

Molecular diffusion in a ternary liquid system with the diffusing component dilute

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(First received 3 October 1968; in revised form 6 February 1969)

Abstract—Experimental molecular diffusivity data were obtained for two ternary liquid systems with a dilute solute diffusing in a very non-ideal solvent mixture and a second dilute solute in a viscous solvent mixture using the diaphragm-cell method. Using only the diffusion data of the solute in each of the two pure solvents and viscosity data of the mixtures, a modified equation was shown to predict the diffusion data over the entire solvent mixture concentration range. A modified Wilke-Chang type equation was also used.

INTRODUCTION

THE THEORY for molecular diffusion of gases in three-component systems has been fairly well established by many investigators. However, less progress on experimental and theoretical work has been reported on molecular diffusion in ternary liquid mixtures. Significant progress has been made for the theory of binary liquid solutions as recently discussed by Cullinan [1].

For three components the process is complex since the interactions between the fluxes appear and, in general, the more nonideal the systems the more the interactions. Many processes for diffusion of liquids such as in absorption and extraction use a solute diffusing through not one but a mixture of solvents. It is often useful or necessary to utilize an effective binary diffusion coefficient for the solute in the solution mixture.

Often the solute diffusing in the solution mixture is relatively dilute. A simple method is needed to predict the diffusivity of this solute using readily available physical properties or parameters which can be predicted. When the mixture of the solution is highly nonideal or relatively viscous the few methods available in the literature given by Tang and Himmelblau [2] and Holmes *et al.* [3] have not been thoroughly tested and might not be applicable.

In the present research, experimental diffusivity coefficients for ternary systems for a dilute solute diffusing in a very nonideal solvent mixture and a second dilute solute in a viscous solvent mixture were obtained. The diaphragm cell method was used. The theory was reviewed for the various binary and multicomponent equations and for the effects of viscosity on the diffusion. A modified equation was shown to predict the diffusion data and that of others [2, 3] over the solvent concentration range. A modified Wilke-Chang type equation was also presented.

THEORY

Diaphragm cell

The basic equations for the diaphragm cell have been derived previously by Smith and Storrow [4], Barnes [5], and Gordon [6]. If the volumes of the two compartments on either side of the diaphragm are equal,

$$\log \left[\frac{C_0'' - C_0'}{C'' - C'} \right] = \beta Dt. \quad (1)$$

The quantity β is determined experimentally using the solute KCl of which the integral diffusion coefficient for dilute concentrations is well known. A value of 1.87×10^{-5} cm²/sec

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from Stokes[7] was used. Perkins[8] and Bidstrup and Geankoplis[9] give a detailed review on the use of this type cell.

Cullinan and Toor[10] showed that in the diaphragm cell method, the flux expression for the component which is dilute will reduce to the uncoupled form. Hence, Eq. (1) will be correct to use and there will be no volume or bulk flow present. This assumes the diaphragm is horizontal and density differences in the two solutions are small. Hartley and Runnicles[11] and Gordon[6] showed that if the pores are 2–5 μ in size streaming is eliminated. The diffusivity of the dilute solute can be considered as the integral coefficient at infinite dilution[12].

Binary diffusion

Using a hydrodynamic theory approach, the following Stokes–Einstein equation is derived [13].

$$D_{12} = \frac{RT}{N6\pi r\eta_2}. \quad (2)$$

This has been shown to apply well to only large solute molecules diffusing in a solvent and D_{12} is inversely proportional to $\eta_2^{1.0}$ [14]. In the absolute reaction rate theory used by Eyring[13] the solute molecule must surmount an energy barrier and D_{12} is inversely proportional to $\eta^{1.0}$. Kamal and Canjar[13] have employed the statistical-mechanical approach for binary liquids. The effect of viscosity is not readily

$$D_{1m} = \frac{D_{13}D_{12}(1-X_1) - X_1D_{12}D_{23}\nabla X_2/\nabla X_1 - X_1D_{13}D_{23}\nabla X_3/\nabla X_1}{X_1D_{23} + X_2D_{13} + X_3D_{12}}. \quad (5)$$

apparent from these equations. Arnold[15] applied the classical kinetic theory of gases to the liquid state and found the diffusivity to be inversely proportional to $\eta^{0.5}$.

Wilke and Chang[16] presented an empirical equation based on the Stokes–Einstein equation and Eyring's rate theory as follows:

$$D_{12}^0 = \frac{7.4 \times 10^{-8}(\rho M_2)^{1/2}T}{\eta_m V_1^{0.6}}. \quad (3)$$

All of the data used were for solutions of limited viscosity range. Many modifications of Eq. (3) have been proposed[14].

When the binary is nonideal the correction factor to the diffusivity is $(1 + \partial \ln \gamma_1 / \partial \ln X_1)$ [17]. Bidlack and Anderson[17] found that the correction factor over corrects by up to several hundred per cent.

To find out the effect of a wide range of viscosity on the diffusion coefficient, Davies *et al.* [15] measured the diffusivity of dilute carbon dioxide in single organic and hydrocarbon liquids. Over a range of viscosity of 0.4–26.5 cP or a range of 65/1, they found their diffusivity data correlated with $1/\eta^{0.5}$ as predicted by the Arnold theory. Hollander and Barker[18] measured the diffusivity of sodium chloride in glycerol with a viscosity of 580 cP. If one compares this to the value in water the diffusivity is approximately proportional to $1/\eta^{0.7}$.

Cullinan[19] derived the following by modifying Eyring's absolute reaction rate theory.

$$D_{ij} = (D_{ij}^0)^{X_j} (D_{ji}^0)^{X_i} (1 + d \ln \gamma_i / d \ln X_i). \quad (4)$$

He finds a very good check of Eq. (4) with experimental data for low viscosity mixtures.

Ternary diffusion

Bird *et al.*[20] used the Stefan–Maxwell equations to derive the diffusivity for component 1 in a mixture m of 1, 2 and 3.

For X_1 small,

$$D_{1m} = \frac{1}{X_2/D_{12} + X_3/D_{13}}. \quad (6)$$

The flux and D_{1m} are related by [21]

$$N_1 = -CD_{1m}\nabla X_1. \quad (7)$$

However, no references are made to the viscosity of the system. Holmes *et al.*[3] and Tang and Himmelblau[2] found that this equa-

tion gave deviations up to 30 per cent for low viscosity mixtures.

Lightfoot *et al.*[21] derived for the diffusion of dilute *A* through *B* and *C* for *A* not associated with the solvent,

$$\frac{1}{D_{Am}} = \frac{\nabla \ln X_A}{\nabla \ln a_A} \left[\frac{X_B}{D_{AB}} + \frac{X_C}{D_{AC}} \right]. \quad (8)$$

Cullinan and Cusick[22] derived Eq. (9) for dilute species 1 in a mixture of two solvents for completely miscible, non-associating systems.

$$D_{1m} = \frac{X_2}{(D_{12}^0)^{X_2} (\alpha_{12}^2 D_{23}^0)^{X_3}} + \frac{X_3}{(D_{13}^0)^{X_3} (\alpha_{13}^2 D_{32}^0)^{X_2}}. \quad (9)$$

The equation predicts well the data for relatively non-viscous and non-associating hydrocarbons of Holmes *et al.*[3] and Cullinan and Toor[10]. Since this holds only for miscible solutions it cannot be used for systems containing solutes such as KCl and CO₂. No provision is included for the effects of highly viscous materials.

Starting with the absolute rate theory equation as modified by Olander[23] and Tang and Himmelblau[2] the following can be written for diffusion of dilute component 1 through a mixture, *m*, of 2 and 3.

$$\left(\frac{\zeta}{k}\right) \left(\frac{D_{1m}\eta_m}{T}\right) \left(\frac{V_m}{N}\right)^{1/3} \cong \exp\left(\frac{\Delta F_{\eta}^* - \Delta F_D^*}{RT}\right)_{1m}. \quad (10)$$

Here the ΔF^* is the free energy of activation for viscous flow and ΔF_D^* for diffusion.

Writing the relation between the viscosity and $\Delta F_{\eta_m}^*$ for the mixture,

$$\eta_m = \frac{hN}{V_m} \exp\left(\frac{\Delta F_{\eta_m}^*}{RT}\right). \quad (11)$$

Olander[23] divided the free energies of activation into two parts for Eq. (10) and this can be written for the bond breaking contribution to give for a mixture[2]

$$(\Delta F_{\eta}^* - \Delta F_D^*)_{1m} = \Delta F_m^j - \Delta F_{1m}^j. \quad (12)$$

He defines the ratio ϵ as $\Delta F_m^j / \Delta F_{\eta_m}^*$.

Combining the above equations, using the exponential mixing rule of Tang and Himmelblau[2] where this is considered as the jump frequency of the molecules, and neglecting the variation with composition of the molar volume to a small power ranging from +0.13 to -0.17, the following is derived.

$$D_{1m}\eta_m^{1-\epsilon} = X_2 D_{12}\eta_2^{1-\epsilon} + X_3 D_{13}\eta_3^{1-\epsilon}. \quad (13)$$

Tang and Himmelblau[2] used a value of ϵ of 0.5 in their derivation as recommended by Olander[23] and did not carry through the general equation containing ϵ . They found

$$D_{1m}\eta_m^{0.5} = X_2 D_{12}\eta_2^{0.5} + X_3 D_{13}\eta_3^{0.5}. \quad (14)$$

Using instead another linear mixing rule by Eyring *et al.*[2] for predicting the viscosity of a liquid mixture, the final equation can be re-derived as

$$\log(D_{1m}\eta_m^{1-\epsilon}) = X_2 \log(D_{12}\eta_2^{1-\epsilon}) + X_3 \log(D_{13}\eta_3^{1-\epsilon}). \quad (15)$$

For $\epsilon = 0.5$ this reduces to the following as used by Tang and Himmelblau[2].

$$\log(D_{1m}\eta_m^{0.5}) = X_2 \log(D_{12}\eta_2^{0.5}) + X_3 \log(D_{13}\eta_3^{0.5}). \quad (16)$$

Holmes *et al.*[3] used the mole fraction average of the activation energies and derived

$$D_{1m}\eta_m = X_2 D_{12}\eta_2 + X_3 D_{13}\eta_3. \quad (17)$$

From the discussion on the effect of viscosity on the binary diffusion coefficients, the exponent of η could be expected to be between 0.5 and 1.0. Hence, it appears that investigating various systems experimentally should help develop the proper expression to use.

EXPERIMENTAL METHODS AND RESULTS

The diaphragm cell used in this work is similar to that of Stokes[7]. The diaphragm was a porous glass disk with pore sizes of 4.5–5.0 μ . Magnetic stirrers in the two compartments were rotated

at 120 RMP by a permanent magnet turning outside the cell. The system was immersed in a bath at $25.0 \pm 0.10^\circ\text{C}$. Details are given elsewhere [8]. The cell constant was determined using 0.1 N KCl solution with calibrations done at four different times spaced apart during the complete series of runs. The average cell constant β was determined to be 0.03440 cm^{-2} with the maximum deviation of a calibration run of 1.6 per cent from the mean value.

Experimental diffusion data were obtained for diffusion of acetic acid in a series of mixtures of ethanol-water and KCl in a series of mixtures of ethylene glycol-water. In all cases the solute was dilute and 0.1 N or less. These coefficients can be considered integral diffusion coefficients. The viscosities of the various mixtures were obtained from the literature [24-26]. The data are tabulated in Table 1. As a check on the accuracy of the data, the diffusivity value for acetic acid in water of $1.295 \times 10^{-5} \text{ cm}^2/\text{sec}$ compares very favorably with the values of $1.210-1.271 \times 10^{-5}$ reported elsewhere [9].

Using the data from Table 1 the diffusivities, D_{1m} , were predicted for the various mixtures using Eqs. (6), (14), (16), and (17). Also various values of ϵ were used in Eq. (13). The best value of ϵ found was 0.2 to give the following.

$$D_{1m}\eta_m^{0.8} = X_2D_2^{0.8} + X_3D_{13}\eta_3^{0.8}. \quad (18)$$

The average absolute deviations of the predicted diffusivities from the experimental values by the various methods are given in Table 2. The data of Tang and Himmelblau [2] and Holmes *et al.* [3] were also used in Table 2. The results for Eq. (6) were very poor as expected and are not tabulated.

DISCUSSION

If Eqs. (13), (14), (17) and (18) are valid, then the value of the right-hand side should be linear with X_2 . A plot of D_{1m} vs. η_{1m} was made on log-log paper for the system of acetic acid in ethanol-water and of KCl in ethylene-glycol-water in Fig. 1. It can be seen that both lines are approximately straight and parallel with a slope of about -0.8. Hence, as an approximation the exponent on the viscosity in Eq. (18) of 0.8 was tried. The range of viscosity changes was 20/1 for the KCl-ethylene glycol-H₂O system which was the greatest. The toluene-hexane-*n*-tetradecane system of Holmes *et al.* [3] was next largest with a 6.6/1 ratio.

In Figs. 2 and 3 the experimental diffusivity data for this work are plotted vs. the composition of the solvent. In Fig. 2 the diffusivity of acetic acid reaches a definite minimum at an intermediate composition of ethanol of about 40 per cent. This is not unexpected since the system is very nonideal and the viscosity also

Table 1. Diffusivity of solutes in various solvents at 25°C

Hydrocarbon (wt. %)	Mole fraction hydrocarbon (X_2)	Viscosity of solution η_m (cP)	Diffusivity of solute, $D_{1m} \times 10^5$ (cm^2/sec)
Acetic acid solute in ethanol-water			
0	0	0.8937	1.295
20	0.089	1.815	0.8906
40	0.207	2.350	0.5706
60	0.370	2.240	0.5972
80	0.610	1.748	0.6547
100	1.000	1.096	1.032
KCl solute in ethylene glycol-water			
0	0	0.8937	1.870
33.11	0.125	1.628	0.9022
60.84	0.311	4.508	0.4442
75.64	0.474	9.242	0.2938
100.00	1.000	18.09	0.1190

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Table 2. Average absolute deviations for predicting D_{1m}

No.	Diffusing solute	Solvents	Average absolute deviations (%)			
			Eq. (14)	Eq. (16)	Eq. (17)	Eq. (18)
I	Acetic acid	Ethanol-H ₂ O	25.3	24.8	14.7	8.5
II	KCl	Ethylene-glycol-H ₂ O	39.5	22.7	19.0	14.6
III	Toluene	<i>n</i> -hexane- <i>n</i> -tetradecane	8.8	5.8	2.2	1.5
IV		<i>n</i> -hexane-cyclohexane	6.5	8.3	2.0	4.3
V		Cyclohexane- <i>n</i> -decane	7.4	7.0	10.0	8.2
VI	CO ₂	Benzene-toluene	0.6	0.6	1.2	0.5
VII		CCl ₄ -benzene	1.6	1.8	2.1	1.6
VIII		Ethanol-H ₂ O	7.0	10.3	31.9	22.2

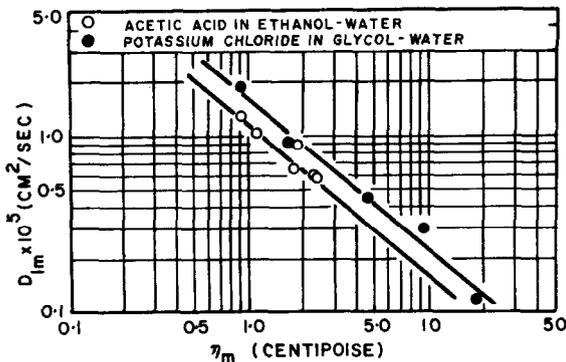


Fig. 1. Diffusivity vs. viscosity for data of this work.

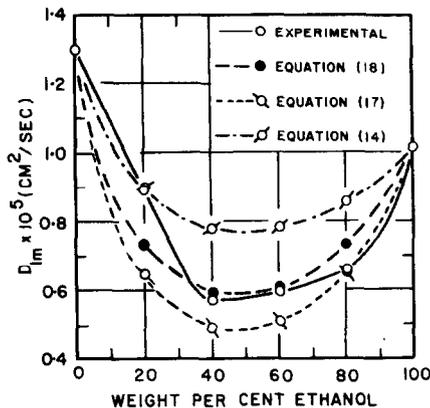


Fig. 2. Experimental and predicted diffusivities of acetic acid in ethanol-water.

behaves in a similar manner reaching a maximum. The system CO₂ in ethanol-water behaves in a similar manner but has a less pronounced dip. Equation (18) predicts the curve quite well

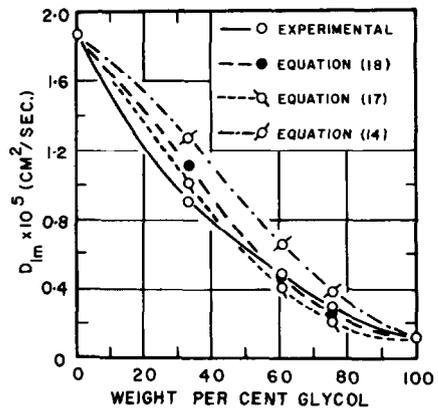


Fig. 3. Experimental and predicted diffusivities of KCl in ethylene glycol-water.

(Fig. 2) with an average deviation of 8.5 per cent as given in Table 2.

The diffusivity of KCl in ethylene glycol-water mixtures in Fig. 3 shows a very large change in going from 0 to 100 per cent glycol. Again Eq. (18) predicts the curve fairly well with an average deviation of 14.6 per cent. In these data the viscosity changes by a factor of 20/1.

In Fig. 4 a plot is made of the diffusivity vs. viscosity for the two systems toluene in *n*-hexane-*n*-tetradecane and toluene in *n*-hexane-cyclohexane of Holmes *et al.*[3]. Again the slopes of the lines are approximately -0.8 which is similar to the slopes in Fig. 1. The other data for the remaining systems were not plotted because of only small changes in viscosity.

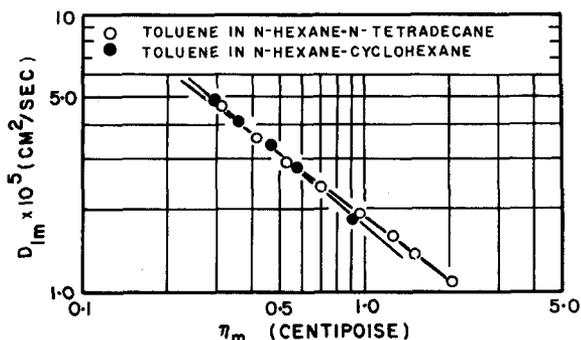


Fig. 4. Diffusivity vs. viscosity for data of Holmes, Olander and Wilke[3].

Comparison of Eqs. (14), (16), (17) and (18) in Table 2 shows that Eq. (18) is to be preferred. For the two very important systems acetic acid-ethanol-water which is very nonideal and KCl-ethylene glycol-water which has a very wide viscosity range, Eq. (18) predicts their behavior quite well and considerably better than the others. It also predicts accurately the hydrocarbon systems III, IV, and V and at least as well as Eqs. (14), (16), and (17) predict. All equations predict accurately the systems of CO_2 in benzene-toluene and in CCl_4 -benzene.

Equation (18) does not predict the CO_2 -ethanol-water system accurately with the average deviation being 22.2 per cent. Equations (14) and (16) perform better here but do not perform well on the very different systems I and II. However, Tang and Himmelblau[2] state that at high ethanol concentrations there is a serious discrepancy between the sources of the solubility data used in determining the diffusivity of CO_2 in a laminar jet of liquid. For Eq. (18) large deviations were found in the high concentration ranges.

There is also some question about the viscosity values for the ethylene glycol-water system at 33.11 and 75.64 wt.% as reported by Dunstan [25, 26]. He tabulates nine experimental points of viscosity covering the complete concentration range and also gives a smoothed curve representing his data. These two intermediate points when plotted on his curve are inconsistent when compared to the rest of the curve. Reading

values off his curve gives viscosities of 2.00 and 7.15 cP for the 33.11 and 75.04 wt.% solutions respectively. Using these new values, the predicted values of D_{1m} come considerably closer to the experimental values. For Eq. (18) the average deviation is reduced considerably from 14.6 per cent to only 4.6 per cent. For the other equations in Table 2 only the deviation for Eq. (17) changes appreciably from 19.0 to 7.6 per cent.

In Fig. 5 all of the experimental diffusivity data are plotted vs. the predicted values for Eq. (18). The data appear to be distributed evenly on both sides of the 45° line except for the CO_2 in ethanol-water system where the predicted values are consistently low. In summary, it is recommended that Eq. (18) be used for predicting the diffusivities of systems similar to those in Table 2. Care must be exercised in using it for systems which are completely different than these. More data are obviously needed.

It is interesting to note that the value of ϵ in Eq. (13) is 0.2 if the exponent of 0.8 is used as in Eq. (18). Bondi[27] states that a value for alcohols is 0.2-0.3 and 0.4-0.6 for hydrocarbons. This is not surprising since in Eq. (14) the value of ϵ is 0.5, and this equation holds well for the hydrocarbons and not as well for the systems with water. It is noted that since the change in viscosity of the hydrocarbons was relatively small, the results should be somewhat

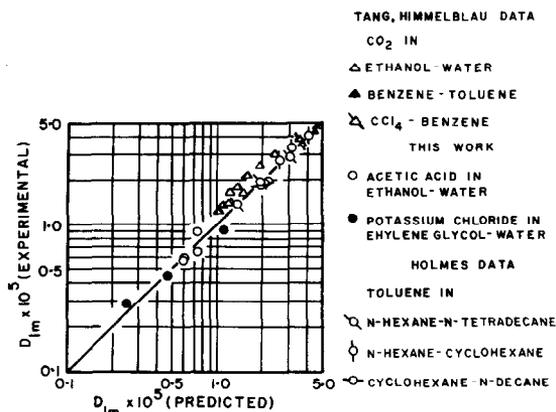


Fig. 5. Experimental diffusivity vs. diffusivity predicted by Eq. (18).

insensitive to the exponent on the viscosity terms. It should be pointed out that many assumptions were used in deriving Eqs. (13-18) so that too much faith should not be put in the value of ϵ found.

Use of the Wilke Eq. (3) was also tried for the estimation of the diffusivities for the acetic acid-ethanol-water system. A new equation can be written as

$$D_{1m} = \frac{7.4 \times 10^{-8} (\bar{\varphi} \bar{M}_{23})^{1/2} T}{\eta_m V_1^{0.6}} \quad (19)$$

The value in the parentheses can be defined as follows using a linear mixing rule.

$$\bar{\varphi} \bar{M}_{23} = X_2 \varphi_2 M_2 + X_3 \varphi_3 M_3 \quad (20)$$

Using the association factor $\varphi_2 = 1.5$ for ethanol and $\varphi_3 = 2.6$ for water [14], values of D_{1m} were predicted for the whole concentration range. The average deviation of the predicted data is 14.1 per cent. The values plotted in Fig. 6 show that this method is surprisingly good for such a nonideal system. No experimental data are needed for this method using the modified Eqs. (19) and (20).

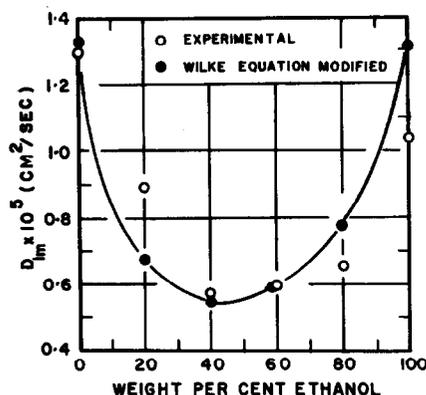


Fig. 6. Comparison of experimental diffusivities for the acetic acid in ethanol-water system and those predicted by the modified Wilke-Chang Eq. (19).

Acknowledgment—The Goodyear Rubber Company provided a fellowship for this work.

NOTATION

- a_i activity
- C total concentration, g mol/cm³
- C'_0 initial concentration in dilute side, g mol/cm³
- C'' final concentration in dilute side, g mol/cm³
- C''_0 initial concentration in concentrated side, g mol/cm³
- C' final concentration in concentrated side, g mol/cm³
- D diffusivity, cm²/sec
- D_{ij} diffusivity of i in j , cm²/sec
- D_{12}^0 diffusivity of 1 at very low concentration in 2, cm²/sec
- ΔF_{η}^* free energy of activation for viscous flow
- ΔF_D^* free energy of activation for diffusion
- ΔF_m^j bond breaking contribution to the free energy for a molecular mixture to move into a vacant site
- ΔF_{1m}^j same as above but the moving molecule is 1 and the mixture m
- h Planck constant
- k Boltzman constant
- M_i molecular weight of solvent i
- N Avagadro number
- R gas constant
- r radius of diffusing molecule
- T temperature, °K
- t time, sec
- V_i molal volume of solute i at normal boiling point, cm³/g mole
- X_i mole fraction of component i
- α_{12}^3 thermodynamic factor of component 3
- β cell constant, cm⁻²
- γ_i activity coefficient of component i
- ϵ factor defined as $\Delta F_m^j / \Delta F_{\eta_m}^*$
- ξ average number of nearest neighbors with respect to which the solute molecule moves (≈ 5.6).
- η viscosity of liquid, poises (centipoises in Eqs. (3) and (19))
- φ association factor of solvent

Subscripts

A, B, C components A, B, C

i, j	components i, j	<i>Superscripts</i>
m	mixture m	0 very low concentration
1,2,3	components 1,2,3	— average value

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Résumé—Les données expérimentales de diffusivité moléculaire ont été obtenues pour deux systèmes de liquide ternaire, avec un soluté dilué se diffusant dans un mélange non-idéal de solvants et avec un second soluté dilué dans un mélange visqueux solvant, au moyen de la méthode diaphragme-cellule. Une équation modifiée qui utilisait seulement les données de diffusion du soluté dans chacun des deux solvants purs et les données de viscosité du mélange, prévoyait les données de diffusion sur toute la gamme de concentration des mélanges de solvants. On a aussi utilisé une équation modifiée du type Wilke-Chang.

Zusammenfassung—Es wurden experimentelle Messwerte nach der Diaphragmazellenmethode für das molekulare Diffusionsvermögen zweier ternärer Flüssigkeitssysteme erhalten, wobei ein verdünnter, gelöster Stoff in eine nichtideale Lösungsmittelmischung und ein zweiter verdünnter, gelöster Stoff in eine zähflüssige Lösungsmittelmischung diffundierten. Unter ausschliesslicher Verwendung der Diffusionswerte des gelösten Stoffes in jedem der beiden reinen Lösungsmittel, und der Viskositätswerte der Mischungen, konnten mit Hilfe einer entsprechend modifizierten Gleichung die Diffusionsdaten über den gesamten Konzentrationsbereich der Lösungsmittelmischung vorausgesagt werden. Eine modifizierte Gleichung des Wilke-Chang Typs wurde ebenfalls verwendet.