.667	0.654	0.665	0.690
0.682	0.834	0.813	0.771	0.812	0.832
0.747	0.984	0.965	0.901	0.963	0.982
0.821	1.254	1.235	1.139	1.233	1.252
0.886	1.633	1.613	1.474	1.610	1.630
0.998	2.976	2.952	2.663	2.948	2.973

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -4.49 to -0.81

Table F.7

List of Five Values of Diffusivity for System 7

y*	$D_{AB}^{(1)}$ cm^2/sec(10^5)	$D_{AB}^{(2)}$ cm^2/sec(10^5)	$D_{AB}^{(3)}$ cm^2/sec(10^5)	$D_{AB}^{(4)}$ cm^2/sec(10^5)	$D_{AB}^{(5)}$ cm^2/sec(10^5)
0.078	0.439	0.421	0.431	0.420	0.438
0.146	0.508	0.487	0.496	0.485	0.507
0.235	0.579	0.554	0.562	0.553	0.578
0.317	0.636	0.609	0.616	0.609	0.635
0.403	0.691	0.664	0.670	0.663	0.691
0.467	0.733	0.704	0.708	0.703	0.731
0.529	0.770	0.752	0.745	0.741	0.769
0.608	0.847	0.822	0.807	0.821	0.846
0.696	1.039	1.016	0.973	1.015	1.038
0.757	1.284	1.260	1.187	1.259	1.282
0.822	1.728	1.703	1.582	1.701	1.727
0.910	3.063	3.031	2.767	3.028	3.060
0.995	7.922	7.863	7.045	7.856	7.916

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -0.41 to -0.74

Table F.8

List of Five Values of Diffusivity for System 8

y*	$D_{AB}^{(1)}$ cm^2/sec(10^5)	$D_{AB}^{(2)}$ cm^2/sec(10^5)	$D_{AB}^{(3)}$ cm^2/sec(10^5)	$D_{AB}^{(4)}$ cm^2/sec(10^5)	$D_{AB}^{(5)}$ cm^2/sec(10^5)
0.132	0.640	0.614	0.632	0.616	0.643
0.269	0.687	0.658	0.668	0.660	0.689
0.368	0.685	0.657	0.662	0.658	0.687
0.437	0.681	0.657	0.651	0.658	0.682
0.541	0.765	0.745	0.716	0.746	0.766
0.640	0.967	0.949	0.892	0.950	0.968
0.702	1.175	1.157	1.076	1.158	1.177
0.812	1.801	1.778	1.633	1.780	1.803

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -4.06 to -1.28

Table F.9

List of Five Values of Diffusivity for System 9

y^*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.092	0.545	0.524	0.538	0.525	0.546
0.207	0.618	0.593	0.602	0.594	0.619
0.301	0.648	0.622	0.628	0.623	0.649
0.383	0.660	0.635	0.637	0.644	0.661
0.489	0.666	0.644	0.635	0.644	0.666
0.593	0.751	0.733	0.702	0.733	0.751
0.653	0.851	0.835	0.788	0.835	0.852
0.710	0.992	0.976	0.911	0.976	0.992
0.797	1.326	1.309	1.207	1.310	1.327
0.901	2.054	2.033	1.854	2.033	2.054

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -3.85 to -1.02

Table F.10

List of Five Values of Diffusivity for System 10

y^*	$D_{AB}^{(1)}$ $cm^2/sec(10^5)$	$D_{AB}^{(2)}$ $cm^2/sec(10^5)$	$D_{AB}^{(3)}$ $cm^2/sec(10^5)$	$D_{AB}^{(4)}$ $cm^2/sec(10^5)$	$D_{AB}^{(5)}$ $cm^2/sec(10^5)$
0.108	0.591	0.565	0.578	0.566	0.592
0.203	0.695	0.664	0.674	0.664	0.695
0.300	0.783	0.748	0.757	0.748	0.783
0.404	0.869	0.832	0.838	0.832	0.869
0.508	0.950	0.912	0.916	0.912	0.950
0.605	1.058	1.024	1.006	1.023	1.058
0.707	1.353	1.321	1.261	1.320	1.353
0.804	1.990	1.956	1.826	1.955	1.989
0.904	3.693	3.650	3.344	3.649	3.692
0.994	9.963	9.883	8.888	9.881	9.961

Range of % DEV of $D_{AB}^{(2)}$ from $D_{AB}^{(1)}$: -4.40 to -0.80

Appendix G

Measurement of the Density

Four different weight concentrations of D-Glucose in the solution were measured for each system. The corresponding weight percentages of D-Glucose in the solutions are 0, 3, 6, and 10%. The D-Glucose used here is anhydrous, but the D-Glucose used by Desai (9) was hydrous. It was, therefore, necessary to correct the equivalent weight from anhydrous to hydrous form. The true weights of anhydrous D-Glucose used are 2.7272 gm, 5.4544 gm, and 9.0907 gm corresponding to 3.0 gm, 6.0 gm, and 10 gm of hydrous D-Glucose.

The procedures for measuring the density are as follow:

1. Measure the weight of empty pycnometer.
2. Place the solution in the pycnometer; then let it be in the constant temperature water bath for about 15 minutes.
3. Dry and weigh.

The weight of pure water at the same temperature was also measured. From equation (G.1) the densities of the solutions can be determined.

$$\text{Density of solution} = (\text{density of water}/\text{weight of water}) \times (\text{weight of solution}) \qquad (G.1)$$

The density of water was obtained from Perry's Handbook (19) as 0.99757 gm/cm^3 at 23°C and 0.99802 gm/cm^3 at 21°C.

Appendix H

Calculation of Differential Diffusion Coefficient of D-Glucose Using Wilke-Chang Correlation and and Clough et al Correlation

The form suggested by Wilke and Chang (24,25) is

$$D_{AB} = \left[(7.4)(10)^{-8}(\psi_B M_B)^{1/2} T\right] / \mu (V_A)^{0.6} \qquad \text{(H.1)}$$

where

D_{AB} = diffusivity of solute A in dilute solution in solvent B, cm^2/sec

M_B = mol. wt. of solvent

T = temperature, °K

μ = viscosity of solution, centipoise

V_A = solute molal volume of the normal boiling point, $\text{cm}^3/\text{cm mole}$

ψ_B = an association factor for the solvent, 2.6 for water as solvent.

The differential diffusion coefficient of D-Glucose in water at 21°C is calculated as follows:

$M_B = 18$

$T = 294\,°\text{K}$

$\mu = 0.9810$ cp

$\psi_B = 2.6$

$V_A = 177.6$

$$D_{AB} = \left[7.4(10)^{-8}(2.6\text{x}18)^{0.5}(294)\right] / \left[(177.6)^{0.6}(0.9810)\right]$$

$$= 0.67(10)^{-5}\text{cm}^2/\text{sec}$$

In a similar way the differential diffusion coefficient of D-Glucose in water at 23°C is calculated to be

$0.71(10)^{-5}$cm^2/sec. The percentage deviation of Wilke-Chang value from the experimental value for each system is given in Table H.1.

The form suggested by Clough et al for predicting the diffusivity of a solute in non-Newtonian solutions is

$$D_{NN}/D = X_{cp}(\xi/\xi cp)(\mu/\mu cp) \tag{H.2}$$

For 1.0% CMC system at 23°C

D = Wilke-Chang value for the diffusivity of a Newtonian (low viscosivity) fluid, $0.71(10)^{-5}$cm^2/sec

X_{cp} = the volume fraction of the continuous phase, 0.97 (4).

$\xi/\xi cp$ = ratio of number of neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter, 15.5/6.0 (4).

μ_{cp} = viscosity of the continuous phase portion of the non-Newtonian fluid.

$$\begin{aligned} D_{NN} &= (0.71)(10)^{-5}(0.97)(15.5/6.0)(0.92/3.0) \\ &= 0.547(10)^{-5}\text{cm}^2/\text{sec} \end{aligned}$$

Comparing this predicted value to the lowest value (the solute concentration is 0.84 gm/cm^3 solution) for the 1.20 wt.% CMC system in the experiments:

$$\begin{aligned} \%\ \text{deviation} &= (0.547(10)^{-5} - 1.181(10)^{-5})/1.181(10)^{-5} \\ &= -53.7\% \end{aligned}$$

Table H.1

The Percentage Deviation of Wilke-Chang Value from the Experimental Values; Wilke-Chang Values: $0.71(10)^{-5} cm^2/sec$ at 23°C and $0.67(10)^{-5} cm^2/sec$ at 21°C

System Number	Temperature °C	Polymer	Polymer conc. wt.%	$D_{AB}^{(1)}$ $(10)^{-5} cm^2/sec$	Y gm/100cm^3 sol.	% Dev
1	23	CMC	2.20	0.512	0.947	-39
2	23	CMC	2.00	0.953	0.775	25
3	23	CMC	1.70	0.572	1.018	-25
4	23	CMC	1.35	0.558	0.825	-27
5	23	CMC	1.20	1.181	0.840	40
6	23	Carbopol	0.28	0.468	0.715	-51
7	21	Carbopol	0.25	0.439	0.734	-52
8	21	Carbopol	0.22	0.640	1.217	- 5
9	23	Carbopol	0.20	0.545	0.870	-29
10	23	Carbopol	0.18	0.591	0.970	-20

Appendix I

Nomenclature

A = concentration dependence of the solution density

A_1, A_2, A_3 = area under the curve of reduced concentration versus distance, cm

a, b, c = constants in Gompertz equation

D = molecular diffusion coefficient of a solute, cm^2/sec

$D_{AB}^{(1)}$ = diffusivity as function of reduced concentration. Calculated with integral I_2 considering volume change, cm^2/sec

$D_{AB}^{(2)}$ = diffusivity as function of reduced concentration. Calculated with integral I_2 neglecting volume change, cm^2/sec

$D_{AB}^{(3)}$ = diffusivity as function of concentration. Calculated with integral I_1 neglecting volume change, cm^2/sec

$D_{AB}^{(4)}$ = diffusivity as function of reduced concentration. Calculated with integral I_1 neglecting volume change, cm^2/sec

$D_{AB}^{(5)}$ = diffusivity as function of reduced concentration. Calculated with integral I_1 for xdy^* and integral I_2 for xy^*dy^* considering volume change, cm^2/sec

G = coordinate, corresponds to distance after the changing of the scale $(G=(x/0.005)-1)$

$\bar{D}$ = integral (average) diffusion coefficient of a solute cm^2/sec

I_1 = integral as $\int xdy*$

I_2 = integral as $\int f(y*)dy*$

j_I^i = ith component of mass diffusion flux of component I relative to mass average velocity, sec.$^{-1}$

M = mol. wt.

p = original interface at x axis, cm.

t = time, seconds

T = temperature, °K

V = volume, cm^3

v = x component of mass average velocity cm/sec

x = coordinate, corresponds to distance cm

Y = concentration of solute, gm/100cm^3

y = concentration of solute, gm/cm^3

y* = reduced concentration W_A/W_{A1}

yp = reduced concentration y* corresponds to p

W = weight fraction of solute, Y/(Y + wt. of Polymer solution)

X = the volume fraction of the continuous phase

n = refractive index

Subscripts:

A = solute A

B = solvent B

A1 = initial weight fraction of solute

AO = solute free weight fraction

NN = diffusivity of a non-Newtonian fluid

cp = properties or parameters of the continuous phase portion of the non-Newtonian fluid.

Greek and Other Letters:

ρ = total mass density, gm/cm^3

ρ_I = mass density of component I, gm/cm^3

ρ_s = density of solute-free polymer solution, gm/cm^3

ϕ = symbol used for sigmoid function

ψ = an association factor for solvent

μ = viscosity of the fluid, centipoise

ξ = number of neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter

η = Boltzmann transformation, $x/2t^{\frac{1}{2}}$, cm/sec$^{\frac{1}{2}}$

Appendix J

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VITA

The author was born on February 4, 1942, in San-Chung, Taipei, Taiwan, Republic of China. She received her Primary education in San-Chung Primary School and Pun-Lai Primary School; and her secondary education in Taipei First Girls' Middle and High School. She entered Tunghai University in Tai-Chung, Taiwan in September 1961 and graduated in June 1965 with a Bachelor of Science Degree in Chemical Engineering.

She has been enrolled in the Graduate School of the University of Missouri at Rolla since September, 1966.