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

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A microinterferometric method was used to determine pseudo-binary, molecular diffusion coefficients for diffusion of D-glucose in aqueous carboxymethylcellulose (CMC) and aqueous carboxypolymethylene (Carbopol) solutions. An initial solute concentration of about 9 wt. % D-glucose in the aqueous polymer solutions was used. The polymer concentrations for the CMC solutions ranged from 1.2 to 2.2 wt. % and for the Carbopol solutions from 0.18 to 0.28 wt. %. Diffusion coefficients were determined as a function of reduced solute concentration, both with and without the effect of solution volume change during diffusion being considered.

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 (10), Longsworth (11), Ambrose (1), Berg (2), Crank and Robinson (4), Robinson (16), Searle (17), Nishijima and Oster (12, 13), and Secor (18). 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 (14) 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 are convenient.

The concentration-dependent (differential) diffusivities, D_{AB}, and average diffusivities, $\bar{D}_{AB}$, were determined in this work for diffusion of D-glucose in aqueous CMC and Carbopol solutions. Five different polymer concentrations of both CMC and Carbopol in water were used as the solution systems. These systems and the initial solute (D-glucose) concentration used are described in Table I.

APPARATUS

The apparatus used in this work was basically the same as that used by Secor (18), except for the Carbopol systems, for which platinum-coated slides were used instead of aluminum-coated slides to eliminate corrosion problems. The range of the apparent viscosity of the polymer solutions

Table I. Polymeric Systems Used[a, b]

System at 23° C.	Polymer	Polymer Concn., Wt. %
1	CMC	2.20
2	CMC	2.00
3	CMC	1.70
4	CMC	1.35
5	CMC	1.20
6	Carbopol	0.28
7	Carbopol	0.25
8	Carbopol	0.22
9	Carbopol	0.20
10	Carbopol	0.18

[a] Water was utilized as the solvent in all cases. [b] D-glucose was the solute, with an initial concentration of 10 grams per 100 cm.³ of solution.

used in the CMC system was from 635 to 9840 cp.; the range of viscosity used in the Carbopol system was from 819 to 17,980 cp. 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.

ANALYSIS OF DATA

Secor (18) used one concentration profile observed at a certain time and assumed no departure from volume additivity—although solution density may be a variable—during the diffusion process. The diffusion coefficient was calculated as a function of concentration, using the following relation:

$$D_{AB}^{3} = \frac{-\int_{0}^{y} x\,dy}{2t\,\dfrac{dy}{dx}} \quad (1)$$

Paul (14) 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 effect 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 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:

$$D_{AB}^{6} = -\frac{2\left[(1 - AW_{A1}y^{*})\int_{0}^{y^{*}}\eta\,dy^{*} + 2AW_{A1}\int_{0}^{y^{*}}\eta y^{*}\,dy^{*}\right]}{(1 + AW_{A1}y^{*})(dy^{*}/d\eta)} \quad (2)$$

where

$$y^{*} = W_{A}/W_{A1} = \text{reduced concentration}$$

$$W_{A} = \text{weight fraction of the solute}$$

$$\rho = \rho_{s}(1 + AW_{A}) = \text{solution density}$$

$$\eta = x/2t^{1/2}$$

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 at one time probably does not contribute significantly to the possible errors mentioned by Paul. However, there are a number of factors in the microinterferometric technique which could disrupt an idealized free diffusion field. By treating the data obtained at one value of time, one is not able to verify positively that the data came from an exact free diffusion experiment.

The time, t, which was a finite known value in the experiments, 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:

$$D_{AB}^{1} = - \frac{(1 - A W_{A1} y^*) \int_0^{y^*} x dy^* + 2 A W_{A1} \int_0^{y^*} x y^* dy^*}{2t (1 + A W_{A1} y^*)(dy^*/dx)} \quad (3)$$

When the volume change was not considered, and solution density assumed to be constant, the above relation was simplified as follows:

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

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 following requirement (18) was used:

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

which demands equal areas under the concentration-distance curve above and below the yp axis (locus of $x = p$), 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 (14) as follows:

$$- \int_0^{yp} x dy^* - 2 A W_{A1} \int_0^{yp} x y^* = \int_{yp}^1 x dy^* + 2 A W_{A1} \int_{yp}^1 x y^* dy^* \quad (6)$$

The iterative procedure used to locate p is described by Huang (9). The noniterative method of Duda and Vrentas (8) could also have been used to locate p for this case.

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:

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

where

$$G(x) = x/r - 1 \quad (7b)$$

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

The method suggested by Davis (5) and used by Secor (18) required first that the data (y^* vs. 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, 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 nonlinear least squares method was used to determine the curve-fit of Equation

7 (which is nonlinear in the constants a, b, and c) directly from the original data—which in general were unequal increments in x. The least squares procedure used resulted in a closer fit of the data to Equation 7 than the procedure of Davis (5).

The integrals $\int_0^{y^*} x dy^*$ and $\int_0^{y^*} x y^* dy^*$ were evaluated by Simpson's numerical method, using Equation 7. However, it was convenient to first transform x to a 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 by Huang (9).

PROCEDURE AND RESULTS

The experimental procedure used here was basically the same as that used by Secor (18).

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 could be determined to ±0.0001.

The densities were measured using a pycnometer, using standard techniques; the density and the concentration dependence of density are given in Table II.

The pseudo binary molecular diffusion results are given (Figures 1 and 2) as the differential diffusion coefficient vs. reduced concentration of the solute. Diffusion coefficients, D_{AB}^{1}, presented were calculated using Equation 3, which considers the density effect on mixing during molecular diffusion.

DISCUSSION

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 10 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.

The rapid rise in D_{AB}^{1} as y^* approaches unity may not be real; this may be indicative of the difficulty of curve-fitting the experimental concentration vs. distance data when y^* is greater than about 0.85.

The integral average diffusivities, $\bar{D}_{AB}^{1}$, for the two polymers are given in Table III. Though the data are somewhat scattered, the integral diffusivities of both D-glucose–CMC

Table II. Density of Pure Solvent and the Concentration Dependence of the Solution Density

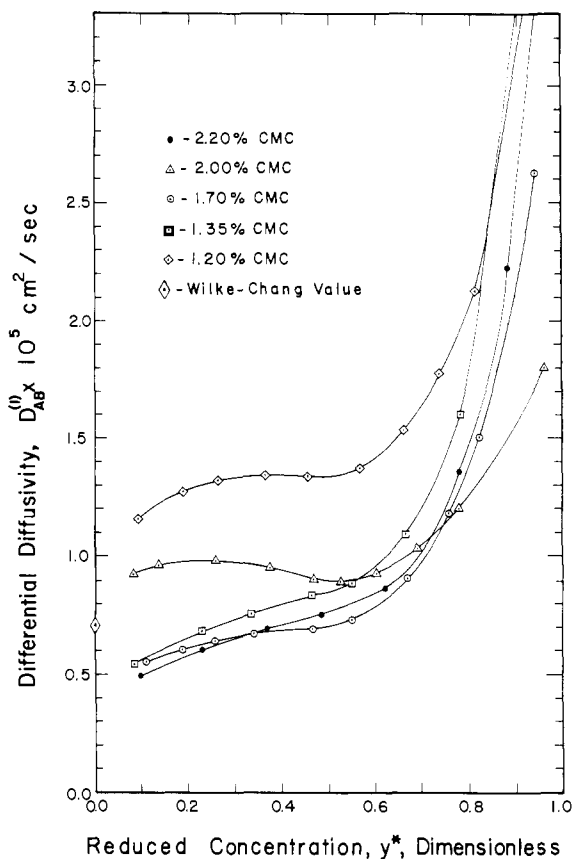| System Number at 23° C.	ρ_s	A	W_{A1}
1	1.0089	0.3387	0.0902
2	1.0070	0.3507	0.0903
3	1.0048	0.3328	0.0905
4	1.0041	0.3132	0.0906
5	1.0029	0.2630	0.0907
6	0.9987	0.3790	0.0910
7[a]	0.9999	0.3890	0.0909
8[a]	0.9991	0.3750	0.0910
9	0.9990	0.3573	0.0910
10	0.9989	0.3558	0.0910

[a] Temperature was 21° C.

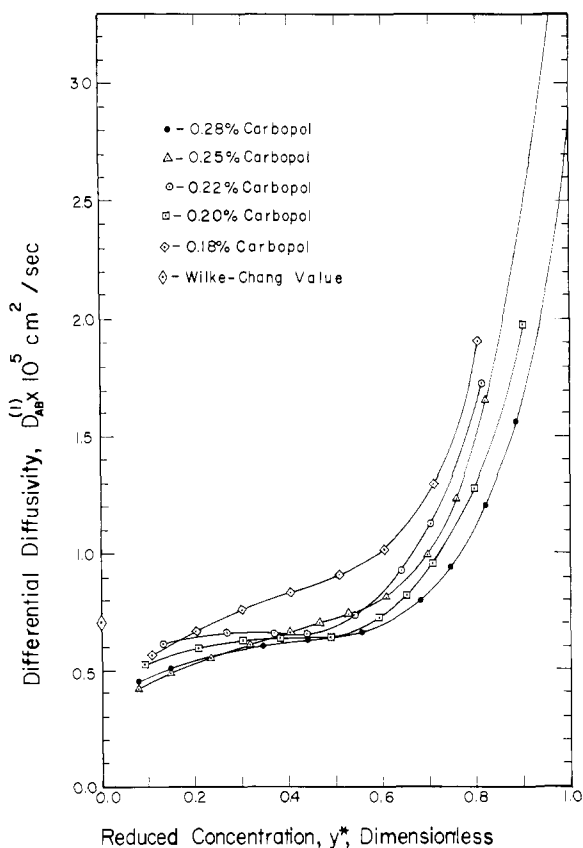Figure 1. Diffusivity of D-glucose in aqueous carboxymethyl-cellulose as a function of solute composition

Figure 2. Diffusivity of D-glucose in aqueous carboxypoly-methylene as a function of solute composition

System Number	Polymer	$\bar{D}_{AB}^{1}$, Cm.^{2}/Sec.(10)^{5}
1	CMC 2.20%	1.140
2	CMC 2.00%	1.121
3	CMC 1.70%	0.969
4	CMC 1.35%	1.292
5	CMC 1.20%	1.717
6	Carbopol 0.28%	0.874
7	Carbopol 0.25%	1.120
8	Carbopol 0.22%	0.878
9	Carbopol 0.20%	0.861
10	Carbopol 0.18%	1.415

[a] Water was utilized as the solvent. [b] D-glucose was the solute, using 10 grams per 100 cm.^{3} of solution.

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 (19) equation for dilute Newtonian solutions, was $0.71(10)^{-5}$ cm.^{2} per second, while at 21° C. it was $0.67(10)^{-5}$ cm.^{2} per second. These predictions may be compared with the experimental values at the lowest value of the 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} per second and $0.439(10)^{-5}$ cm.^{2} per second. 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 semitheoretical equation for predicting the diffusivity of a solute in non-Newtonian solutions.

$$D_{NN}/D_N = X_{cp} \, (\zeta/\zeta_{cp})(\mu/\mu_{cp}) \qquad (8)$$

Ree and Eyring (15) show that the average of ζ is about 6.0 in nonpolar, organic fluids, and the best available average value of ζ is 15.5 in aqueous systems. Therefore, (ζ/ζ_{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 10 systems were not performed in this study. Clough et al. studied β-napthol diffusing through a 1% aqueous solution of sodium carboxymethylcellulose. None of 10 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 $\mu_{cp} = 3.0$cp. 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 (19) value of the diffusivity (in pure water) was calculated to be $0.71(10)^{-5}$ cm.^{2} per second and was used as the diffusivity of Newtonian fluid, D_N. Then D_N for System 5, using Equation 9, is predicted to be $0.54(10)^{-5}$ cm.^{2} per second. The lowest experimental value of the diffusivity for this system (at the solute concentration of 0.84 gram per 100 cc. of solution) is $1.18(10)^{-5}$ cm.^{2} per second. 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 particular system, the Wilke-Chang relation seemed to be slightly more accurate than the relation of Clough et al. (3).

Despite the somewhat wide use of the wedge micro-interferometric technique, the accuracy of this technique

appears not to have been rigorously established. Thus, the authors plan in the future to measure, with the wedge microinterferometer, the diffusion coefficients of several systems for which the diffusivities are already known—i.e., determined by a well-established method, such as that which uses the Gouy interferometer.

NOMENCLATURE

a, b, c = constants in Gompertz equation
A = constant in the linear solution density vs. concentration function
D_{ij}^n = pseudo-binary (differential or concentration dependent) molecular diffusion coefficient of solute i in solution j using method n, cm.^{2}/sec.
$\bar{D}_{ij}^n$ = integral (concentration-averaged) value of D_{ij}^n, cm.^{2} per second =

$$\int_{y_1^*}^{y_2^*} y^* D_{ij}^n \, dy^* / (y_2^* - y_1^*)$$

$G(x)$ = a scaled distance coordinate, dimensionless
p = location of the original interface on the x axis, cm.
t = time measured from the beginning of mass transfer, sec.
W = weight fraction of the solute in the solution
x = distance coordinate, cm.
X_{cp} = volume fraction of the continuous phase portion of the polymer solution
y = concentration of solute, grams per 100 cm.^{3}
y^* = reduced solute concentration = W_A / W_{A1}
yp = value of y^* at x equal to p

Subscripts

A = solute A
B = solution B, polymer plus solvent, as indicated in Table I
$A1$ = initial weight fraction of solute
$A0$ = solute-free weight fraction
NN = diffusivity of a non-Newtonian fluid
N = diffusivity of a Newtonian fluid

1 = zero value of reduced concentration
2 = the largest value of reduced concentration
cp = parameter of the continuous phase portion of the non-Newtonian fluid

Greek Letters

μ = viscosity of the fluid, centipoise
ζ = number neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter
η = Boltzmann transformation = $x/2t^{1/2}$, cm. per second$^{1/2}$
ρ = total solution density, gram per cm.^{3}
ρ_s = solute-free solution density, gram per cm.^{3}

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Surface Thermodynamic Properties of n-Long-Chain Alcohols, Alkoxy Ethanols, Propanols, and Butanols

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The surface thermodynamic properties of even-membered straight-chain alcohols (C_{20} and C_{22}), alkoxy ethanols (C_{16} to C_{22}), alkoxy propanols (C_{16} to C_{22}), and alkoxy butanols (C_{16} and C_{18}) have been derived from surface tension measurements at different temperatures. There is no significant variation in the thermodynamic properties with the introduction of different extended polar groups to the hydrophobic chain.

TO ELUCIDATE the nature of interaction of monolayers of fatty alcohols and alkoxy ethanols, a recent communication (4) from this laboratory reported the results of surface tension studies on a number of alcohols (C_6 to C_{18}), lower homologs of alkoxy ethanols, and carbitols, and derived the surface thermodynamic quantities. In this communication, the results of a similar study on the long-chain alcohols (C_{20} and C_{22}), alkoxy ethanols (C_{16} to C_{22}), propanols (C_{16} to C_{22}), and butanols (C_{16} and C_{18}) are reported.

EXPERIMENTAL

Materials. Alcohols commercially obtained (from B.D.H. or Fluka) were first subjected to the triangular method of fractional recrystallization, with dry acetone as the solvent, followed by a process of acetylation and deacetylation of the corresponding fractions of the acetates. Thereafter, they were fractionally distilled through a 65-cm. column packed with borosilicate glass helices. Alkoxy ethanols, pro-