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ABSTRACT

The diffusion of toluene, in two-component hydrocarbon solvent mixtures, at very dilute concentrations and at constant temperature was studied by a stirred diaphragm cell technique.

The diffusion coefficient - viscosity products, for the n-hexane - n-tetradecane, n-hexane - cyclohexane and cyclohexane - n-decane solvent mixtures, were best correlated as a linear function of the solvent composition expressed in mole fraction. The latter solvent mixture gave a definite minimum in its diffusion coefficient - viscosity product composition data, corresponding to a similar minimum in the viscosity versus composition data.

An extensive study was made of the effect of free and forced convection resistances outside of the diaphragm. It was found that the mass transfer resistance external to the diaphragm was small (0.3 per cent of the total resistance at 350 rpm stirring speed) and was nearly a constant for all the fluids investigated. Under these conditions the cell constant exhibited negligible variation with fluid properties.

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INTRODUCTION

The molecular diffusion coefficient of liquid systems has been found to be an important variable in processes such as absorption, extraction, distillation, and ion exchange. Correlation of mass-transfer coefficients requires a knowledge of the diffusion coefficient. Little is known about mass transfer by molecular diffusion in liquid mixtures of more than two components, although Gosting and others have studied the effects of interacting flows for systems of two solutes in one solvent.^{1,6,8} However, there have been no data or specific theory published on the diffusion of a dilute solute in a multicomponent solvent.

The purpose of this study was to determine if diffusion in a mixed solvent could be related to the binary diffusion coefficients of the solute in each of the pure solvents and to the mixture viscosity.

Diffusion coefficients of very dilute toluene (5.0×10^{-3} mole per liter) in mixed hydrocarbon solvents were measured by using a stirred diaphragm cell technique. Counterdiffusion of the solvent was not measured, since the solvent is essentially stagnant when the solute is very dilute. Each system may thus be considered, for diffusion purposes, to be a binary of one solute and a two-component solvent.

The usual correction for nonideality, $(1 + \partial \ln \gamma_1 / \partial \ln X_1)$, may be omitted, since the solute is very dilute.

Johnson and Babb have presented an excellent review of current diffusion theory and data for binary nonelectrolytes.¹² For conditions under which the solute is very dilute, the Eyring, thermodynamic, Stokes-Einstein, and thermodynamics-of-irreversible-processes theories give the

following form for correlation:

$$\frac{D\mu}{T} = \psi, \quad (1)$$

where ψ is a correlation coefficient which is dependent on molecular size, shape, and other variables.

The Eyring theory for diffusion and viscosity⁹ gives the following form for the correlation coefficient. The diffusion coefficient is given by

$$D = \lambda_D \frac{kT}{h} \exp \{ - \Delta F_D^\ddagger / RT \}. \quad (2)$$

The viscosity is

$$\mu = \frac{h}{\lambda_\mu} \frac{(\lambda_1/\lambda_2\lambda_3)}{2} \exp \{ \Delta F_\mu^\ddagger / RT \}. \quad (3)$$

Combining these equations gives Eyring's general expression,

$$\frac{D\mu}{T} = k (\lambda_1/\lambda_2\lambda_3) (\lambda_D/\lambda_\mu)^2 \exp \{ \Delta F_\mu^\ddagger - \Delta F_D^\ddagger / RT \}. \quad (4)$$

Normally for self-diffusion it is assumed that the free energies of activation are equal for diffusion and viscosity and that λ_D equals λ_μ . Douglass and McCall have shown these assumptions to be approximately true for self-diffusion in paraffin hydrocarbons.⁵ The familiar Eyring expression results from applying these assumptions to Eq. (4):

$$\frac{D\mu}{T} = k (\lambda_1/\lambda_2\lambda_3). \quad (4a)$$

The group $(\lambda_1/\lambda_2\lambda_3)$ arises from the viscosity development, and for very dilute solutes it would be a function of the solvent only. If $\lambda_1\lambda_2\lambda_3$ represents the volume occupied by a single molecule, Eq. (4a) becomes

$$\frac{D\mu}{T} = k (N^0/v')^{1/3} \quad (4b)$$

Since $(N^0/v')^{1/3}$ is dependent only on the solvent properties, it is proportional to $(\rho_m/M_m)^{1/3}$ for mixed solvents. In the absence of a more theoretical treatment for mixtures, one might expect D_μ and $(N^0/v')^{1/3}$ to be linear functions of the relative amounts (mol fraction) of the solvent components. If the free energies of activation are not equal or if λ_μ does not equal λ_D , D_μ may not be linear in solvent composition, since these factors are dependent on the solute as well as the solvent.

Wilke and Chang²⁰ and others^{11,14,15} have developed empirical correlations which attempt to replace the size-shape parameter of Eq. (1) with easily measured macroscopic properties of the system. The Wilke and Chang correlation for solutes at very low concentrations in binary systems is

$$\frac{D_\mu}{T} = 7.4 \times 10^{-8} (x^0 M)^{1/2} / v^{0.6} \quad (5)$$

If the solute is the same in all cases, the form of the correlation is

$$D_\mu / T (x^0 M)^{1/2} = \text{constant} \quad (6)$$

If this correlation is applicable to a mixed solvent system, supplying the correctly averaged molecular weight of the solvent should correlate the diffusion-viscosity data by Eq. (6). A mol fraction and volume fraction average molecular weight are the obvious ones to try. The association parameter of the solvent, x^0 , is 1.0 for hydrocarbons.

Bird, Steward, and Lightfoot speculated that the following equation, derived from the Maxwell-Stefan diffusion equations, may work for ternary liquid systems:³

$$D_{lm} = \frac{D_{13} D_{12} (1-x_1) - x_1 D_{12} D_{23} \sqrt{x_2} / \sqrt{x_1} - x_1 D_{13} D_{23} \sqrt{x_3} / \sqrt{x_1}}{x_1 D_{23} + x_2 D_{13} + x_3 D_{12}} \quad (7)$$

For this study x_1 was very small and Eq. (7) reduces to

$$D_{lm} = \frac{1}{x_2 / D_{12} + x_3 / D_{13}} \quad (8)$$

Wilke has shown the validity of this equation for some gaseous systems.¹⁹ Equations (7) and (8), unlike the theories of liquid diffusion, contain no reference to the viscosity of the system.

EXPERIMENTAL PROCEDURE

Apparatus

The diaphragm cell method was used for all diffusion-coefficient measurements. The principles and general technique of this method were reviewed by Gordon.¹⁰ An extensive study of convection effects was made by this author and the pre-run suggested by Gordon has been omitted. The details of these technique modifications are discussed under Special Problems.

The diaphragms used here were Ace Glass, E porosity. They were 5.0 cm in diameter and 0.5 cm thick. The pore diameter was specified to be three to eight microns. The cells were used with the diaphragm in a vertical position. The two cell compartments which had volumes of about 125 cc and were stirred with 1-inch-long Teflon-covered bar magnets. A cell is shown in Fig. 1. The vertical-diaphragm type of cell has the advantages of ease of filling and sampling, and the cell constant is not altered by collection of small amounts of air on the diaphragm.

Equation (13) was found to satisfactorily describe the transport in the diffusion cell. The cells were calibrated with 0.2 N HCl and the data of Stokes¹⁸ for the diffusion-coefficient reference.

The densities were measured with a Westphal balance and were reproducible to 0.2%. The viscosities were measured with an Ostwald viscometer calibrated with distilled water. The viscosities were reproducible to 0.5%.

The constant-temperature water bath and magnetic stirring apparatus are shown in Fig. 2. All data were taken at 25.1 ± 0.1 °C. Four variable stirring speeds are possible with this apparatus. All experiments were made at 350 rpm stirring speed as checked with a stroboscope.

Procedure

One compartment of the cell was filled with the solvent, and by applying pressure to this compartment some of the solvent was forced through the diaphragm. Care must be taken to sweep the air from the diaphragm with the solvent so that a reproducible cross section is obtained.

ZN-2428

Fig. 1. Diaphragm diffusion cell.

ZN-2429

Fig. 2. Constant temperature and stirring apparatus.

The concentrated solution was then used to wash and fill the other compartment.

The experiments were made for a time sufficient to make the ratio of the initial concentration difference to the final concentration difference about two. The run times varied from three to ten days. At the end of the experiment, the contents of the cell were removed and analyzed. An analysis of the initial concentrated solution was reported as the initial concentration difference, since pure solvent was used in the other compartment at the start of the experiment.

For the organic systems, the solute was toluene and the solvents were n-hexane, n-tetradecane, n-decane, and cyclohexane. The toluene, on the average, had an initial concentration of 5×10^{-3} mole per liter. The diffusion coefficients therefore may be considered to be integral coefficients at essentially infinite dilution.

Solvents

The hexane, cyclohexane, and decane were obtained from Phillips Petroleum Company. The hexane and decane were Pure Grade and the cyclohexane was Spectro Grade. The tetradecane was obtained from Matheson, Coleman, and Bell and had a specified melting point of 4 to 6 °C. The toluene was Baker and Adamson Reagent Grade.

The solvents were dried by passing them through a column of silica gel which was about 1 meter long and 2 cm in diameter. They were then batch-distilled and the fraction within 0.5 °C of their boiling point was recovered. The tetradecane freezing point was measured after being vacuum-distilled, and was found to be 5.4 to 5.6 °C, compared to the accepted value of 5.5 °C.

It was found that the solvents were permanently contaminated after the toluene was added and therefore fresh solvents were used for all runs.

Analysis

The analysis of the 0.2 N HCl, used for calibration, was a titration with standard 0.1 N NaOH to a phenolphthalein end point. The reproducibility was about ± 0.0005 N in acid.

The analysis for toluene in the hydrocarbon solvents was made with a Beckmann quartz spectrophotometer. At 2620 Å, the optical density was not strictly proportional to the concentration of toluene (Beer's law was not obeyed). Calibration curves were used to determine the concentrations. The reproducibility of these measurements was ± 1.0 to 1.5%

Reliability of the data

The reproducibility of the calibration titrations was found to be 0.0005 mole per liter of acid. The value of the initial concentration difference was 0.2 N and the final concentration difference was 0.1 N on the average. Considering a 0.1% error in the pipettes, the maximum error in the cell constant was slightly more than 2.2%. In all cases the cell constants were reproducible to better than 2.2% or the cells were not used.

The accuracy of the spectrophotometer readings was 1.0 to 1.5%. This gave a maximum error in the diffusion coefficient of about 6.0%. In most cases the actual data reproduced better than 5.0%.

Averages of at least three runs were used for the cell-constant values. Two or more determinations were used for the organic systems.

SOME SPECIAL PROBLEMS

External Mass-Transfer Resistance

Assuming pseudo-steady-state conditions, the equation which describes the transport in a diaphragm cell is

$$\log \Delta C_i / \Delta C_f = \beta D t, \quad (9)$$

with

$$\beta = [1/V_1 + 1/V_2] \left[\frac{1.0}{2D/kA + 1/A'} \right] \quad (10)$$

Equation (9) is derived in Appendix A. The nomenclature may be found in Appendix G.

Normally one finds the $2D/kA$ term omitted from the cell constant β . This term accounts for the external mass-transfer resistance due to laminar fluid layers on the diaphragm. By including this term one can correct for a cell constant which apparently varies with stirring speed and fluid properties. It may be omitted from the cell constant only when the cell is perfectly stirred and there is no external mass-transfer resistance. In actual practice these conditions are not fully realized.

Other users of the diaphragm cell have investigated the effect of stirring,^{13,16,17} but have not actually considered $2D/kA$ in the cell constant.

Lewis used a cell with very efficient stirring.¹³ He found that, above 120 rpm, all the cell constants were constant, and he concluded that the cells should be run at this speed to obtain reproducible results.

Other investigators have essentially done the same thing and used some minimum speed, determined for their cell geometry, for all experiments.^{16,17} This procedure requires many calibration runs for each cell, and then the assumption that the minimum calibration speed works for all other fluid properties.

To use Eq. (9), one needs to know k , the mass-transfer coefficient, as a function of stirring speed and fluid properties. A correlation of mass-transfer coefficients, for a specific cell geometry, as a function of stirring speed and fluid properties would provide a convenient means for estimating the external resistance term.

Electrochemical limiting-current experiments were performed to determine the mass-transfer coefficient for the cell geometry used in this study. A special half-cell was constructed and the limiting current, for three different copper sulfate solutions, was measured as a function of stirring speed. The cell is shown on Fig. 3. The limiting currents were used to calculate the mass-transfer coefficients. Appendix C presents a discussion of the technique and validity of using limiting-current measurements for predicting mass-transfer coefficients.

The mass-transfer coefficients were correlated in the forced-convection range in the usual dimensionless group manner. The least-squares fit of 32 datum points gives

$$Nu' = 0.050 Re^{0.79} Sc^{0.38}. \quad (11)$$

The data are plotted in Fig. 4 and the numerical data are presented in Appendix C.

It was assumed that the correct length parameter was the stirring bar length, but this was not varied. Therefore the correlation should be applied only to this specific cell geometry. It was also assumed that the mass-transfer coefficient was the same for the sintered glass diaphragm as it was for the copper cathode.

A free-convection correlation was obtained from the limiting current measurements on each of the three copper sulfate solutions. It is

$$Nu' = 0.58 [Sc \cdot Gr]^{1/4}. \quad (12)$$

It compares quite favorably with the equation given by Wilke et al., who obtained

$$Nu' = 0.66 [Sc \cdot Gr]^{1/4} \quad (13)$$

for free vertical plates, from electrochemical measurements and the dissolution of benzoic acid. The difference between the correlations is thought to be due to wall and shape effects.

Free-convection calculations for 0.1 N KCl and 0.2 N HCl show that the cell constant will be about 3.8% lower for KCl and about 6.8%

ZN-2430

Fig. 3. Electrochemical cell used for convection study.

MU-19957

Fig. 4. Forced-convection mass-transfer correlation.

lower for HCl than in a cell stirred at 350 rpm. Chang⁴ and Stokes¹⁷ found about 6.0% difference between stirred and nonstirred experiments for 0.1 N KCl. The present author, like Lewis,¹³ found a variation from cell to cell in the difference between free- and forced-convection data. See Table I. In this work, the variation may be due to mechanical vibrations, which would not give the same free-convection conditions from run to run.

Table I

Comparison of free- and forced-convection cell constants for 0.1 N HCl			
Cell	Free convection	At 350 rpm	Difference (%)
12	2.21×10^{-2}	2.33×10^{-2}	5.2
13	2.44	2.66	8.3
14	2.27	2.45	7.3
25	1.85	1.94	4.6

The average difference between free convection and 350-rpm experiments is about 6.4%, compared to 6.8% calculated from Eq. (13).

A cell calibrated by using free-convection conditions with a solution whose density is a strong function of concentration obviously could not be accurately used to determine the diffusion coefficient for a solution in which the density is a very weak function of concentration. For work with very dilute solutions, free-convection conditions would give very low mass-transfer coefficients, owing to the low density differences that would arise.

For a typical cell used in this work $1/A'$ is about 0.23 cm^{-1} (estimated from forced-convection data). Equation (10) indicates that if $2D/kA$ is large compared with $1/A'$, it must be included in the cell constant. Since the mass-transfer coefficient is a function of the stirring speed and fluid properties, and if $2D/kA$ is not negligible, the cell constant varies with stirring speed and fluid properties. The magnitudes of $2D/kA$ for 200-rpm and 350-rpm stirring speeds are shown on Table II.

Table II

Calculated mass-transfer resistance term				
Solvent	Solute	At 200 rpm $1/\text{cm}^2 \times 10^3$	At 350 rpm $1/\text{cm}^2 \times 10^4$	Free convection $1/\text{cm}^2$
Water	0.1 N KCl	1.1	7.0	8.8×10^{-3}
Water	0.2 N HCl	1.3	8.5	1.6×10^{-2}
Hexane	Toluene	1.1	7.7	
Cyclohexane	Toluene	1.2	7.6	
Decane	Toluene	1.4	8.0	
Tetradecane	Toluene	1.5	9.1	

The correction resulting from including $2D/kA$ is about 0.5% at 200 rpm and about 0.3% at 350 rpm. One should note that $2D/kA$ is part of the cell constant and about the same, at one speed, for all fluids. Therefore one stirring speed was used (350 rpm) for all measurements and the correlations were not used directly to determine the cell constants or diffusion coefficients.

The Effect of Bulk Flow Through A Vertical Diaphragm

The effect of bulk flow through a vertical diaphragm was studied by Chang.⁴ It was concluded that the effect was negligible.

Steady-State Assumption

Equation (9) was derived by assuming that there is a linear concentration gradient present in the diaphragm at the start of the experiment and that it remains throughout the experiment.

Gordon gives the semi-empirical equation $t = 1.2 (l^2/D)$ for the time required to set up a linear gradient from the initial condition of pure solvent in the diaphragm and in one compartment and the concentrated solution in the other compartment.¹⁰ Since the concentrations are unknown after this pre-run, the solutions are replaced with known concentrations and the run is started. It is probably impossible to remove and replace the solutions without altering the concentration gradient in the diaphragm.

Barnes found the exact solution for two different initial conditions for diffusion through a diaphragm.² Barnes's case number II was reduced by Gordon to Eq. (9), without the external mass-transfer resistance term. The initial condition is that there must be a linear concentration gradient present in the diaphragm at time zero.

It is shown in Appendix B that Barnes's case number I reduces to

$$\log \{ \Delta C_1 / \Delta C_f (1 - \lambda/6) \} = \beta' D t (1 - \lambda/6), \quad (14)$$

where

$$\beta' = A'/l [1/V_1 + 1/V_2], \quad (15)$$

and λ is the ratio of the free volume to the diaphragm to the volume of one of the cell compartments and equals about 0.02 for a typical cell. The initial conditions for case I are that the diaphragm and one of the compartments are filled with the solvent and the other compartment filled with the concentrated solution. Since $1 - \lambda/6$ appears on both sides of Eq. (17) and $\lambda/6$ is small, the factors tend to cancel. Including $1 - \lambda/6$ on the right introduces a decrease of 0.3%. Including it on the left decreases the left side by 0.44%. Therefore the total correction is 0.14%. It is believed that the elimination of the technique step of setting up a linear gradient helps the reproducibility of the experiments and saves time and materials. Some preliminary calibration data with KCl showed that omission of the pre-run was valid within the experimental accuracy.

All cell calibrations and diffusion coefficients reported here were obtained with the following initial conditions:

1. The pure solvent was in the diaphragm and one of the cell compartments at time zero.
2. The concentrated solution was in the other cell compartment at time zero.

RESULTS AND DISCUSSION

The diffusion coefficient data are shown in Figs. 5, 6, and 7. The viscosity data are shown on Figs. 8, 9, and 10. All experimental data are tabulated in Appendix E.

Table III compares the diffusion coefficients and viscosities for the pure solvents with those measured by Chang,⁴ and compares the diffusion coefficients with those predicted by Eq. (5). The difference in the experimental diffusion coefficients may be due to quality differences in the solvents or due to a possible error in Chang's assumption that Beer's law was obeyed for the spectrophotometric analysis.

Table III

Diffusion of toluene in pure solvents					
Solvent	$D \times 10^5$ (cm ² /sec)			μ (cp)	
	This study	Chang	Calc. Eq. (6)	This study	Chang
	at 25.1°C	at 25.0°C	at 25.0°C	at 25.1°C	at 25.0°C
Hexane	4.62	4.21	3.81	0.308	0.304
Decane	2.24	2.09	1.79	0.840	0.860
Tetradecane	1.08	1.02	0.87	2.035	2.12
Cyclohexane	1.81		1.32	0.881	

Correlation of D_u with solvent mol fraction

Figures 11 and 12 show that, for the hexane-tetradecane and hexane-cyclohexane systems, D_u is a linear function of the composition (mol fraction) of the solvents. Figure 13 shows that D_u versus mol fraction cyclohexane for the decane-cyclohexane solvent exhibits a definite minimum which corresponds to a similar minimum in the viscosity data for that solvent. The first two systems did not show a minimum or maximum in their viscosity-versus-composition curves. Even though the decane-cyclohexane system exhibited a definite minimum in its D_u and μ data, a linear mol fraction average of D_u gave a correlation accurate to 10% over the entire composition range. This method of correlation was accurate to better than 5% for the other two systems.

MU-19958

Fig. 5. Diffusion coefficient of toluene in hexane-tetradecane.

MU - 19959

Fig. 6. Diffusion coefficient of toluene in hexane-cyclohexane.

MU - 19960

Fig. 7. Diffusion coefficient of toluene in cyclohexane-decane.

MU-19961

Fig. 8. Viscosity of the hexane-tetradecane system.

MU-19962

Fig. 9. Viscosity of the hexane-cyclohexane system.

Fig. 10. Viscosity of the cyclohexane-decane system.

Fig. 11. Diffusion coefficient - viscosity product for the hexane-tetradecane system.

MU - 19965

Fig. 12. Diffusion coefficient - viscosity product for the hexane-cyclohexane system.

MU-19966

Fig. 13. Diffusion coefficient - viscosity product for the cyclohexane-decane system.

Correlation with the Eyring parameters

Table IV shows that the maximum deviation from linearity in mol fractions for the group $(\rho_m/M_m)^{1/3}$ is about 3% for all three systems. This is consistent with the assumption that D_μ is linear in mol fraction. However, division of D_μ by $(\rho_m/M_m)^{1/3}$ does not give a constant as suggested by Eq. (4b). It is interesting to note that $D_\mu (M_m/\rho_m)^{1/3}$, for the arbitrary units used, is almost identically equal to the average number of carbon atoms in the solvent molecules. The minimum in the D_μ data for the decane-cyclohexane system indicates that the free energies of activation for diffusion and viscosity are not the same or that (λ_D/λ_μ) is not unity.

Correlation using the Wilke-Chang equation

The addition of the solvent size parameter $(x^o M_m)^{1/2}$, suggested by Eq. (6), should make $D_\mu/(x^o M_m)^{1/2}$ a constant. Table V shows that although the $D_\mu/(x^o M_m)^{1/2}$ group is relatively constant for the hexane-tetradecane solvent, it varies by up to 17% for the other two solvent mixtures. This variation is probably due to the inability of the correlation to predict the binary diffusion coefficients. It is also shown on Table V that Eq. (5) is as applicable to a mixed solvent as it is to a single solvent if a mole fraction average molecular weight is used. Using Eq. (5) gives results accurate to 15 to 27%. Using an average value of $D_\mu/(x^o M)^{1/2}$ group for the binary data only, gives the mixture diffusivities accurate to better than 15% if the mixture viscosity is known. It would be preferable to use experimental binary diffusivities to determine the constant for Eq. (6) rather than using Eq. (5) for prediction of the diffusion coefficient for a mixed solvent.

Test of Eq. (8)

Table VI shows that Eq. (8) does approximately predict the diffusion coefficients for the hexane-tetradecane and decane-cyclohexane systems when the binary diffusion coefficients are known. The equation predicts the wrong trend for the hexane-cyclohexane system, with a maximum error of about 30%. The validity of using Eq. (8) for weighting the binary diffusivities without considering the system viscosity is doubtful for liquid mixtures.

Table IV

Correlation with the Eyring parameters								
Hexane-Tetradecane System								
Mol fraction hexane	1.00	0.887	0.785	0.664	0.499	0.328	0.197	0.00
$(\rho_m/M_m)^{1/3}$	0.196	0.188	0.183	0.178	0.172	0.166	0.162	0.151
$D\mu(M_m/\rho_m)^{1/3} \times 10^5$	7.23	7.82	8.36	9.27	10.9	11.9	12.7	14.0
Hexane-Cyclohexane System								
Mol fraction hexane	1.00	1.00	0.768	0.452	0.262	0.00		
$(\rho_m/M_m)^{1/3}$		0.196	0.120	0.204	0.206	0.209		
$D\mu(M_m/\rho_m)^{1/3} \times 10^5$		7.23	7.32	7.67	7.73	7.65		
Decane-Cyclohexane System								
Mol fraction hexane		1.00	0.754	0.492	0.241	0.00		
$(\rho_m/M_m)^{1/3}$		0.209	0.198	0.187	0.179	0.173		
$D\mu(M_m/\rho_m)^{1/3} \times 10^5$		7.65	7.70	8.40	9.18	10.3		

Correlation using the Wilke-Chang equation

Hexane-Tetradecane System

Mol fraction hexane	1.00	0.887	0.785	0.664	0.499	0.328	0.197	0.00
------------------------	------	-------	-------	-------	-------	-------	-------	------

(a) $D \times 10^5$	4.62	3.57	2.90	2.38	1.92	1.58	1.37	1.08
(b) $D \mu / (x^\circ M_m)^{1/2}$	0.153	0.150	0.145	0.147	0.157	0.156	0.155	0.156
(c) $D \times 10^5$	3.81	3.08	2.52	2.04	1.58	1.28	1.12	0.87
(d) $D \times 10^5$	4.65	3.77	3.08	2.49	1.89	1.56	1.36	1.06

Mol fraction hexane	1.00	0.768	0.452	0.262	0.00
------------------------	------	-------	-------	-------	------

(a) $D \times 10^5$	4.62	4.10	3.37	2.78	1.81
(b) $D\mu/(x^\circ M_m)^{1/2}$	0.153	0.157	0.169	0.173	0.174
(c) $D \times 10^5$	3.81	3.29	2.51	2.02	1.32
(d) $D \times 10^5$	4.91	4.26	3.26	2.64	1.72

Mol fraction cyclohexane	1.00	0.754	0.492	0.241	0.00
-----------------------------	------	-------	-------	-------	------

(a) $D \times 10^5$	1.81	1.87	1.94	2.00	2.24
(b) $D\mu / (x^\circ M_m)^{1/2}$	0.174	0.153	0.147	0.145	0.158
(c) $D \times 10^5$	1.32	1.54	1.66	1.75	1.79
(d) $D \times 10^5$	1.73	2.03	2.19	2.30	2.35

- (a) Experimental diffusion coefficient.
- (b) Experimental diffusion coefficient and viscosity data and a mol fraction average molecular weight. ($\times 10^2$)
- (c) D calculated with equation (5) using experimental viscosity data and a mol fraction average molecular weight.
- (d) D calculated using mean value of $D_H/(x^0 M)^{1/2}$ and experimental viscosity data.

Table VI

Correlation with Equation (8),

$$D_{lm} = \frac{1.0}{x_2/D_{12} + x_3/D_{13}}$$

Hexane-Tetradecane System

Mol fraction hexane	1.00	0.887	0.785	0.664	0.499	0.328	0.197	0.00
(a) $D \times 10^5$	4.62	3.57	2.90	2.38	1.92	1.58	1.37	1.08
(b) $D \times 10^5$	4.62	3.38	2.79	2.20	1.75	1.53	1.27	1.08

Hexane-Cyclohexane System

Mol fraction hexane	1.00	0.768	0.452	0.262	0.00
(a) $D \times 10^5$	4.62	4.10	3.37	2.78	1.81
(b) $D \times 10^5$	4.62	3.40	2.49	2.15	1.18

Decane-Cyclohexane System

Mol fraction cyclohexane	1.00	0.754	0.492	0.241	0.00
(a) $D \times 10^5$	1.81	1.87	1.94	2.00	2.24
(b) $D \times 10^5$	1.81	1.90	2.00	2.12	2.24

(a) Experimental diffusion coefficient.

(b) D calculated by Eq. (8).

CONCLUSIONS

A general correlation for diffusion in mixed solvents can not be obtained without more data on other types of solutes and on solvents of more than two components. For the three systems studied, a linear mol fraction average of the diffusion coefficient - viscosity product for the pure solvents correlated the data for the mixed solvent accurately to about 10%. However, the decane-cyclohexane system showed a definite minimum when correlated this way.

If the binary diffusivities are not available, the Wilke and Chang correlation (with a mol fraction average molecular weight) can be used to estimate the mixture diffusion coefficient if the mixture viscosity is known. The validity of this procedure appears to be limited by the accuracy with which the correlation can predict the binary diffusion coefficients.

The harmonic weighting of the binary diffusivities [Eq. (8)] suggested by Bird et al. was found to be invalid for liquid mixtures.

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APPENDIX A DERIVATION OF CELL EQUATION CONSIDERING EXTERNAL MASS-TRANSFER RESISTANCE

The process of mass transfer from one compartment of a diaphragm cell to the other consists of three steps:

- (a) The transfer through the boundary layer in the compartment containing the concentrated solution.
- (b) The diffusion through the sintered glass disk.
- (c) The transfer through the boundary layer in the compartment containing the dilute solution.

Considering the pseudo-steady-state operation,

$$N = k_1 A (C_1 - C_{1i}) = DA' / l (D_{1i} - C_{2i}) = k_2 A (C_{2i} - C_2),$$

$$N = \frac{C_1 - C_{1i}}{1/kA} = \frac{C_{1i} - C_{2i}}{1/DA'} = \frac{C_{2i} - C_2}{1/k_2 A},$$

$$N = \frac{C_1 - C_2}{1/k_1 A + 1/DA' + 1/k_2 A}.$$

Assume k_1 equals k_2 ; then

$$N = \frac{C_1 - C_2}{2/kA + 1/DA'}.$$

If the volume of the diaphragm is neglected, a material balance on each side of the diaphragm gives

$$V_1 \frac{dC_1}{dt} + \frac{C_1 - C_2}{2/kA + 1/DA'} = 0,$$

$$V_2 \frac{dC_2}{dt} + \frac{C_2 - C_1}{2/kA + 1/DA'} = 0;$$

let $\theta = [2/kA + 1/DA']$,

then $dC_1 + (C_1 - C_2)/V_1 \theta = dC_2 + (C_2 - C_1)/V_2 \theta$,

$$d C_1 - d C_2 = [(C_1 - C_2)/V_1] \theta dt + [(C_1 - C_2)/V_2] \theta dt,$$

$$d \Delta C / \Delta C = (1/V_1 + 1/V_2) \theta dt.$$

Assume D and k are constant; then

$$\ln \Delta C_1 / \Delta C_f = (1/V_1 + 1/V_2) t / \theta,$$

$$\theta = (2/kA + 1/DA') = 1/D (2D/kA + 1/A').$$

Therefore

$$\ln \Delta C_1 / \Delta C_f = (1/V_1 + 1/V_2) \left[\frac{1}{2D/kA + 1/A'} \right] D t$$

or

$$\ln \Delta C_1 / \Delta C_f = \beta D t, \quad (9)$$

which reduces to the more common expression for the cell equation, where the external mass transfer resistance is neglected or $k \rightarrow \infty$,

$$\ln \Delta C_1 / \Delta C_f = (1/V_1 + 1/V_2) (A'/1) D t,$$

$$\ln \Delta C_1 / \Delta C_f = \beta' D t.$$

APPENDIX B

APPLICATION OF THE SOLUTION BY BARNES TO A DIFFUSION CELL

Barnes² has derived the following equations, which describe the diffusion through a diaphragm with the initial conditions

- (a) The diaphragm and one of the compartments are filled with the pure solvent at time zero.
- (b) The other compartment is filled with the concentrated solution at time zero.

$$C_1 = \frac{C_1^0}{2} \left[1 - \frac{\lambda}{2} + \frac{\lambda^2}{4} + \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{60} \right) \exp \left\{ - \frac{2DA't}{1V_1} \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{45} \right) \right\} \right] \\ + \sum_{i=1}^{\infty} \frac{4\lambda}{\pi^2 i^2} \left(1 - \frac{6\lambda}{2\pi^2} \right) \exp \left\{ - \frac{Dt}{1^2} (i^2 \pi^2 + 4\lambda) \right\}, \quad (a)$$

$$C_2 = \frac{C_1^0}{2} \left[1 - \frac{\lambda}{2} + \frac{\lambda^2}{4} - \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{60} \right) \exp \left\{ - \frac{2DA't}{1V_2} \left(1 - \frac{\lambda}{6} + \frac{\lambda^2}{45} \right) \right\} \right] \\ + \sum_{i=1}^{\infty} (-1)^i \frac{4\lambda}{i^2 \pi^2} \left(1 - \frac{6\lambda}{2\pi^2} \right) \exp \left\{ - \frac{Dt}{1^2} (i^2 \pi^2 + 4\lambda) \right\}, \quad (b)$$

where λ is the ratio of the free volume in the diaphragm to the volume of one compartment; $\lambda \approx 0.02$ for a typical cell. Therefore the λ^2 , 4λ , $6\lambda/i^2 \pi^2$ terms are small and can be dropped.

Considering only the summation terms, subtract (b) from (a):

$$\frac{4\lambda}{\pi^2} \left[\sum_{i=1}^{\infty} \frac{1}{i^2} \exp \left\{ - \frac{Dt}{1^2} i^2 \pi^2 \right\} - \sum_{i=1}^{\infty} (-1)^i \frac{1}{i^2} \exp \left\{ - \frac{Dt}{1^2} i^2 \pi^2 \right\} \right].$$

Expansion shows that the even terms of the first summation are canceled by the even terms of the second summation, and the odd terms after the first are very small compared with the first.

This leaves

$$\frac{4\lambda}{\pi^2} \left[\exp \left\{ -\frac{Dt \pi^2}{l^2} \right\} + \exp \left\{ -\frac{Dt \pi^2}{l^2} \right\} \right],$$

or

$$\frac{8\lambda}{\pi^2} \exp \left\{ -\frac{Dt \pi^2}{l^2} \right\}, \quad (c)$$

for the summation terms only.

In order that the ratio of the initial concentration difference to the final concentration difference should be about 2.0 for Eq. (13), the Dt product is held constant for all runs. For example, the calibration run uses a time of about 3.5×10^5 sec and D is about 3.0×10^{-5} cm²/sec. Therefore the combined summation terms (c) reduce to $0.0163 e^{-140}$, which is very small compared with the first terms of (a) and (b). The summation terms may be dropped completely.

Now, combining the first terms of (a) and (b) gives

$$\begin{aligned} C_1 - C_2 &= \frac{C_1^0}{2} \left(1 - \frac{\lambda}{2}\right) - \frac{C_1^0}{2} \left(1 - \frac{\lambda}{2}\right) + \left[\frac{C_1^0}{2} \exp \left\{ -\frac{2 DA' t}{l V_1} \left(1 - \frac{\lambda}{2}\right) \right\} \right] \left(1 - \frac{\lambda}{2}\right) \\ &+ \left[\frac{C_1^0}{2} \exp \left\{ -\frac{2 DA' t}{l V_2} \left(1 - \frac{\lambda}{2}\right) \right\} \right] \left(1 - \frac{\lambda}{2}\right), \end{aligned}$$

$$C_1 - C_2 = C_1^0 \left(1 - \frac{\lambda}{2}\right) \exp \left\{ \frac{2 DA' t}{l} \left(1 - \frac{\lambda}{2}\right) \left(\frac{1}{V_1} + \frac{1}{V_2}\right) \right\},$$

$$\ln \frac{C_1^0}{C_1 - C_2} \left(1 - \frac{\lambda}{2}\right) = \frac{Dt A'}{l} \left(1 - \frac{\lambda}{2}\right) \left(\frac{1}{V_1} + \frac{1}{V_2}\right),$$

or

$$\ln \left\{ \frac{\Delta C_1}{\Delta C_f} \left(1 - \frac{\lambda}{2}\right) \right\} = \beta' Dt \left(1 - \frac{\lambda}{2}\right)$$

$$\beta' = \frac{A'}{l} \left(\frac{1}{V_1} + \frac{1}{V_2}\right).$$

APPENDIX C

ELECTROCHEMICAL EXPERIMENT

Wilke, Tobias, and Eisenberg^{21,22} and Fenech⁷ have found that limiting current measurements in copper sulfate and silver perchlorate solutions are convenient means of obtaining mass-transfer coefficients for free flat electrodes and natural convection conditions. Wilke et al. confirmed that limiting current experiments were mass-transfer controlled by obtaining similar results from experiments on the dissolution of solid benzoic and salicylic acid plates.

The electrochemical method was used in this study to obtain a correlation of mass-transfer coefficients external to the diaphragm of a diaphragm diffusion cell. Both natural and forced convection were studied by using an electrochemical cell which was geometrically similar to one of the diffusion cell compartments.

Under limiting current conditions in electrolysis, the transport of ions to the cathode is controlled by diffusion and convection effects. An effective mass-transfer coefficient may be defined by

$$N = k (C_B - C_1) . \quad (a)$$

The rate of deposition, under limiting current conditions, is given by

$$N = (1 - t) I_L / n F , \quad (b)$$

where t is the proper effective transference number of the ion being deposited at the cathode averaged over the mass-transfer film, and I_L is the limiting current density. In the steady state (a) may be equated to (b):

$$N = (1 - t) I_L / n F = k (C_B - C_1) . \quad (c)$$

At the point of limiting current, C_1 is zero. Therefore a simple measurement of the limiting current gives the average mass-transfer coefficient from Eq. (c).

By varying the fluid properties and convection conditions, one can thus obtain a mass-transfer correlation for a specific cell and cathode geometry.

The experimental apparatus, other than the special cell used in this work, was discussed in detail by Fenech. The apparatus consisted of the electrolytic cell, shown in Fig. 3, for deposition of copper from copper sulfate - sulfuric acid solution on the copper cathode which was in the same position as the diaphragm of the diffusion cell. Auxiliary equipment was provided for recording the total cell current as a function of the cathode polarization.

The electrolytic cell was geometrically the same as the diffusion cell. The cathode was a smooth copper disk 5.0 cm in diameter. The cell volume was about 125 cm³. A 1-inch-long stirring bar was used to stir the cathode compartment. The copper anode was above and separated from the cathode compartment by a sintered glass disk. The anode compartment was stirred mechanically. The area of the anode was much greater than that of the cathode. The reference cell was a copper rod immersed in the same solution as was being used in the cell. It was connected to the cell by a capillary which ended inside the cell about 3 mm from the cathode. The measuring circuit was designed so that the amount of current through the reference cell was negligible.

The experimental procedure consisted of measuring the plateau in the current-potential curve for various convection conditions and solution properties.

The electrical circuit is shown schematically below.

A typical curve obtained for either free or forced convection conditions is shown below.

These curves were recorded on an X - Y recorder as the applied cell potential was slowly increased by a motor-driven rheostat.

APPENDIX D
CONVECTION CORRELATION DATA

A. Forced Convection

Solution	Stirring speed (rpm)	$Re = d^2 n \rho / \mu$	k (cm/sec)	$Nu' = kd/D$
I $Sc=2,520$	285	2355	0.883×10^{-3}	437
	283	2318	0.883	437
	500	4096	1.350	668
	490	4014	1.318	652
	455	3727	1.227	607
	470	3850	1.255	621
	510	4178	1.328	657
	715	5857	1.484	735
	705	5775	1.485	735
	180	1475	0.555	275
	125	1024	0.446	221
	213	1745	0.660	327
	308	2523	0.981	486
	417	3416	1.076	533
II $Sc=62,490$	520	723	2.440×10^{-4}	508
	390	542	2.133	444
	260	362	1.367	285
	190	264	1.186	247
	295	410	1.800	375
	225	313	1.186	247
	420	584	2.093	436
	400	556	2.100	533
III $Sc=14,880$	220	680	3.316×10^{-4}	359
	155	479	2.213	240
	440	1360	4.913	533
	550	1700	6.110	663
	635	1962	8.460	918
	250	772	3.359	364
	300	927	3.841	417
	360	1112	5.036	547
	410	1267	5.394	585
	510	1576	6.708	728

B. Free Convection

Solution	$Nu' = kr/D$	$Gr = r^3 g(\rho_B - \rho_i) \rho_{av} / \mu_{av}^2$	$Sc = \mu / \rho D$
I	154	2,479,000	2,316
II	161	86,720	62,360
III	182	788,200	12,800

APPENDIX D (cont'd.)

C. Physical Properties

Solution	Concentration			Density (gm/cm ³)	Viscosity (cp)	Dx10 ⁵ (cm ² /sec)
	H ₂ SO ₄	CuSO ₄ (mols/liter)	Glycerol			
I	1.495	0.259	0.00	1.124	1.457	0.513
II	0.745	0.380	5.90	1.205	9.310	0.122
III	1.143	0.587	3.10	1.177	4.093	0.234

APPENDIX E
CELL CONSTANT SUMMARY

Cell	$\beta \times 10^2$ (cm ⁻²)						Average	Maximum deviation (%)
1 ^a	2.949	2.718	3.041	3.058	3.070	2.758	2.93	7.2
2	3.628	3.542	3.578	3.530	3.676		3.61	2.0
3	3.245	3.374	3.276	3.343	3.329		3.31	2.0
4	3.446	3.491	3.349				3.44	1.4
5	3.328	3.319	3.360	3.369			3.34	0.7
9	2.468	2.442	2.478	2.506			2.47	1.3
10 ^a	2.949	3.048	3.077	2.975	3.062		3.02	2.4
12	2.332	2.312	2.330	2.365			2.33	1.3
13	2.637	2.660	2.655	2.689			2.66	1.1
14	2.467	2.471	2.414				2.45	1.5
25	1.936	1.916	1.945				1.94	1.3

^aCells 1 and 10 were not used to determine any diffusion coefficients.

APPENDIX F

(DATA)

Diffusion of toluene in hexane-tetradecane at $25.1 \pm 0.1^\circ\text{C}$

Mol fraction hexane	$D \times 10^5$ (cm^2/sec)	Average $D \times 10^5$	μ (cp)	$D_1 \times 10^5$	M_m (g/mol)	ρ (g/cm^3)
1.00	4.57 4.62 4.69 4.62	4.62	0.308	1.42	86.2	0.655
0.887	3.59 3.55	3.57	0.411	1.47	101	0.676
0.785	2.98 2.82	2.90	0.529	1.53	112	0.694
0.664	2.42 2.34	2.38	0.695	1.65	126	0.710
0.499	1.90 1.93	1.92	0.957	1.87	144	0.727
0.328	1.58	1.58	1.254	1.98	162	0.740
0.197	1.39 1.35	1.37	1.504	2.06	177	0.749
0.00	1.08 1.11 1.04 1.07	1.08	2.035	2.20	198	0.75

Diffusion of toluene in hexane-cyclohexane at $25.1 \pm 0.1^\circ \text{C}$

Mol fraction hexane	$D \times 10^5$ (cm^2/sec)	Average $D \times 10^5$	μ (cp)	$D \times 10^5$	M_m (g/mol)	ρ (g/cm^3)
1.00	4.57 4.62 4.69 4.62	4.62	0.308	1.42	86.2	0.655
0.768	4.10 4.09	4.10	0.355	1.46	85.7	0.679
0.452	3.43 3.31	3.37	0.464	1.56	85.1	0.715
0.262	2.83 2.74	2.78	0.574	1.59	84.7	0.737
0.00	1.87 1.84 1.72	1.81	0.881	1.60	84.2	0.774

Diffusion of toluene in cyclohexane-decane at $25.1 \pm 0.1^\circ\text{C}$

Mol fraction cyclohexane	$D \times 10^5$ (cm^2/sec)	Average $D \times 10^5$	μ (cp)	$D_\mu \times 10^5$	M_m (g/mol)	ρ (g/cm^3)
1.00	1.84 1.87 1.72	1.81	0.881	1.60	84.2	0.774
0.754	1.92 1.83	1.87	0.813	1.52	98.5	0.754
0.492	1.95 1.94	1.94	0.810	1.57	114	0.741
0.241	2.03 1.97	2.00	0.820	1.64	128	0.732
0.00	2.27 2.16 2.29	2.24	0.840	1.88	142	0.726

APPENDIX G

NOMENCLATURE

A	Area of the diaphragm	cm ²
A'	Area of the diaphragm open to mass transfer	cm ²
C	Solute concentration	mol/liter
ΔC_i	Initial concentration difference	mol/liter
ΔC_f	Final concentration difference	mol/liter
d	Diameter of stirring bar	cm
D	Diffusion coefficient	cm ² /sec
F	Faraday	Coulombs/g-eq.
$\Delta F^\ddagger$	Free energy of activation	calories
g	Gravity constant	cm/sec ²
h	Planck's constant	cm/sec ²
I	Planck's current density	ma/cm ²
k	Average mass-transfer coefficient or Boltzman constant	cm/sec
l	Effective pore length in the diaphragm	cm
M	Molecular weight	g/mol
n	Valence charge of an ion	
N ^O	Avogadro number	molecules/mol
R	Thermodynamic constant	
r	Radius of diaphragm	cm
T	Absolute temperature	°K
t	Transference number	
v	Molal volume at the normal boiling point	cm ³ /g mol
v'	Molal volume of solvent	cm ³ /g mol
V	Volume of a cell compartment	cm ³
x	Mol fraction	
x ^O	Association parameter for diffusion	
∇x	Gradient of mol fraction	

β	Cell constant	cm^{-2}
γ	Activity coefficient	
ρ	Density	g/cm^3
ψ	Size-shape parameter for diffusion	$\text{cm}^2\text{-cp}/\text{sec-}^\circ\text{K}$
μ	Viscosity	centipoise (cp)
λ	Volume of free space in diaphragm/volume of one cell compartment or Intermolecular and jump distances in Eyring theory	cm

Special sub- and superscripts

av	Properties averaged over the film resistance
B	Bulk solution properties
i	Properties at the interface
m	mol fraction average for a mixture
o	initial
1,2,...	components of a mixture or cell compartment number

Dimensionless Groups

Gr	Grashoff number for mass transfer
Nu'	Nusselt number for mass transfer
Re	Reynolds number
Sc	Schmidt number

	Forced Convection	Free Convection
Gr	----	$r^3 g(\rho_B - \rho_i) \rho_{av} / \mu_{av}^2$
Nu'	$(kd/D)_B$	$(kr/D)_{av}$
Re	$(d^2 n \rho / \mu)_B$	----
Sc	$(\mu / \rho D)_B$	$(\mu / \rho D)_{av}$

BIBLIOGRAPHY

1. R. L. Baldwin, P. J. Dunlop, and L. J. Gosting, J. Am. Chem. Soc. 77, 5235 (1955).
2. Colin Barnes, Physics 5, 4 (1934).
3. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Notes on Transport Phenomena (Wiley, New York, 1958).
4. Pin Chang, Measurement and General Correlation of Diffusion of Non Electrolytes (Thesis) (Ph.D. in Chemical Engineering), University of California, Jan. 1954.
5. D. C. Douglass and D. W. McCall, J. Phys. Chem. 62, 1102 (1958).
6. P. J. Dunlop and L. J. Gosting, J. Am. Chem. Soc. 77, 5238 (1955).
7. Eugene J. Fenech, UCRL-3586, Nov. 1956.
8. H. Fujita and L. J. Gosting, J. Am. Chem. Soc. 78, 1099 (1956).
9. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes (McGraw-Hill, New York, 1941).
10. A. R. Gordon, Ann. N. Y. Acad. Sci. 46, 285 (1945).
11. R. S. Hufstedler, Statistical Correlation of Liquid Diffusion Coefficients for Dilute Binary Solutions (Thesis) (Ph.D. in Chemical Engineering), Colorado School of Mines, 1958.
12. P. A. Johnson and A. L. Babb, Chem. Revs. 56, 387 (1956).
13. J. B. Lewis, J. Appl. Chem. (London) 5, 228 (1955).
14. D. F. Othmer and M. S. Thakar, Ind. Eng. Chem. 45, 589 (1953).
15. E. G. Scheibel, Ind. Eng. Chem. 46, 2007 (1954).

16. I. E. Smith and J. A. Storrow, J. Appl. Chem. 2, 225 (1952).
17. R. H. Stokes, J. Am. Chem. Soc. 72, 763 (1950).
18. R. H. Stokes, J. Am. Chem. Soc. 72, 2243 (1950).
19. C. R. Wilke, Chem. Eng. Progr. 46, 95 (1950).
20. C. R. Wilke and P. Chang, A. I. Ch. E. Journal 1, 264 (1955).
21. C. R. Wilke, M. Eisenberg, and C. Tobias, J. Electrochem. Soc. 100, 513 (1953).
22. C. R. Wilke, C. Tobias, and M. Eisenberg, Chem. Eng. Progr. 49, 633 (1953).

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