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Diffusivity of Urea in Concentrated, Saturated and Supersaturated Solutions

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A relatively simple and extremely versatile optical method of obtaining diffusion coefficient data known as Gouy interferometry was employed to measure diffusion coefficients in undersaturated and supersaturated aqueous urea solutions at 25°C. The use of laser light as a monochromatic light source in the interferometer greatly simplified the procedure for obtaining diffusivity data from the interferometer. A novel design of a real image camera was employed to record the interferometric data. Values obtained from the interferometric data for low concentration (0–4 molar) aqueous urea solutions were within ±5% of literature values.

The diffusion coefficient was found to decrease linearly with increasing concentration up to the saturation point of the aqueous urea solutions, and to decrease drastically with increasing concentration in the supersaturated region. This behavior is similar to that observed in liquid-liquid systems near the consolute point (Cussler, 1980). It is speculated that this phenomenon is a result of molecular aggregation of the urea molecules in supersaturated aqueous solutions. Very little experimental data have previously been obtained in the supersaturated region due to crystallization problems. Supersaturated diffusion coefficient data are important in the study and design of crystallization processes.

The solid-solute-liquid solvent binary systems urea-water and sucrose-water were modeled as a saturated solution solute-liquid solvent system in order to test various concentration dependent diffusion relationships. Two of these relationships, the Vignes and Leffler-Cullinan equations, showed improved correlation with experimentally determined diffusivity data for aqueous urea and aqueous sucrose solutions at undersaturated conditions.

SCOPE

The measurement of diffusion coefficients in supersaturated solutions is of fundamental importance in further understanding the mechanism of diffusion. In particular, diffusion data in the supersaturated range are necessary for the rational design of crystallization processes. Virtually no data of this kind exists, however, resulting in the use of values obtained through the extrapolation of lower concentration data to the supersaturated region. Diffusion coefficients obtained through this extrapolation could be seriously in error as a result of molecular aggregation postulated to occur in supersaturated solutions. In addition, the prediction of diffusion coefficients in concentrated solid solute-liquid solvent systems are limited by the fact that many of the widely used equations employed in the prediction of concentration dependent diffusion coefficients were designed for use with liquid-liquid systems. The purpose of this study is as follows: (1) the experimental measurement of diffusion coefficients in concentrated, saturated and supersaturated solutions of nonelectrolytes (2) comparison of results obtained in the supersaturated region with those predicted by existing correlations and by extrapolation of data in the undersaturated region, and (3) comparison of results obtained in both the undersaturated and supersaturated region with modifications of predictive equations normally used in liquid-liquid systems.

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CONCLUSIONS AND SIGNIFICANCE

The diffusion coefficients of urea in aqueous solutions were obtained at concentrations ranging from 0.125 to 11.5 molar at 25°C. The experimental results at several lower concentrations were compared to the values obtained by Gosting and Akely (1952) and were consistent to better than 5%. Experimental results in this work extend the concentration range of experimental D_{AB} values into the supersaturated region (saturation being 10.47 molar at 25°C).

Experimental results show a linear decrease in the diffusion coefficient with increasing concentration in the undersaturated region. Experimental results in the supersaturated region ($\bar{C} \geq$ 10.5 molar) exhibit a much more rapid decrease with increasing concentration than in the undersaturated region so that the linear relationship between the diffusion coefficient and concentration determined for the undersaturated region is no longer applicable. These results show that the common practice of extrapolating undersaturated diffusion data into the supersaturated region can lead to serious error.

The rapid decrease in the diffusion coefficient with increasing concentration in the supersaturated region is similar to behavior observed in liquid-liquid systems near the consolute point (Cussler, 1980). It is speculated that this phenomenon is a result of molecular aggregation of the solute in the solution. It is postulated that these aggregates form as a prelude to crystallization. The urea molecules would, therefore, diffuse as aggregates of varying size, thus altering the nature of the diffusion process.

The solid solute-liquid solvent binary systems urea-water and sucrose-water were redefined as liquid solvent-liquid solute systems where the liquid solute was a saturated solution of the solid solute. This was done in order to allow estimation of the term D^0_{BA}, the infinite dilution diffusivity of solvent B in solute A, required for use in several important predicative equations.

With D^0_{BA} available, results predicted by the Vignes (1966), Leffler-Cullinan (1970) and Sanchez-Clifton equations (1977) were compared to those predicted by the Gordon (1937) equation (which does not require D^0_{BA} term and is, therefore, usually used when solid solutes are involved) and to experimental data. Results indicate that the Vignes and Leffler-Cullinan equations, in most cases, will show improvement over the Gordon equation in prediction of diffusion coefficients in the undersaturated region. The method employed in estimating D^0_{BA}, however, can at times effect the results obtained. The prediction of diffusion coefficients in the supersaturated region awaits quantitative description of the aggregation phenomena.

INTRODUCTION

The basic method employed in this study for the measurement of diffusion coefficients is that of free diffusion. In the free diffusion method, a sharp boundary is formed in a vertical diffusion cell. Diffusion across the boundary causes a change in concentration on either side of the boundary with time. In the early stages, concentrations at the extreme ends of the diffusion cell remain constant at their initial values, and during this time the system is a true free diffusion process.

The majority of methods used in obtaining diffusion coefficients in free diffusion processes employ optical techniques which analyze changes in concentration in the vicinity of the diffusion boundary. The concentration changes around the boundary are usually characterized by a refractive index gradient. The passage of light through this gradient yields time dependent patterns that can be photographed and analyzed to yield diffusion coefficients.

The most widely used optical methods of measuring diffusion coefficients in free diffusion processes utilize interferometric techniques. Reviews of these techniques appear in Dunlop et al. (1972) and Tyrell (1961). The experimental technique employed in this study is known as the Gouy interference method.

GOUY INTEFERENCE METHOD

The Gouy interferometer is an extremely simple optical system, consisting of a monochromatic light source which illuminates a horizontal slit, and is focused by a lens of long focal length onto a screen or photograph plate. If light leaving the lens passes through the diffusion boundary of a system, horizontal interference fringes (known as Gouy fringes) can be viewed and recorded. A schematic diagram of the Gouy interferometer appears in Figure 1. The qualitative explanation of the fringes is given by Gouy (1980). A number of investigators (Longsworth, 1945, 1947, 1950; Kegels and Gosting, 1947; Coulson et al., 1948), have developed and refined

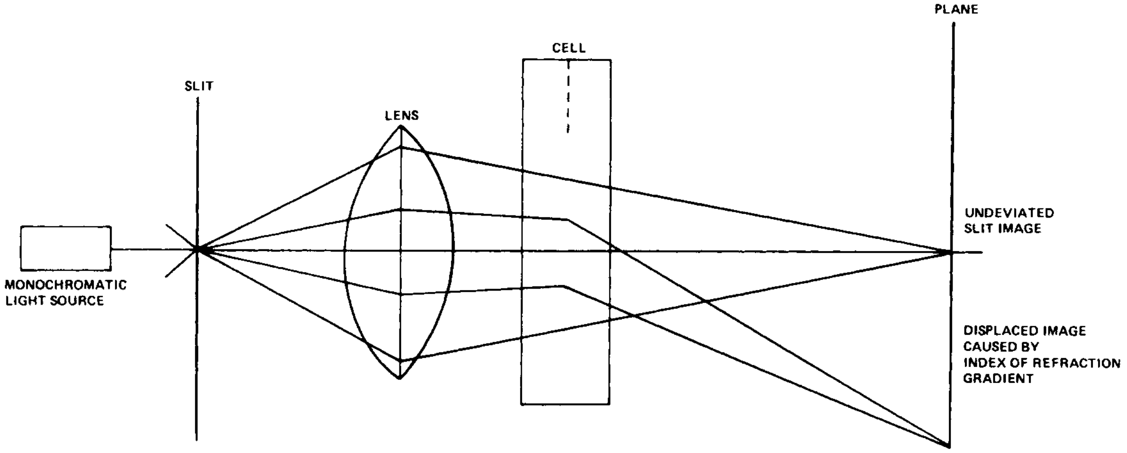

Figure 1. Gouy interferometer.

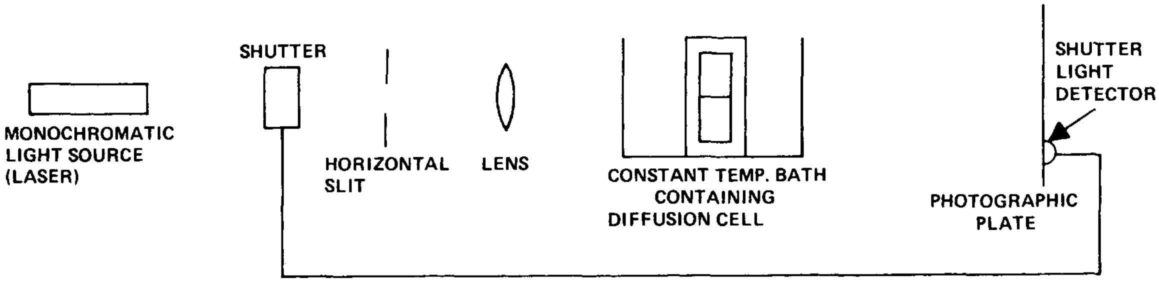

Figure 2. Experimental apparatus.

a quantitative theory relating the spacing of the horizontal (Gouy) fringes to the diffusion coefficient. A description of the theoretical treatment can be found in Sorell (1981).

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the Gouy interferometer apparatus employed in diffusion studies appears in Figure 2. A detailed description of the apparatus can be found in Sorell (1981). Illumination of the system was provided by a Spectra Physics Model 146 randomly polarized helium-neon laser. Fringe data were photographically recorded employing a lensless real image camera developed by O'Shea (1977).

The diffusion cell employed appears in Figure 3, and is a modification of the one described by Caldwell et al. (1957). A single plexiglass temperature bath was employed to control the temperature of the solution reservoirs, valving, inlet and outlet tubing connected to the diffusion cell, and the diffusion cell itself. In this way temperature gradients within the system and crystallization problems in the tubing were minimized.

The temperature in each bath was regulated by a Model 72 Immersion Circulator manufactured by Fisher Scientific. The control of temperature was 0.01°C.

The system urea-H_2O was chosen for study because solubility, density, viscosity, and activity coefficient data were available as function of concentration, (Scatchard et al., 1938; Gucker et al., 1938) and diffusion coefficients had been reported at concentrations up to 4 molar (Gosting and Akely, 1952). In addition the viscosities of saturated urea solutions were low enough to allow formation of a sharp boundary in the diffusion cell.

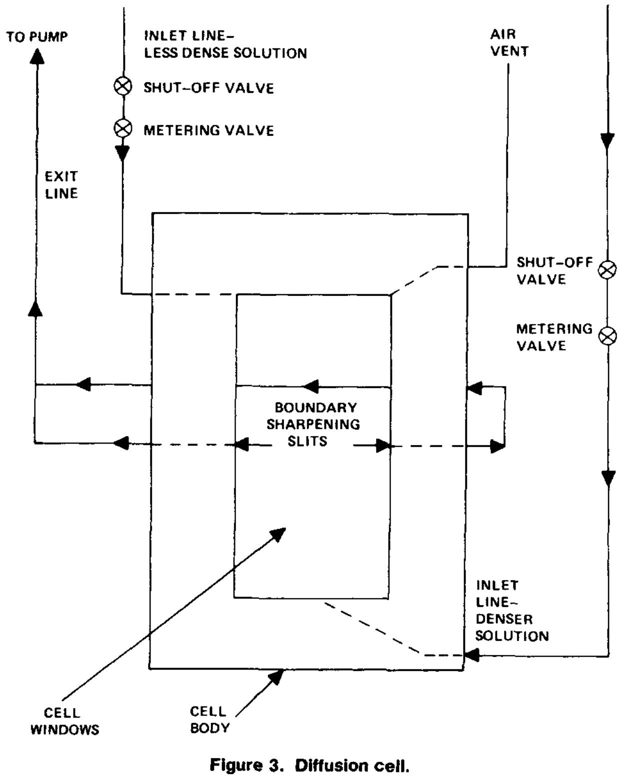

Figure 3. Diffusion cell.

After solutions of the desired concentrations were prepared and the system brought to the appropriate temperature, the diffusion cell was filled with the two solutions and the boundary sharpening procedure was begun. A detailed description of this procedure can be found in Sorell (1981). The sharpness of the boundary could be qualitatively judged by the appearance of the fringe pattern observed during the process. When a fringe pattern of acceptable quality was obtained, flow to the diffusion cell from the solution reservoirs was stopped. At this point the diffusion process is in the free diffusion mode. A timer was immediately started in order to record the difference in time between the beginning of the free diffusion process and the subsequent photographic exposures of the Gouy fringe pattern.

The photographic exposures taken at each time were analyzed to yield experimental fringe distances between the undeviated slit image and each of the bottom eleven fringes in the photograph. This analysis was done employing a comparator (Model #267A) manufactured by the Gaertner Scientific Corporation.

The total number of fringes present in the interference pattern (J_m) was also determined from the fringe photographs. A combination of the methods discussed by Tyrell (1961) and English (1947) were employed to evaluate J_m for each experiment.

Upon analyses of the fringe photographs as mentioned above, an uncorrected diffusion coefficient could be calculated for each fringe photograph taken at a given time. This uncorrected diffusion coefficient can be calculated from the relation

$$D' = \frac{J_m{}^2 \lambda\, b^2}{4(\overline{C}_t)^2_{t'}} \tag{1}$$

A plot of D' vs. $1/t'$ extrapolated to $1/t' = 0$ yields the true diffusion coefficient at a concentration of $\overline{C} = (C_2 + C_1)/2$ (where C_1 and C_2 are the concentrations of the solutions used). The slope of the plot is equal to $D\Delta t$ where Δt is the zero time correction. The zero time correction is a measure of the extent of initial boundary imperfection in the experiment. The smaller the zero time correction, the better the initial boundary.

RESULTS AND DISCUSSION

The experimental values of the diffusion coefficient, D_{AB}, for the urea water system at different mean concentrations $\overline{C} = (C_2 + C_1)/2$ were obtained at concentrations ranging from 0.125 to 11.50 molar. The concentration difference between the two solutions ($\Delta C = C_2 - C_1$) was 0.25 molar for all experiments.

The experimental results at several lower concentrations were compared to the values obtained by Gosting and Akely (1952) who employed Gouy interferometry to measure the diffusion coefficients of urea up to concentrations of 4 molar. Results of the work are consistent with their results to better than 5%.

Experimental results obtained in this work extend the concentration range of experimental D_{AB} values into the supersaturated concentration region. The solubility data of Scatchard, Homer and Wood (1938) indicate that at 25°C a saturated solution of urea and water exists at a concentration of 10.47 molar.

Experimental values D_{AB} in the supersaturated region were obtained up to a mean concentration $\overline{C} = 11.50$ molar, at which point crystallization problems in the system prevented further experiments. The experimental values obtained in this work along with those previously determined by Gosting and Akely (1952) appear in Figure 4. The results show a linear decrease in the diffusion coefficient with increasing concentration in the undersaturated region. This result is in general agreement with other workers (Gosting and Morris, 1949; Gosting and Akely, 1952;

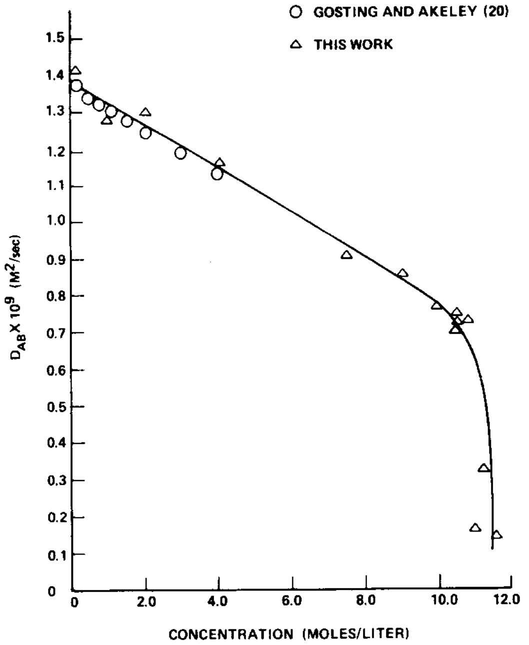

Figure 4. Diffusivity of aqueous urea solutions at 25°C.

Sandquist and Lyons, 1954), who have examined the diffusion of solid nonelectrolytes in aqueous undersaturated solutions.

Determination of the constants in a quadratic equation by the method of least squares yields the relation

$$D_{AB} \times 10^9 = 1.40171 - 5.91362 \times 10^{-2}\,\overline{C} - 3.90011 \times 10^{-4}\,\overline{C}^2 \quad (2)$$
$$(\mathrm{m^2/s})$$

Which expresses the undersaturated values of D_{AB} determined experimentally in this work with an average deviation of less than 3%. A value of the infinite dilution diffusivity obtained from this expression is within 2% of the value reported by Longsworth (1954).

Experimental results in the supersaturated region ($\overline{C} \geq 10.5$) also appear in Figure 4. It is observed that the slope of the D_{AB} vs. $\overline{C}$ curve becomes markedly steep once the point of saturation is reached. The linear relationship between the diffusion coefficient and mean concentration determined for the undersaturated region is no longer applicable. These results show that the common practice of extrapolating undersaturated diffusion data into the supersaturated region can lead to serious error.

The rapid decrease in diffusion coefficient with increasing concentration in the supersaturated region is similar to behavior observed in liquid-liquid systems near the consolute point. Claersson and Sundelof (1957) and Haase and Siry (1968) experimentally demonstrated that the diffusion coefficient rapidly goes to zero as the consolute point is approached. Attempts to explain this phenomena have been made on thermodynamic grounds (Turner 1975 a,b) and by postulating the failure of Fick's law near the consolute point (Anisimov and Perelman, 1966). Cussler (1980) explained this behavior by assuming that concentration fluctuations including both single molecules and cluster of molecules dominate behavior near the consolute point.

The concept of molecular clusters is often employed in the analysis of crystallization phenomena. It is postulated that molecular clusters form as a prelude to the crystallization process. In a stable supersaturated solution, the molecules would diffuse as clusters of many sizes thus altering the nature of the diffusion process. Studies of the diffusion coefficients of detergent solutions near the critical micelle concentration (Mijnlieff, 1962, 1963) have demonstrated that the formation of the micelles (clusters of 5–50 molecules) will result in a rapid drop in the diffusion coefficient.

The rapid decrease in diffusion coefficient with concentration in the supersaturated region of the urea-water system was not observed in studies of sucrose-water (English and Dole, 1950). As previously mentioned, it has been reported (Cussler, 1980) that the diffusion coefficient rapidly decreases toward zero in liquid-liquid systems near the consolute point. The analogous situation in a solid liquid system might be considered the spinodal curve which defines the limits of metastability in the supersaturated solution. If it is postulated that the diffusion coefficient rapidly approaches zero near the spinodal, the observed behavior of a given system will depend on the location of the spinodal and the ability to make measurements in that region. Diffusion measurements made in supersaturated urea solutions, therefore, could have been significantly closer to the spinodal than those made in the sucrose water system. The difference between the two systems might also be explained in terms of their ability to form molecular clusters. Examination of the energies of cluster formation (O'Hara and Reid, 1970) indicates that certain physical properties of the molecules effect their ability to form clusters. Further studies of diffusion coefficients in supersaturated solutions will be necessary, however, before any general description on this behavior can be developed.

COMPARISON OF RESULTS WITH PREDICTIVE EQUATIONS

Many investigators (Gosting and Morris, 1959; Dunlop and Gosting, 1953; Gosting and Akely, 1952; English and Dole, 1950) have compared experimentally determined diffusivity data with the Gordon equation (Gordon, 1937; James et al., 1939) although Gordon (1950) himself points out the limited applicability of the equation over a wide concentration range. The widespread use of the Gordon equation to predict concentration dependent diffusion is no doubt a reflection of the need for a method of accurately describing the diffusion process in solid solute-liquid solvent systems. Other widely used predictive equations such as those of Vignes (1966), Leffler and Cullinan (1970), and Sanchez and Clifton (1977) are less applicable to the study of solid solute-liquid solvent systems, due to their dependence on D^0_{BA}, the infinite dilution diffusivity of the solvent B in the solute A. In the case of a solid solute A and liquid solvent B the term D^0_{BA} has little physical meaning and has, therefore, prevented the use of these equations when a solid solute was involved. In order to employ these equations for the case of a solid solute dissolved in a liquid some assumption about the nature of D^0_{BA} must be made. The assumption made in this work was that the liquid solvent B-solid solute A type system can be redefined as a system comprising a liquid solvent B and a liquid solute A (where the liquid solute A is actually a saturated solution of solute A in solvent B). This redefinition of the system allows estimation of the parameter D^0_{BA}.

With this parameter available, results predicted by the Vignes, Leffler-Cullinan, and Sanchez-Clifton equations can be compared to those predicted by the Gordon equation and to experimental data. These four predictive equations appear below:

Gordon

$$D_{AB} = D^0_{AB}\left(1 + \frac{d\ln \gamma_A}{d\ln X_A}\right)\frac{\mu B}{\mu_{AB}} \quad (3)$$

Vignes

$$D_{AB} = (D^0_{AB})^{X_B}\,(D^0_{AB})^{X_A}\left[1 + \frac{d\ln \gamma_A}{d\ln X_A}\right] \quad (4)$$

Leffler-Cullinan

$$D_{AB}\,\mu_{AB} = (D^0_{AB}\,\mu_B)^{X_B}\,(D^0_{BA}\,\mu_A)^{X_A}\left(1 + \frac{d\ln \gamma_A}{d\ln X_A}\right) \quad (5)$$

Sanchez-Clifton

$$D_{AB} = (X_A\,D^0_{BA} + X_B\,D^0_{AB})\left(1 - q + q\frac{d\ln \gamma_A}{d\ln X_A}\right) \quad (6)$$

TABLE 1. ESTIMATED D^0_{BA} VALUES AND SANCHEZ-CLIFTON q PARAMETERS FOR UREA-WATER AND SUCROSE-WATER SYSTEMS

Estimation Technique	$D^0_{BA} \times 10^9$ m/s (Urea-Water)	$D^0_{BA} \times 10^{11}$ m^2/s (Sucrose-Water)	q Urea-Water	q Sucrose-Water
Wilke-Chang	2.001	2.550	0.296	1.607
Wilke-Chang with Olander Modification	0.87001	1.1087	0.057	1.583
Scheibel	2.051	2.478	0.303	1.606
Reddy-Doraiswamy	1.2174	1.144	0.152	1.583

The four equations above were employed to predict the diffusivity of urea and of sucrose in aqueous solutions as a function of concentration. The values of D^0_{BA} required for use Eqs. 3–5 were obtained using four techniques (Wilke-Chang, Wilke-Chang with Olander Modification, Scheibel, Reddy-Doraiswamy) which are summarized by Skelland (1974) and Reid et al. (1977). The D^0_{BA} values for each of the techniques, as well as, the empirically determined parameter in the Sanchez-Clifton equation are summarized in Table 1. Thermodynamic and viscosity data required for use with Eqs. 3–6 were obtained from the literature (English and Dole, 1950; Gosting et al., 1952; Scatchard et al., 1938) up to saturation concentrations. Data in the supersaturated region was obtained through extrapolation. It is recognized that data obtained in the supersaturated region through extrapolation is suspect, however, currently no other technique is available for the prediction of such data.

Figures 5–8 illustrate the values predicted for the diffusivity of urea (D_{AB}) in water by the Gordon, Vignes, Leffler-Cullinan, and Sanchez-Clifton equations for various values of D^0_{BA}. The Gordon equation deviates negatively from the experimental D_{AB} curve in the undersaturated concentration region, and is independent of the D^0_{BA} value chosen.

The Vignes and Leffler-Cullinan equation closely parallel one another for all four values of D^0_{BA} employed. Both equations poorly fit the experimental data when the relatively high D^0_{BA} values estimated by the Wilke-Chang and Scheibel techniques were used. When the lower values of D^0_{BA} estimated via the Olander modified Wilke-Chang and Reddy Doraiswamy techniques are employed, the Vignes and Leffler-Cullinan equation fit the data well. Both equations exhibit negative deviation from experimental data in the undersaturated region, but show improved correlation with the experimental data as compared to the Gordon equation.

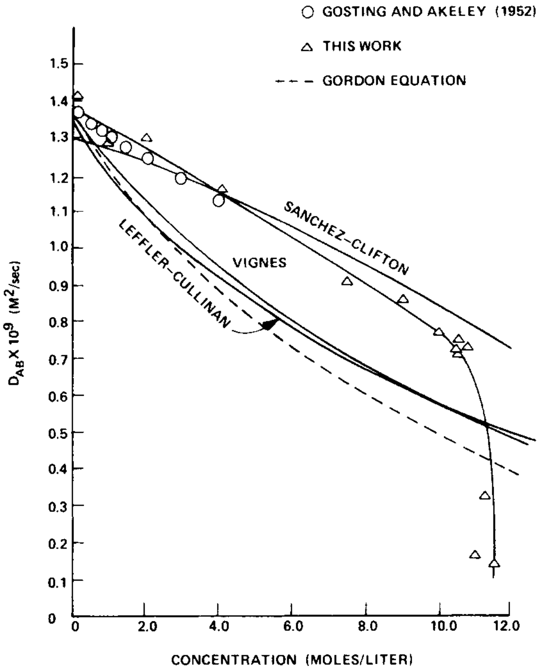

Figure 6. Predicted vs. experimental results for urea-water system using D^0_{BA} (Wilke-Chang with Olander modification).

The Sanchez-Clifton fits the experimental data poorly except in the case where the Olander modified Wilke-Chang value of D^0_{BA} is used. In this case the equation fits the experimental data well,

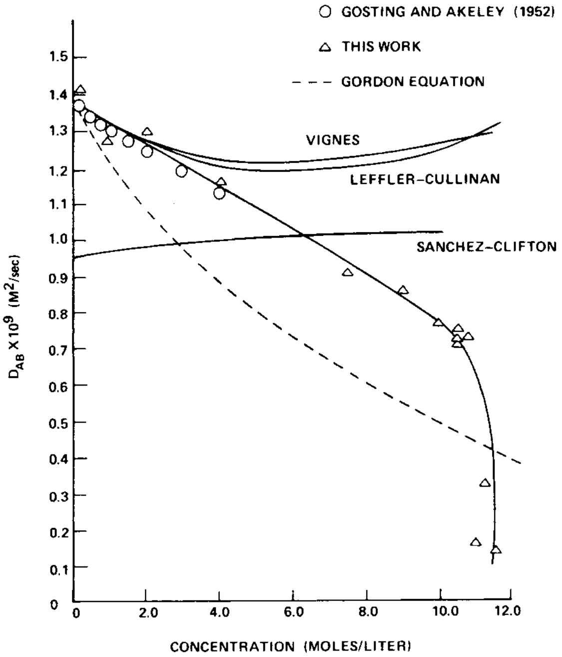

Figure 5. Predicted vs. experimental results for urea-water system using D^0_{BA} (Wilke-Chang).

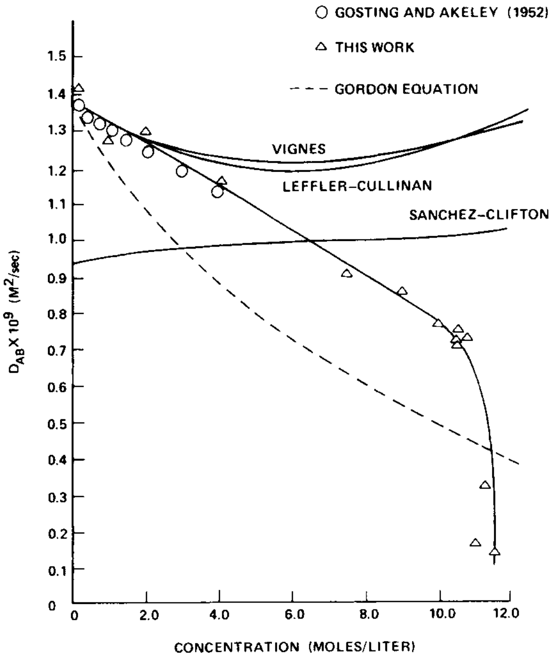

Figure 7. Predicted vs. experimental results for urea-water system using D^0_{BA} (Scheibel).

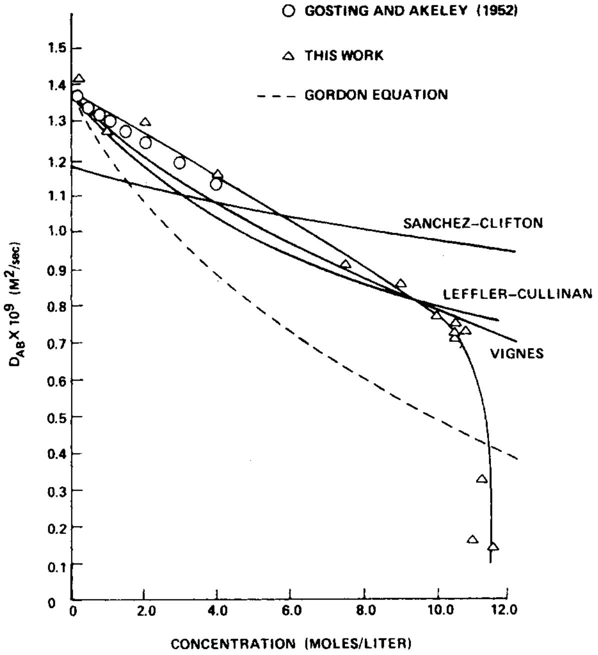

Figure 8. Predicted vs. experimental results for urea-water systems using D^0_{BA} (Reddy-Doraiswany).

particularly in the high concentration ranges of the undersaturated region.

None of the equations tested predict the rapid drop in the diffusion coefficient with concentration in the supersaturated region. This is probably due to the use of extrapolated thermodynamic and viscosity data. In order to successfully predict diffusion coefficients in supersaturated solutions correlations without thermodynamic correction factors will have to be developed, or thermodynamic and viscosity data in supersaturated solutions will have to be experimentally determined.

Figures 9–12 illustrate the values predicted for diffusion of sucrose in water by the Gordon, Vignes, Leffler-Cullinan, and Sanchez-Clifton equations for various values of D^0_{BA}. The Gordon equation, as in the urea-water system, deviates negatively from the experimental D_{AB} curve.

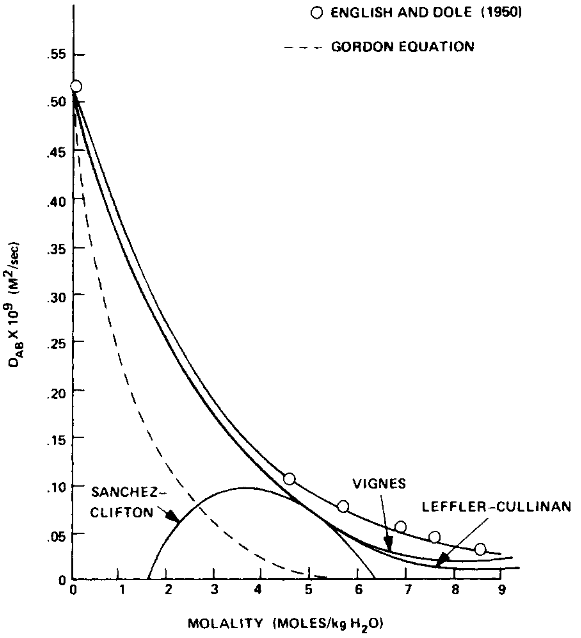

Figure 9. Predicted vs. experimental results for the sucrose-water system using D^0_{BA} (Wilke-Chang).

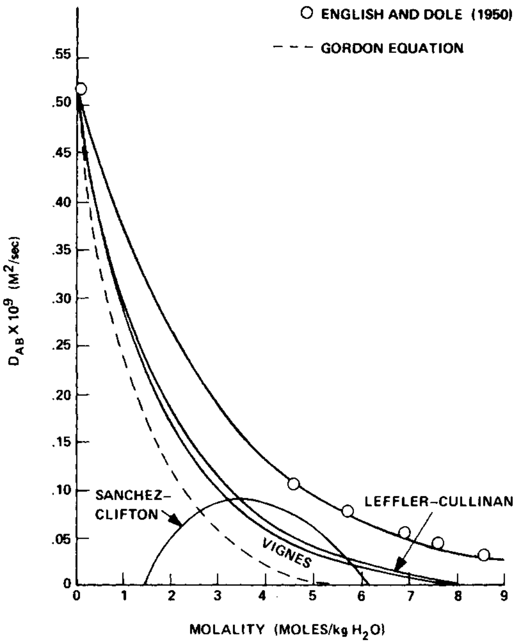

Figure 10. Predicted vs. experimental results for sucrose-water systems using D^0_{BA} (Wilke-Chang with Olander modification).

The Vignes and Leffler-Cullinan equations appear to best fit the data when the values of D^0_{BA} estimated from the Wilke-Chang and Scheibel techniques are used. However, the results predicted by these equations employing all four values of D^0_{BA} are superior to those predicted by the Gordon equation. The Sanchez-Clifton equation, however, correlates poorly with experimental data for all values of D^0_{BA} employed.

DISCUSSION

On the basis of the urea-water and sucrose water systems used in the preceding analysis of experimental vs. predicted D_{AB} values, it appears that the Vignes and Leffler-Cullinan equations offer a

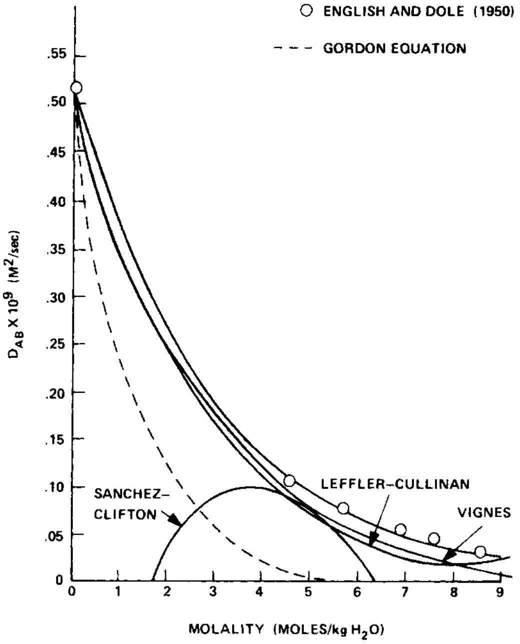

Figure 11. Predicted vs. experimental results for sucrose-water system using D^0_{BA} (Scheibel).

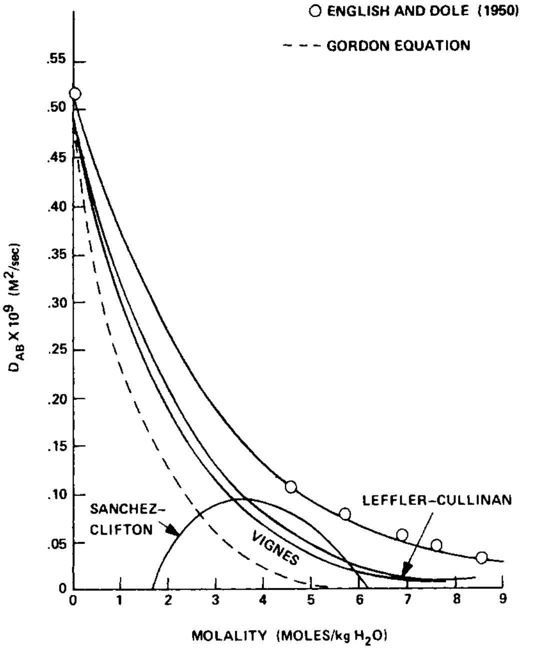

Figure 12. Predicted vs. experimental results for sucrose-water system using D^0_{BA} (Reddy-Doraiswamy).

fair degree of agreement with experimental results. While the precision of this agreement varies with the assumptions made in obtaining a D^0_{BA} value, the Vignes and Leffler-Cullinan equation generally show improvement over the Gordon equation in the prediction of diffusion coefficients. The only exception to this is in the urea-water system employing the Wilke-Chang and Scheibel values of D^0_{BA}.

Similar testing of other solid solute-liquid solvent systems experimental data employing the assumptions and predictive equations described above are necessary before any overall conclusion can be drawn. However it does appear that modeling the solid solute-liquid solvent system as a saturated solution solute-liquid solvent system can yield acceptable values of $D^0_{BA}$for use in equations for the prediction of diffusion coefficients. The prediction of diffusion coefficients in supersaturated solution, however, will remain difficult until the effect of molecular aggregation on the diffusion coefficient can be quantified.

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NOTATION

b = optical path length
$\overline{C}_t$ = parameter obtained from fringe photographs
D' = uncorrected diffusion coefficient
D_{AB} = diffusion coefficient of solute A in solvent B at a given concentration
D^0_{AB} = infinite dilution diffusivity of solute A and in solvent B
D^0_{BA} = infinite dilution diffusivity of solvent B in solute B
J_m = total number of fringes
t = time after beginning free diffusion
q = empirical constant in Eq. 1
X_A = mole fraction A
μ_B = viscosity of solvent B
μ_{AB} = viscosity of the solution
γ_A = activity coefficient of solute A

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An Experimental Study of Floc Strength

Photographic observation of the disintegration of individual flocs upon interaction with a turbulent jet has been used to quantify the binding force of kaolin-polymer and kaolin-Fe^{+III} aggregates. The data suggest that the strength per unit mass decreases with increasing floc size, thereby supporting the multiple-level model for aggregation.

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SCOPE

An important characteristic of flocs in coagulation processes is their binding force, i.e., the ability of the aggregate structure to resist deaggregation. The impact of the physicochemical environment during coagulation upon floc strength is perhaps qualitatively understood, but present knowledge is not adequate to permit rational process improvement. The objectives of this investigation were to observe the disintegration of individual flocs photographically and to deduce, if possible, the magnitude of the force required to produce breakup. Different floc structures were studied at various levels of acidity to produce quantitative information about the effects of these parameters upon aggregate resistance.

Previous studies of floc strength have relied upon indirect measurements to deduce relative binding force. Hannah et al. (1967) measured the size distribution of fragments produced when a parent aggregate was drawn through a 70 μm orifice; they manipulated mixing intensity, pH, and coagulant type. Tambo and Hozumi (1979) observed maximum floc diameter in a paddle flocculator as a function of pH, dissipation rate, and coagulant type. Either of these cited investigations can serve as the basis for valuable generalizations, but neither can be used to make a quantitative estimate of floc strength.

CONCLUSIONS AND SIGNIFICANCE

Photographic observation of the breakup of individual flocs in a turbulent jet has been used to quantify the binding force of aggregates as a function of the flocculator environment during coagulation. Flocs formed from a dispersed phase of kaolin with an anionic macromolecular coagulant-aid were found, at a given size, to be more than twice as strong as those formed with an inorganic acid salt ($FeCl_3$) alone. This result is interpreted as a consequence of structural differences, with interparticle bridging in the case of the clay-polymer structures producing mechanically-linked flocs that are quite resilient when subjected to minor deformation. Floc growth in the case of the Fe^{+III} coagulant occurs under alkaline conditions by particle capture by enmeshment; structures thus produced are relatively weak. The variation of binding force with pH was investigated for both types of coagulants and increased alkalinity produced stronger floc in both systems. This effect was more pronounced in the case of kaolin-Fe^{+III} structures. It was found that floc binding force in all cases examined could be correlated with floc size in a manner consistent with the spectral model of Tambo and Hozumi (1979), even though their model is not a physically realistic portrait of the breakup process in conventional coagulation environments.

Increased floc strength could be used in a coagulation process to produce larger, more settlable aggregates. Floc growth rates could also be enhanced since stronger structures are better able to tolerate fluid velocity gradients required for orthokinetic flocculation. It is likely, however, that stronger flocs would be more difficult to dewater.

The information contained in this paper contributes to the understanding of deaggregation and can be used for the refinement of floc breakage models that contain binding force as a parameter; indeed, Glasgow and Luecke (1980) have demonstrated the pressing need for this type of investigation. The photographic observations of the breakup of individual aggregates in a turbulent environment appear to be the first of their kind in the literature. In addition, the data obtained from them should facilitate optimization of coagulation processes where particular objectives or constraints must be satisfied.

INTRODUCTION

It is evident that any model of floc breakage will require floc binding force, or strength, as a parameter. Thomas (1963) has used an expression developed by Hamaker (1937) to roughly estimate the force of attraction between colloidal particles

$$F = \frac{Ar}{12h^2} \tag{1}$$

By representing the number of particle-particle contacts per unit volume floc as n_c, Thomas was able to write an expression for the

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