

recycle rate 200% of the feed rate, a detention time of about 35 min., the provision of adequate contact time between the dichromate and surfactant, and the provision of adequate mixing of the polymer with the dichromate-surfactant particulates. A typical air requirement was 5.1 liters (at STP)/hr., delivered at 40 lb./sq. in. gauge, or 0.043 liters air (at STP)/liter of feed. With these conditions, feed streams containing from 25 to 100 mg./liter of dichromate could be treated effectively, producing effluent streams containing 10 mg./liter of dichromate and 30 mg./liter of surfactant (or containing 5 mg./liter of dichromate with a feed ratio of 2.7). For the 100 mg./liter of feed, for example, the total of 10,800 mg. of dichromate could be concentrated in a liquid volume (collapsed foam) of 0.9 liters, producing a foam concentration of 12,000 mg./liter and an enrichment ratio of 1,200.

Compared with diffused-air ion flotation in a 4-in. column, also at a 40-min. detention time and molar feed ratio of 2, but with no polymer and a feed rate of 3 liters/hr., the air requirement would be 27 liters of air (at STP)/liter feed, delivered at 3 lb./sq. in. gauge. A 100 mg./liter dichromate feed could be reduced to 40 mg./liter and a 25 mg./liter feed to 11 mg./liter, but at the expense of foam stream rates from 3 to 16% of the feed rate.

The dissolved-air ion flotation of dichromate, with a polymer flocculant aid, appears to be particularly promising for dichromate removal and recovery. The dichromate (and surfactant and probably the polymer) can be concentrated in a very small volume of liquid; this volume leads to further steps for the economical recovery of dichromate and of surfactant.

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NOTATION

- x_b = concentration of surfactant (EHDA-Br) in effluent stream, mg./liter
- x_1 = concentration of surfactant in feed stream, mg./liter
- x'_1 = concentration of surfactant in feed stream, mole/liter
- y_1 = concentration of polymer in feed stream, mg./liter
- z_b = concentration of dichromate, as Cr_2O_7 , in effluent stream, mg./liter
- z_f = concentration of dichromate in foam, mg./liter
- z_1 = concentration of dichromate in feed stream, mg./liter
- z'_1 = concentration of dichromate in feed stream, mole/liter

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A Predictive Theory for Diffusion in Mixed Solvents

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A relationship for the diffusion coefficient of a dilute species in a mixture of two solvents is developed. The result, based on the linear additivity of the frictional activation energy which is valid for completely miscible, nonassociated systems, predicts the diffusion coefficient of the solute in terms of the limiting values of the diffusion coefficient of the solute in each of the solvents, the limiting values of the solvent pair diffusion coefficient, and two thermodynamic factors. The equation is confirmed for some recent experimental data.

In systems consisting of more than two components, the characterization of the diffusion process is considerably more complex than that of the simple binary case in which only one properly defined diffusion coefficient is required. This, of course, is due to the appearance of interactions between the several flows, and, in general these effects are more pronounced the more nonideal the system.

In order to describe adequately the diffusional behavior

of such systems, one must adopt more general linear relations in which the flux of any species depends on all of the independent concentration gradients. In certain regions of the composition field of multicomponent systems, a simpler description is possible. A trivial example is the case in which all species are dilute in a single solvent. In this case the matrix of multicomponent diffusion coefficients reduces to diagonal form, the flux of each dilute

species depending only on its corresponding gradient with coefficient equal to the binary diffusion coefficient of the dilute species in the solvent.

A nontrivial case of such a reduction to uncoupled behavior (and one that is approximated in many absorption and extraction processes) is the diffusion of a single dilute species through a mixture of solvents. In this case the flux of the dilute species depends only on its own gradient, but the coefficient cannot, in general, be directly related to any binary diffusion coefficient. However, this coefficient must reduce to the appropriate binary diffusion coefficient as the solvent becomes pure.

In view of some recent successful predictions of the variation of the binary mutual diffusion coefficient with composition (4, 13) and the extension of these results to multicomponent systems (5), it appears possible to develop predictive relationships for the process of diffusion in mixed solvents. For simplicity, as well as to allow comparison with experimental data, the diffusion of a dilute species in a mixture of two concentrated species will be considered here.

THE THEORY

For a multicomponent system, isothermal isobaric diffusion in the absence of external forces may be described by the relations (2, 11)

$$-\nabla \mu_i = \sum_j F_{ij} c_j (\underline{V}_i - \underline{V}_j); \quad i = 1, 2, \dots, n \quad (1)$$

which serve to define the multicomponent friction coefficients. Consider the diffusion of a trace amount of species 1 through a mixture of 2 and 3. Equation (1) then takes the form

$$-\nabla \mu_1 = (F_{12} c_2 + F_{13} c_3) \underline{V}_1 \quad (2)$$

since the terms involving \underline{V}_2 and \underline{V}_3 vanish, because 1 is present in such small quantity that it imparts no bulk velocity to the other species (2). Furthermore, since the process can be viewed as one in which the trace species moves through a uniform environment (that is, the solvent is effectively stationary), the gradient of activity coefficient does not contribute to the flux (2). In this limiting case, one can write

$$\nabla \mu_1 = \lim_{c_1 \rightarrow 0} \frac{\partial \mu_1}{\partial c_1} \nabla c_1 = \frac{RT}{c_1} \nabla c_1 \quad (3)$$

Also, since the volume average velocity is effectively zero, the usual form is obtained

$$\underline{J}_1 = c_1 \underline{V}_1 = -(\lim_{c_1 \rightarrow 0} D_{11}) \nabla c_1 \quad (4)$$

where the coefficient appearing has been identified as the limiting value of the main ternary diffusion coefficient in the 1-2-3 mixture.

Combination of Equations (2) and (3) and comparison with Equation (4) show that

$$\lim_{c_1 \rightarrow 0} D_{11} = \frac{RT}{c} \frac{1}{x_2 \lim_{c_1 \rightarrow 0} F_{12} + x_3 \lim_{c_1 \rightarrow 0} F_{13}} \quad (5)$$

For ideal gases, the friction coefficients may be directly related to the corresponding binary diffusion coefficients, and Equation (5) used to generate the usual limiting Stefan-Maxwell equation for the effective coefficient in terms of the corresponding diffusion coefficients in each of the solvents (9, 12).

In liquid systems the friction coefficients are composition dependent and the above approach is no longer a valid one. However, recent results (4, 5, 13) with binary and ternary completely miscible, nonassociated liquid mixtures have demonstrated that if an activation energy is assigned

to each frictional interaction as follows

$$F_{ij} = \frac{hN}{ca^2} e^{\Delta G_{ij}/RT} \quad (6)$$

then the following mixture rule is valid

$$\Delta G_{ij} = \sum_k x_k \lim_{x_k \rightarrow 1} \Delta G_{ij} \quad (7)$$

which is equivalent to the requirement that the partial molar activation energies be independent of composition.

Substitution of Equation (7) into Equation (6) gives the friction coefficient in terms of the various limiting values of the activation energy. If Equation (6) is used once again to replace these activation energies in terms of limiting values of the friction coefficient, the following result is obtained by passing to the indicated limit:

$$c \lim_{x_i \rightarrow 0} F_{ij} = \frac{\prod_{k \neq i} (\lim_{x_k \rightarrow 1} F_{ij})^{x_k}}{\prod_{k \neq i} (V_k)^{x_k}} \quad (8)$$

Thus, for the case at hand, the friction coefficients appearing in Equation (5) are given in terms of their values at either extreme of the solvent composition field. These, in turn, may be written in terms of various limiting values of binary diffusion coefficients.

First of all, from the known binary limit (2)

$$\lim_{x_i + x_j \rightarrow 1} F_{ij} = \frac{RT}{\mathcal{D}_{ij} c} \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \quad (9)$$

one obtains directly

$$\lim_{x_j \rightarrow 1} F_{ij} = \frac{RT V_j}{\mathcal{D}_{ij}^0} \quad (10)$$

so that the coefficients,

$$F_{12} \text{ and } F_{13} \text{ at } x_2 \rightarrow 1 \text{ and } x_3 \rightarrow 1$$

are determined, and it remains to characterize the coefficients

$$F_{12} \text{ and } F_{13} \text{ at } x_3 \rightarrow 1 \text{ and } x_2 \rightarrow 1$$

In this regard, it has been shown that (5)

$$\lim_{x_k \rightarrow 1} F_{ij} = \frac{RT V_k}{\alpha_{ij}^k \mathcal{D}_{jk}^0} \quad i, j \neq k \quad (11)$$

where the α_{ij}^k 's are thermodynamic parameters given by

$$\alpha_{ij}^k = - \left[\frac{1}{RT V_k} \lim_{x_k \rightarrow 1} \mu_{ij}^k \right]^{-1} \quad (12)$$

and μ_{ij}^k is of the form

$$\left(\frac{\partial \mu_i}{\partial c_j} \right)_{c_\ell}, \quad \ell \neq j, k$$

The use of Equations (10), (11), and (8) in Equation (5) yields

$$\lim_{c_1 \rightarrow 0} D_{11} = \left[\frac{x_2}{(\mathcal{D}_{12}^0)^{x_2} (\alpha_{12}^3 \mathcal{D}_{23}^0)^{x_3}} + \frac{x_3}{(\mathcal{D}_{13}^0)^{x_3} (\alpha_{13}^2 \mathcal{D}_{32}^0)^{x_2}} \right]^{-1} \quad (13)$$

which gives the diffusion coefficient of the solute in terms of the limiting binary diffusion coefficients and the two thermodynamic parameters. Clearly, the utility of this relationship rests on the accessibility of these parameters. Certainly, in the absence of detailed thermodynamic data, evaluation of these directly from their definition as given by Equation (12) is impossible. However, evaluation by this route is unnecessary. A combination of results from classical and irreversible thermodynamics provides an independent means of evaluation.

On the one hand, since the friction coefficients obey the

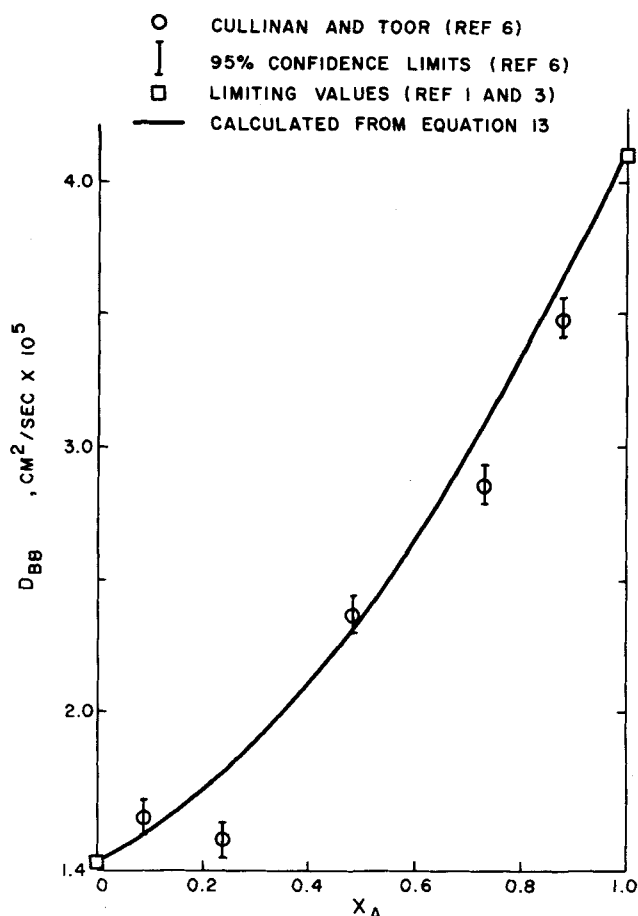


Fig. 1. The diffusion coefficient of benzene dilute in acetone, carbon tetrachloride at 25°C.

reciprocal relations, it follows directly from Equations (11) and (12) that

$$\mathcal{D}_{ik}^0 \lim_{x_k \rightarrow 1} \mu_{ij}^k = \mathcal{D}_{jk}^0 \lim_{x_k \rightarrow 1} \mu_{ji}^k \quad (14)$$

On the other hand, the derivatives μ_{ij}^k are themselves subject to symmetry requirements on purely thermodynamic grounds. For the derivatives in question here, these take the form

$$RTV_i + \lim_{x_k \rightarrow 1} \mu_{ij}^k = RTV_j + \lim_{x_k \rightarrow 1} \mu_{ji}^k \quad (15)$$

which can be obtained directly from a relationship given by Fitts (8).

Combination of Equations (12), (14), and (15) yields the desired result

$$\alpha_{ij}^k = \frac{V_k \left(1 - \frac{\mathcal{D}_{ik}^0}{\mathcal{D}_{jk}^0} \right)}{(V_i - V_j)} \quad (16)$$

In the evaluation of the thermodynamic parameters from Equation (16), difficulty is encountered in cases in which either $\mathcal{D}_{ik}^0/\mathcal{D}_{jk}^0$ or V_i/V_j is close to unity. When all species are similar (that is, an ideal solution), it can be shown that α_{ij}^k must be unity (5). Thus, in cases in which species i and j are similar, one expects $V_k/(V_i - V_j)$ to be on the order of $[1 - \mathcal{D}_{ik}^0/\mathcal{D}_{jk}^0]^{-1}$. On this basis, then, it can be shown that the error in the estimate of α_{ij}^k will be equal to the error in the estimate of the diffusivity ratio multiplied by a factor on the order of the reciprocal of $1 - \mathcal{D}_{ik}^0/\mathcal{D}_{jk}^0$. Hence, if $\mathcal{D}_{ik}^0/\mathcal{D}_{jk}^0$ is close to unity, large errors are to be expected.

This problem may be circumvented by recourse to the statistical mechanical theory of Bearman (2), in which it

is shown that the ratio of tracer diffusion coefficients is given by

$$\frac{D_i^{i-k}}{D_k^{i-k}} = \frac{V_k}{V_i} \quad (17)$$

for binary solutions in which the radial distribution functions are independent of composition and there is no volume change on mixing.

For solutions of this type then

$$\lim_{x_i \rightarrow 0} \frac{D_i^{i-k}}{D_k^{i-k}} - \frac{\mathcal{D}_{ik}^0}{\mathcal{D}_{jk}^0} = \frac{V_k}{V_i} \quad (18)$$

so that if both the i - k and j - k binaries follow Equation (17), it follows that

$$\frac{\mathcal{D}_{ik}^0}{\mathcal{D}_{jk}^0} = \frac{V_j}{V_i} \quad (19)$$

In this case Equation (16) becomes simply

$$\alpha_{ij}^k = \frac{V_k}{V_i} \quad (20)$$

Since Equation (17) is only expected to hold for mixtures of species of similar size (2), Equation (20) will only be valid for species of similar volumes.

On the basis of the above analysis, it appears reasonable to use Equation (20) in place of Equation (16) whenever $|1 - \mathcal{D}_{ik}^0/\mathcal{D}_{jk}^0| < 0.25$, provided that the resulting α_{ij}^k is not far removed from unity. This is particularly reasonable when the diffusivity ratio must be estimated from empirical correlations (14).

In addition to the thermodynamic factors, the limiting values of the diffusion coefficient of the dilute species in each of the solvents as well as the limiting values of the solvent mixture diffusion coefficient are required in Equa-

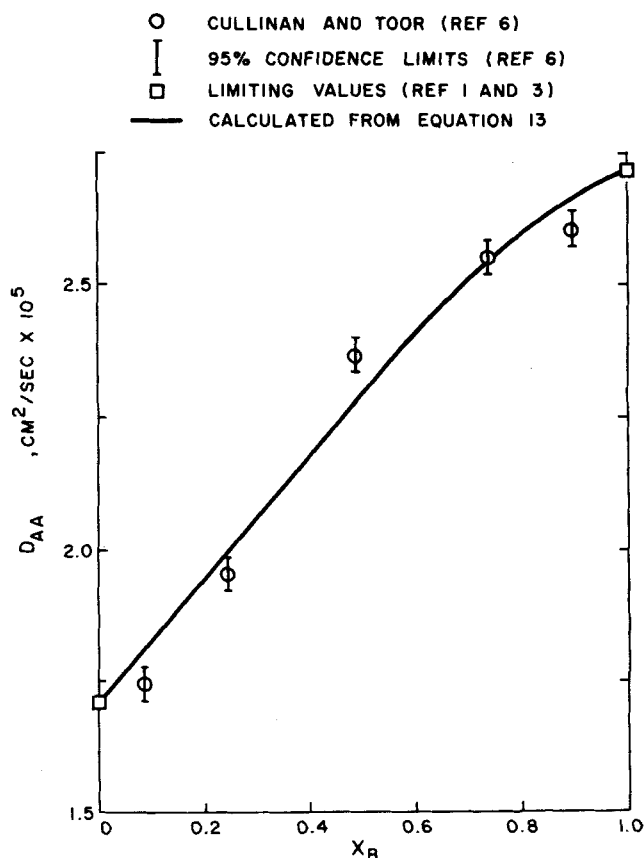


Fig. 2. The diffusion coefficient of acetone dilute in benzene, carbon tetrachloride at 25°C.

tion (13). It might also be pointed out that this equation may be obtained directly from the more general expressions of Cullinan and Cusick (5) for the friction coefficients of a multicomponent mixture using inverted forms of Dunlop's relations (7).

COMPARISON WITH EXPERIMENT

Several experimental investigations have been performed on diffusion in mixed solvents. Holmes et al. (9) studied the diffusion of dilute toluene in various solvent pairs (*n*-hexane, *n*-dodecane; *n*-hexane, cyclohexane; and cyclohexane, *n*-decane). Tang and Himmelblau (12) investigated the diffusion of carbon dioxide through mixtures of benzene, toluene; carbon tetrachloride, benzene; and ethanol, water. Cullinan and Toor (6) reported data for acetone dilute in benzene, carbon tetrachloride and benzene dilute in acetone, carbon tetrachloride.

Since the present theory is only applicable to completely miscible systems, the data of Tang and Himmelblau (12) do not fall within the present framework.

For the data of Cullinan and Toor (6), experimental values of all of the required limiting binary diffusion coefficients appearing in Equation (13) are available (1, 3, 6). In the calculation of the thermodynamic factor α_{AB} , the diffusivity ratio in Equation (16) is 1.20, so Equation (20) was used instead. Since the volume ratio on the right side of Equation (19) is also 1.20 in this case, the use of Equation (20) is clearly justified. For the factor α_{BC} the diffusivity ratio in Equation (16) is 1.17, so Equation (20) was again employed. In this case the volume ratio in Equation (19) is 1.10, indicating a small error of less than 6% in the use of Equation (20). For α_{AC} , Equation (16) was used directly since the diffusivity ratio was 1.44. The results were $\alpha_{AB} = 1.313$, $\alpha_{BC} = 0.828$, $\alpha_{AC} = 1.693$. Note that the factors calculated from Equation (20) are both reasonably close to unity.

In Figures 1 and 2 the experimental values are compared with the predictions of Equation (13). The data are somewhat scattered, yet the fit is essentially optimum in both cases. To confirm this, a univariate (sectioning) search on an IBM 7044 computer was performed which indicated that a response surface of the sum of the squares of the deviations of the coefficients calculated by Equation (13) from the measured values possessed a ridge which was essentially constant and minimum in the sum of squares. By employing the pattern search of Hooke and Jeeves (10), it was determined that the above values of the thermodynamic factors did indeed lie on the ridge.

Experimental values of the limiting diffusion coefficients of the various solvent pairs employed by Holmes et al. (9) are not available, thus precluding a direct test of Equation (13) for these systems. By using values estimated by the Wilke-Chang correlation (14) predictions were obtained with an average percent error of 6.0%, well within the accuracy of the required estimates.

CONCLUSIONS

A relationship giving the diffusion coefficient of a species dilute in a mixture of two solvents has been developed based upon the linear additivity of the frictional activation energy as expressed by Equation (7). This mixing rule has been confirmed (4, 5, 13) for binary and ternary diffusion in completely miscible, nonassociated liquid systems. Hence it is expected that the present result is valid for systems of this type. The direct utility of the result depends on a knowledge of the limiting binary diffusion coefficients of the solute in each of the solvents as well as those of each solvent in the other. It is felt that the rational scheme for the most efficient evaluation of the thermodynamic factors presented here will, in general, yield the best results. Unfortunately, a comprehensive test of these procedures is

not possible because of the absence of sufficient data for systems of this type.

The agreement with experiment as given here also provides further confirmation of the general theory (4, 5). It is also interesting to note that in the special case of diffusion in mixed solvents no thermodynamic data are required for the application of the results. Finally, these results are only valid when the solute is dilute. In nonideal systems, if the solute is present in appreciable amount, interaction effects must be taken into account and the simplified description is no longer valid.

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NOTATION

- a = distance between equilibrium positions
- c_i = molar concentration of species i
- c = total molar concentration
- D_{11} = main diffusion coefficient in multicomponent mixture
- \mathcal{D}_{ij} = binary mutual diffusion coefficient
- D_i^{i-j} = tracer diffusion coefficient of species i in an i - j binary
- D_k^k = self-diffusion coefficient of species k
- F_{ij} = friction coefficient
- ΔG_{ij} = activation energy for the i - j frictional interaction
- h = Planck constant
- J_1 = diffusional flux of species 1, volume reference frame
- N = Avagadro's number
- R = gas constant
- T = absolute temperature
- V_i = molar volume of species i
- \underline{V}_i = velocity of species i
- x_i = mole fraction of species i
- ∇ = gradient

Greek Letters

- α_{ij}^k = thermodynamic factor as defined by Equation (12)
- γ_i = activity coefficient of species i
- μ_i = chemical potential of species i
- μ_{ij} = derivative in Equation (12)

Subscripts

- i, j, k, ℓ = component i, j, k, ℓ
- 1, 2, 3 = component 1, 2, 3

Superscript

- 0 = infinite dilution of indicated species

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