GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: April 15, 1980

Project Title: Concentration Dependent Diffusion Coefficients of Non-Electrolytes in Supersaturated Solutions (Cottrell Research Grant)

Project No: E-19-611

Project Director: Dr. A. S. Myerson

Sponsor: Research Corporation; New York, New York 10017

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Defense Priority Rating: None

Assigned to: Chemical Engineering

(School/Department)

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SPONSORED PROJECT TERMINATION SHEET

Date __4/19/82_________________

Project Title: Concentration . . . Supersaturated Solutions

Project No: E-19-611

Project Director: Myerson

Sponsor: Research Corp.

Effective Termination Date: __3/31/82_________________

Clearance of Accounting Charges: _______________________

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [ ] Final Fiscal Report
- [ ] Final Report of Inventions: N/A All closing actions completed.
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other ___________________

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FORM OCA 10.781
Concentration Dependent Diffusion Coefficients of Nonelectrolytes in Supersaturated Solutions

Annual Report

Submitted To: Research Corporation

Allan S. Myerson
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332
Abstract

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. 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 modelled 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. The purpose of this study is the experimental measurement of diffusion coefficients in supersaturated solutions of nonelectrolytes and comparison of these results with those predicted by extrapolation of existing data and by modifications of existing theoretical correlations.
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 ($\bar{C} > 10.5$ 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 may be attributed to 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 $D_{BA}^0$, the infinite dilution diffusivity of solvent B in solute A, required for use in several important predictive equations.
With $D_{BA}^O$ 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 or $D_{BA}^O$ 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 $D_{BA}^O$ 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, concentration at the extreme ends of the diffusion cell remains 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 Interference 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 (1880). A number of investigators
(Longsworth, (1945,1947,1950), Kegeles and Gosting (1947), Coulson et.al. (1948)), have developed and refined 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 was 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 crystalization problems in the tubing were minimized.

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

The system urea-H₂O 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 viscosity of saturated urea solutions were low enough to allow formation of a sharp boundary in the 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 pat-
tern 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 begin-
ing 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 (Jm) was
also determined from the fringe photographs. A combination of the methods dis-
cussed by Tyrell (1961) and English (1947) were employed to evaluate Jm 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

\[ D' = \frac{J_m \lambda^2 b^2}{4(C_t)^2 t} \]

where

- \( D' \) = uncorrected diffusion coefficient
- \( J_m \) = total fringe number
- \( \lambda \) = wavelength of light used
- \( b \) = optical path length
- \( t \) = time after beginning free diffusion
- \( C_t \) = parameter obtained from fringe photographs
A plot of $D'$ vs $1/t'$ extrapolated to $1/t' = 0$ yields the true diffusion coefficient at a concentration of $	ilde{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 $\Delta t$ 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 $\tilde{C} = (C_2 + C_1)/2$ 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 this 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 of $D_{AB}$ in the supersaturated region were obtained up to a mean concentration $\tilde{C} = 11.50$ 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) 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

\[ D_{AB} \times 10^9 = 1.40171 - 5.91362 \times 10^{-2} C - 3.90011 \times 10^{-4} C^2 \]  

\[ (m^2/sec) \]  

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 \((C > 10.5)\) also appear in Figure 4. It is observed that the slope of the \( D_{AB} \) vs \( C \) 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 the diffusion coefficient with increasing concentration in the supersaturated region may be attributed to molecular aggregation of the solute in the solution. It is postulated that these aggregated form as a prelude to the crystallization process. The urea molecules would then diffuse as aggregates of various sizes, thereby altering the nature of the diffusion process. When molecules of the solute are postulated to diffuse as aggregates, diffusion theory (Skelland (1974)) predicts the decrease in diffusion coefficients experimentally observed in this work.

The rapid decrease in diffusion coefficient with concentration in the supersaturated region observed for the urea-water system was not observed in
studies of the sucrose-water system (English and Dole (1950)). This could be a result of differences in the physical properties of the two systems, hence, differences in their abilities to form aggregates. Supersaturated sucrose-water solutions are considerably more viscous than urea-water solutions. In addition, the sucrose molecule is larger than the urea molecule. Both of these factors could hinder aggregate formation. Additional experimental studies of diffusion coefficients of solid nonelectrolytes in supersaturated solutions will be required, however, before a general description to this phenomena 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 $D_{\text{BA}}^0$, 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 $D_{\text{BA}}^0$ 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 $D_{\text{BA}}^0$ 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 $D_{BA}^0$.

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

$$D_{AB} = D_{AB}^0 + 1 + \frac{d \ln \gamma_A}{d \ln X_A} \frac{\eta_B}{\eta_{AB}}$$

(3)

Vignes

$$D_{AB} = D_{AB}^0 \frac{X_B}{D_{BA}} \frac{X_A}{D_{AB}} 1 + \frac{d \ln \gamma_A}{d \ln X_A}$$

(4)

Leffler-Cullinan

$$D_{AB} \gamma_{AB} = D_{AB}^0 \gamma_B \gamma_A \frac{X_B}{D_{BA}} \frac{X_A}{D_{AB}} 1 + \frac{d \ln \gamma_A}{d \ln X_A}$$

(5)

Sanchez-Clifton

$$D_{AB} = X_A D_{BA}^0 + X_B D_{AB}^0 1 - q + q \frac{d \ln \gamma_A}{d \ln X_A}$$

(6)

where $D_{AB}^0$ = infinite dilution diffusivity of solute A in solvent B

$X_A$ = mole fraction A

$\gamma_A$ = activity coefficient of solute A

$\eta_B$ = viscosity of the solvent

$\eta_{AB}$ = viscosity of the solution

$D_{BA}^0$ = infinite dilution diffusivity of solvent B in solute A

$q$ = empirical constant

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
required for use of Equations 3-5 where 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 \( D_{BA}^0 \) values for each of the techniques, as well as, the empirically determined parameter in the Sanchez-Clifton equation are summarized in Table 1.

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 \( D_{BA}^0 \). The Gordon equation deviates negatively from the experimental \( D_{AB} \) curve in the undersaturated concentration region, and is independent of the \( D_{BA}^0 \) value chosen.

The Vignes and Leffler-Cullinan equation closely parallel one another for all four values of \( D_{BA}^0 \) employed. Both equations poorly fit the experimental data when the relatively high \( D_{BA}^0 \) values estimated by the Wilke-Chang and Scheibel techniques were used. When the lower values of \( D_{BA}^0 \) 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.

The Sanchez-Clifton equation fits the experimental data poorly except in the case where the Olander modified Wilke-Chang value of \( D_{BA}^0 \) is used. In this case the equation fits the experimental data quite well, particularly in the high concentration ranges of the undersaturated region. None of the equations, however, predicted the rapid drop in the diffusion coefficient with concentration in the supersaturated region.

Figure 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 $D_{BA}^O$. The Gordon equation, as in the urea-water system, 
deviates negatively from the experimental $D_{AB}$ curve.

The Vignes and Leffler-Cullinan equation appear to best fit the data 
when the values of $D_{BA}^O$ estimated from the Wilke-Chang and Scheibel techniques 
are used. However, the results predicted by these equation employing all four 
values of $D_{BA}^O$ are superior to those predicted by the Gordon equation. The 
Sanchez-Clifton equation, however correlates poorly with experimental data 
for all values of $D_{BA}^O$ 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 fair degree of agreement with 
experimental results. While the precision of this agreement varies with the 
assumptions made in obtaining a $D_{BA}^O$ 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-Change and Scheibel values of $D_{BA}^O$.

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 modelling the solid solute-liquid solvent system as a saturated solution 
solute-liquid solvent system can yield acceptable values of $D_{BA}^O$ for use in 
equations for the prediction of diffusion coefficients. The prediction of dif-
fusion coefficients in supersaturated solution, however, will remain difficult 
until the effect of molecular aggregation on the diffusion coefficient can be 
quantified.
Acknowledgements

The authors would are indebted to the Research Corporation for partial support of this research. Acknowledgement is made to the donors of The Petroleum Research Fund Administered by the ACS, for partial support of this research.
Notation

\( b \) = optical path length

\( \bar{C}_t \) = parameter obtained from fringe photographs

\( D' \) = uncorrected diffusion coefficient

\( D_{AB} \) = diffusion coefficient of solute A in solvent B at a given concentration

\( D_{AB}^\circ \) = infinite dilution diffusivity of solute A in solvent B

\( D_{BA}^\circ \) = infinite dilution diffusivity of solvent B in solute A

\( J_m \) = total number of fringes

\( t \) = time after beginning free diffusion

\( q \) = empirical constant in Eq.1

\( X_A \) = mole fraction A

\( \nu_B \) = viscosity of solvent B

\( \nu_{AB} \) = viscosity of the solution

\( \gamma_A \) = activity coefficient of solute A
References


1. Schematic Diagram of Gouy Interferometer
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5. Predicted vs. Experimental Results for the Urea-Water System Using $D_{\text{BA}}^\text{O}$ (Wilke-Chang)
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1. Estimated $D_{BA}^0$ Values and Sanchez-Clifton $q$ Parameters for Urea-Water and Sucrose-Water Systems.
CELL IMAGE

PLANE

UNDEVIATED SLIT IMAGE

CAUSED BY INDEX OF REFRACTION GRADIENT

MONOCHROMATIC LIGHT SOURCE

SLIT

LENS

CELL

IMAGE PLANE

DISPLACED IMAGE

CAUSED BY INDEX OF REFRACTION GRADIENT
$D_{AB} \times 10^9$ (m²/sec) vs. Concentration (Moles/Liter)

- ○ GOSTING AND AKELEY (20)
- △ THIS WORK
GOSTING AND AKELEY (1952)

THIS WORK

GORDON EQUATION

LEFFLER–CULLINAN

VIGNES

SANCHEZ–CLIFTON

$D_{AB} \times 10^9$ (M$^2$/sec)

CONCENTRATION (MOLES/LITER)
\[D_{AB} \times 10^9 \text{ (M}^2\text{sec)}\]

CONCENTRATION (MOLES/LITER)

○ GOSTING AND AKELEY (1952)
△ THIS WORK
--- GORDON EQUATION

SANchez-CLIFTON
LEFFLER-CULLINAN
VIGNES
The figure shows a graph plotting the diffusion coefficient $D_{AB} \times 10^9$ (m$^2$/sec) against concentration (moles/liter). The data points and lines are labeled as follows:

- ○ GOSTING AND AKELEY (1952)
- △ THIS WORK
- --- GORDON EQUATION
- VIGNES
- LEFFLER–CULLINAN
- SANCHEZ–CLIFTON

The concentration range is from 0 to 12 moles/liter, and the diffusion coefficient range is from 0 to 1.5 $D_{AB} \times 10^9$ (m$^2$/sec). The graph includes a legend and axis labels for both the x-axis (CONCENTRATION) and y-axis ($D_{AB} \times 10^9$).
\[ D_{AB} \times 10^9 \text{ (m}^2/\text{sec)} \]

\[ \text{CONCENTRATION (MOLES/LITER)} \]
ENGLISH AND DOLE (1950)

---

GORDON EQUATION

---

DAB \times 10^9 \text{ (m}^2/\text{sec)}

MOLALITY (MOLES/kg H_2O)
ENGLISH AND DOLE (1950)

--- GORDON EQUATION

--- --- ---

\[
D_{AB} \times 10^9 (\text{M}^2/\text{sec})
\]

MOLALITY (MOLES/kg H$_2$O)

○ ENGLISH AND DOLE (1950)

--- --- ---

GORDON EQUATION

LEFFLER–CULLINAN

SANCHEZ–CLIFTON

VIGNES

0 1 2 3 4 5 6 7 8 9
<table>
<thead>
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<th>Estimation Technique</th>
<th>$D_{BA}^0 \times 10^9 \frac{m^2}{sec}$ (urea-water)</th>
<th>$D_{BA}^0 \times 10^{11} \frac{m^2}{sec}$ (sucrose-water)</th>
<th>$q_{urea-water}$</th>
<th>$q_{sucrose-water}$</th>
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<tbody>
<tr>
<td>Wilke-Chang</td>
<td>2.001</td>
<td>2.550</td>
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<tr>
<td>Wilke-Chang with Olander Modification</td>
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<td>1.1087</td>
<td>0.057</td>
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<tr>
<td>Scheibel</td>
<td>2.051</td>
<td>2.478</td>
<td>0.303</td>
<td>1.606</td>
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<tr>
<td>Reddy-Doraiswamy</td>
<td>1.2174</td>
<td>1.144</td>
<td>0.152</td>
<td>1.583</td>
</tr>
</tbody>
</table>
April 12, 1982

Dr. R. Scott Pyron
Regional Director
Grants Program
Research Corporation
6075 Roswell Road, NE
Atlanta, GA 30328

Dear Dr. Pyron:

Enclosed is the final report on my research corporation grant. I would like to take this opportunity to thank the Research Corporation for its support.

Sincerely,

Allan S. Myerson
Assistant Professor

Enclosure
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. 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 under saturated conditions.
STUDENT PARTICIPATION (Give names of students working on the project, their role in the research, their achievements and their career plans.)

Louis Sorrell, M.S. March 1981 - Constructed experimental apparatus. Studied the urea-water system. 
Mr. Sorrell is currently employed at the Texaco Research Center in Beacon, N.Y.

Elizabeth Seely, M.S., expected January 1983. Ms. Seely will study the glycine-water system, other systems of nonelectrolytes and will be involved in theoretical predictions of diffusion coefficients.

Robert Ramsdell, B.S., June 1982. Mr. Ramsdell was involved in developing new techniques for the predicting of diffusion coefficients. Mr. Ramsdell will be attending graduate school.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers or talks resulting from the work. Attach two copies of any reprints available, if not previously forwarded.)


OTHER SUPPORT (List amounts and sources—including institutional—of other contributions received or expected for this work.)

Proposal "Concentration Dependent Diffusion Coefficients in Supersaturated Solutions" Submitted to the National Science Foundation.

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (The terminal report should be approved by an authorized officer of the institution.)

a. Equipment, supplies (Itemize major expenditures) $7,000

Temperature Control Equipment $1,500
Pumps $1,000
Stereo Zoom Microscope $1,000
Optical Components $1,000

b. Stipends (Academic status, rates, periods of appointment)

c. Other expenditures (Itemize and give purpose)

Signature of principal investigator ________________________________ Date ___________________

Signature of authorized officer of institution (required for terminal report only) ________________________________ Date 4/13/82

Name and position of authorized officer of institution ________________________________