Diffusion in the Ternary System d-Tartaric Acid—*l*-Tartaric Acid-Water at 25°C

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Ternary diffusion coefficients at 25°C. of the system 0.5 g./cc. *d*-tartaric acid—0.5 g./cc. *l*-tartaric acid-water are reported. The results allow experimental verification of the theory for the diffusion of two indistinguishable solutes and clearly illustrate the difference between mutual and tracer diffusion. Moreover, the results allow calculation of ternary mass transfer coefficients and ternary tray efficiencies for the case of two similar species dissolved in a third.

Since the first accurate experiments of Dunlop and Gosting in 1955 (*1*), multicomponent diffusion has been extensively studied. Of the various flux equations investigated, no single form has been found most convenient for all experimental cases. The generalized Fick's law form is most useful for liquids, while its firm basis in kinetic theory makes the Stefan-Maxwell equations best for dilute gases (*2*). The solution of both forms of flux equations by matrix techniques is understood for a large class of physical situations (*3, 4*). A surprising variety of ternary systems, including gases (*5*), electrolyte solutions (*6*), organic liquid mixture (*7*), and polymer solutions (*8*) have been reported. At least one four component study is in progress (*9*).

But in contrast with gases, the physical significance of ternary liquid diffusion coefficients has remained obscure. For example, the apparent magnitude of the coefficients can be changed by the choice of one component as the solvent, or by the use of molar concentration gradients rather than mass concentration gradients (*2*). Restraints such as electroneutrality or the Gibbs-Duhem equation, which are included in the flux equations, are also misleading. Wendt (*10*) showed that most ternary electrolyte data reported in the literature could be explained by writing general flux equations without restraints, assuming all cross terms were zero, and then building in the restraints. The restraints had effectively obscured any true nature of the diffusion coefficients.

This work attempts illumination of the physical significance of ternary diffusion coefficients by an experimental study of the system of *d*-tartaric acid—*l*-tartaric acid-water. The two solutes of this system react identically with water, since water is symmetric; for example, the activity coefficients of *d*-isomer solutions are within 0.1% of those of *l*-isomer solutions and those of racemic solutions (*11*). Hence, except for their reaction to polarized light, the solutes should be even closer to being indistinguishable than in tracer diffusion, where the different isotropic mass of the radioactive tracer plays an unknown role. However, one experimental fact belies the notion that the tartaric isomers are completely indistinguishable: the solubility of the racemate is one seventh of that of either isomer alone. While other compounds such as alanine do not show this solubility effect, the price of their individual isomers is prohibitive.

Various theories reported in the literature have attempted to calculate the physical significance of the ternary diffusion coefficients. One is a simple extension of the Stokes-Einstein equation in which the system is assumed to contain two kinds of spheres moving through a stagnant fluid (*12*); the cross term diffusion coefficients are simply hydrodynamic interactions between the spheres. Other methods have assumed a crystal lattice (*13*) or a modified Eyring model (*14*). Three papers have specifically discussed ternary systems with two indistinguishable solutes. Dunlop (*15*) used the Onsager reciprocal relations and knowledge of the limiting values of the diffusion coefficients in an attempt to derive a relation between tracer diffusion and binary diffusion. While the equations are correct, they contain indeterminate ratios of experimental quantities. The model of Albright and Mills (*16, 17*), which makes specific assumptions about the fluxes and gradients, obtains relations between the four ternary diffusion coefficients in terms of two independent quantities. Curran, Taylor, and Solomon (*18*) showed that Dunlop's equations reduced to those of Albright and Mills without any specific assumptions. These results are discussed in more detail below. In this discussion, we will assume that all diffusion coefficients are independent of concentration and that the optical isomers used here are equivalent to isotropic solutes.

THEORY

Diffusion in an isothermal, isobaric ternary system is described by the flux equations

$$-j_i = \sum_{j=1}^{2} D_{ij} \nabla C_j \quad i = 1, 2 \tag{1}$$

The quantities C_j and j_i may refer to either molar concentrations and fluxes, or mass concentrations and fluxes. The four diffusion coefficients are subject to the Onsager reciprocal relation, so that in general only three are independent. However, if two of the species in the system are indistinguishable, the diffusion coefficients are subject to still another restraint, so that only two coefficients are independent. More specifically, the coefficients may be shown to be (*15* to *18*)

$$D_{11} = \left(\frac{C_1}{C_1 + C_2}\right) D + \left(\frac{C_2}{C_1 + C_2}\right) D^{\dagger}$$

$$D_{12} = \left(\frac{C_1}{C_1 + C_2}\right) (D - D^{\dagger})$$

$$D_{21} = \left(\frac{C_2}{C_1 + C_2}\right) (D - D^{\dagger}) \tag{2}$$

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$$D_{22} = \left(\frac{C_2}{C_1 + C_2} \right) D + \left(\frac{C_1}{C_1 + C_2} \right) D^{\dagger}$$

where the subscripts 1 and 2 refer to *d* and *l* isomer, respectively. The quantities D and $D^{\dagger}$ are the eigenvalues of this matrix of diffusion coefficients. Their physical significance can be clarified by considering two special cases. First, regardless of the individual values of the fluxes, their sum

$$-(j_1 + j_2) = (D_{11} + D_{21}) \nabla C_1 + (D_{12} + D_{22}) \nabla C_2 = D \nabla (C_1 + C_2) \quad (3)$$

reduces to the binary form of Fick's law. Thus the eigenvalue D is seen to be the usual mutual diffusion coefficient, that which we would obtain for the diffusion of a racemic mixture.

The second case is that of intradiffusion, where the gradients of solutes 1 and 2 sum to zero. Intradiffusion occurs when *d* isomer diffuses into the ternary system *d* isomer—*l* isomer—water. Tracer diffusion occurs when *d* isomer, which is present only in small concentration, diffuses into either *d* isomer—water or *l* isomer—water. Self-diffusion occurs when radioactively labeled water diffuses into unlabeled water. In the case of intradiffusion, the combination of Equations (1) and (2) gives

$$-j_i = D^{\dagger} \nabla C_i \quad (i = 1, 2) \quad (4)$$

which again represents a binary flux equation. Parallel to the above, the eigenvalue $D^{\dagger}$ is seen to be the intradiffusion coefficient. Albright and Mills (*16, 17*) assumed Equation (4) to be correct, although the experimental basis of this assumption is uncertain. However, this assumption is unnecessary (*15, 18*).

One interesting feature of Equation (2) is that the mutual diffusion coefficient D and the intradiffusion coefficient $D^{\dagger}$ remain as independent parameters. This is sensible: Equation (1) contains four diffusion coefficients; if the Onsager reciprocal relations are valid, only three of these coefficients are independent, and if two species are indistinguishable, only two independent coefficients remain. Thus no phenomenological argument can give a relation between D and $D^{\dagger}$. Any relation between these quantities, such as the Hartley-Crank equation (*19*), must be empirical.

The physical significance of this result is best seen by considering the diffusion coefficients for a dilute gas mixture. These can be found from the Stefan-Maxwell relations (*2*) to be

$$\begin{aligned}
D_{11} &= \mathcal{D} \left(\frac{x_2 + x_3}{\mathcal{D}} + \frac{x_1}{\mathcal{D}_{12}} \right) \Big/ \left(\frac{x_3}{\mathcal{D}} + \frac{x_1 + x_2}{\mathcal{D}_{12}} \right) \\
D_{12} &= \mathcal{D} x_1 \left(\frac{1}{\mathcal{D}_{12}} - \frac{1}{\mathcal{D}} \right) \Big/ \left(\frac{x_3}{\mathcal{D}} + \frac{x_1 + x_2}{\mathcal{D}_{12}} \right) \\
D_{21} &= \mathcal{D} x_2 \left(\frac{1}{\mathcal{D}_{12}} - \frac{1}{\mathcal{D}} \right) \Big/ \left(\frac{x_3}{\mathcal{D}} + \frac{x_1 + x_2}{\mathcal{D}_{12}} \right) \qquad (5) \\
D_{22} &= \mathcal{D} \left(\frac{x_1 + x_3}{\mathcal{D}} + \frac{x_2}{\mathcal{D}_{12}} \right) \Big/ \left(\frac{x_3}{\mathcal{D}} + \frac{x_1 + x_2}{\mathcal{D}_{12}} \right)
\end{aligned}$$

where x_i is the mole fraction of species i, $\mathcal{D} = \mathcal{D}_{13} = \mathcal{D}_{23}$ is the mutual diffusion coefficient of the indistinguishable solutes, and $\mathcal{D}_{12}$ is the self-diffusion coefficient of the solutes. These equations imply that the concentration units used here are in moles per cubic centimeters and that the gaseous solutions are ideal. The two eigenvalues of these coefficients are

$$D = \mathcal{D} \quad (6)$$

and

$$D^{\dagger} = \left[\frac{x_3}{\mathcal{D}} + \frac{x_1 + x_2}{\mathcal{D}_{12}} \right]^{-1} \quad (7)$$

By use of these relations, the coefficients of Equation (5) may be rearranged to give the coefficients of Equation (2). Again, we see that D and $D^{\dagger}$ are independent since they refer to different weighted averages of different molecular collusions. No relation between these quantities can be found without reference to kinetic theory. Furthermore, Equation (7) shows that the intradiffusion coefficient will differ most from the binary diffusion coefficient if $\mathcal{D}_{12}$ is very different from $\mathcal{D}$ and if the solution is concentrated (that is, x_3 small). For example, the system Cl^{35}-Cl^{37}-H_2 would show much larger ternary effects than the system Cl^{35}-Cl^{37}-A.

The purpose of the experiments reported below in which $C_1 = C_2$ is to provide experimental verification of the analysis above. In these experiments, the solutes *d* tartaric acid and *l* tartaric acid will be used exactly as in a conventional ternary experiment. The analysis should evaluate all four ternary coefficients. If the analysis is correct, and if the solutes are truly indistinguishable, three conditions must be met:

1. When $\Delta C_{10} - \Delta C_{20} = 0$, the system should behave as a binary.
2. When $\Delta C_{10} + \Delta C_{20} = 0$, the system should behave as a binary.
3. Since $C_1 = C_2$, D_{12} should equal D_{21} and D_{11} should equal D_{22}.

EXPERIMENTAL PROCEDURE

Urea, *d* tartaric acid, and *l* tartaric acid were recrystallized once from solution. Reagent grade glycine and sucrose were used as received. Doubly distilled water was used in all experiments. All solutions were prepared by weight by using a Mettler B-6C200 balance, and weights corrected to vacuum by using densities of 1.330, 1.601, 1.984, 1.588, and 0.997047 g./cc. for urea, tartaric acid, potassium chloride, sucrose, and water, respectively. Solution densities were calculated from data in the literature (*20*).

Diffusion experiments were made by the diaphragm cell method (*21, 22*). The cell, which is constructed of 24 mm. Pyrex tubing, is shown in Figure 1. The cross bar of the T shaped cell forms a polarimeter cell 100 mm. in length, mounted directly in the optical path of the polarimeter. The vertical bar of the T is broken by an O ring seal. A 0.1μ Millipore filter (type VC) used in place of the usual fritted glass diaphragm was clamped across this O ring seal. Before use, the filter was soaked in water for 24 hr. The entire cell was stirred magnetically at 72 rev./min. with stirrers of thin walled glass tubing containing soft iron wire (*23*). The cell was sealed with stoppers similar to those used by Albright and Mills (*16*) and was emptied and filled with pipettes which discharged parallel to the filter (*22*). The cell compartments above and below this filter had volumes of 90.5 and 89.0 cc., so that the measured diffusion coefficients should correspond closely to the diffusion coefficient of the average concentration between compartments.

The accuracy of these experiments was limited to ±2% by a sharp compromise in the cell design. Obviously, if the length of the polarimeter cell were doubled, the solution concentration could be measured twice as accurately, or to the same accuracy with one half as large an initial concentration difference. But such a cell can not be stirred sufficiently fast so that the solution in the upper T shaped compartment remains homogeneous. Trial experiments with ink in the apparatus described above showed that the solutions in both the upper and the lower compartments were homogeneous during diffusion of the ink. As an additional precaution, the solution of greater density was placed in the top compartment so that free convection augmented the mechanical stirring. The filter position was horizontal to 0.002 in. to eliminate free convection between compartments (*24*).

The calibration constants of the Millipore filters were measured with urea by using diffusion and density data in the literature (25). Initial and final solution concentrations were measured with a differential refractometer. The calibration constants varied less than 1% (the experimental error) over 200 hr. of operation. In both these calibrations and in the tartaric acid experiments, the bottom compartment of the cell was filled. Then the top compartment was rinsed and filled, starting the experiment. Because the Millipore filter has a volume of less than 0.1 cc., the usual preliminary diffusion period was unnecessary (*26*). Furthermore, the small average pore size of the filters gives a low Darcey's law permeability, minimizing the possibility of accidental mixing of the solutions. After the start of an experiment with optically active solutes, the optical rotation in the upper compartment was measured at about 2-hr. increments for a one to two day diffusion period. Calibration experiments lasted about one day.

The analysis of the ternary experiments was not based on the general theory developed earlier (22) because the data were of insufficient accuracy to merit such an analysis. To be sure, the data could have been screened to remove points showing large deviations and then the technique of nonlinear least squares applied, but it seems inconsistent to precede an objective analysis with a subjective one. The analysis for the diffusion coefficients begins with the usual equations for ternary diffusion in the diaphragm cell:

$$\Delta C_1 = \left[\left(\frac{1+S}{2} \right) e^{-\beta\sigma_1 t} + \left(\frac{1-S}{2} \right) e^{-\beta\sigma_2 t} \right] \Delta C_{10} + \left[b_2\, e^{-\beta\sigma_1 t} - b_2\, e^{-\beta\sigma_2 t} \right] \Delta C_{20} \qquad (8)$$

$$\Delta C_2 = \left[-\, b_1\, e^{-\beta\sigma_1 t} + b_1\, e^{-\beta\sigma_2 t} \right] \Delta C_{10} + \left[\left(\frac{1-S}{2} \right) e^{-\beta\sigma_1 t} + \left(\frac{1+S}{2} \right) e^{-\beta\sigma_2 t} \right] \Delta C_{20} \qquad (9)$$

The other constants in these equations are functions of the four D_{ij}:

$$S = [1 + 4\, b_1\, b_2]^{1/2} \qquad (10)$$

$$b_1 = [D_{21}/(\sigma_2 - \sigma_1)] \qquad (11)$$

$$b_2 = [D_{12}/(\sigma_1 - \sigma_2)] \qquad (12)$$

$$\sigma_1 = \frac{1}{2} \left[D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}} \right] \qquad (13)$$

$$\sigma_2 = \frac{1}{2} \left[D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}} \right] \qquad (14)$$

The convention adopted in these equations is that $D_{11} > D_{22}$, so that the diffusion of species 1 is dominated by the eigenvalue σ_1; this differs from the convention of Gosting and co-workers in which $D_{11} < D_{22}$, and the diffusion of species 1 is dominated by σ_2 (*1*). If the theory presented above is correct, Equations (8) and (9) take on the following form when $\Delta C_{10} - \Delta C_{20} = 0$:

$$\frac{\Delta C_1 + \Delta C_2}{\Delta C_{10} + \Delta C_{20}} = e^{-\sigma_1 \beta t} \qquad (15)$$

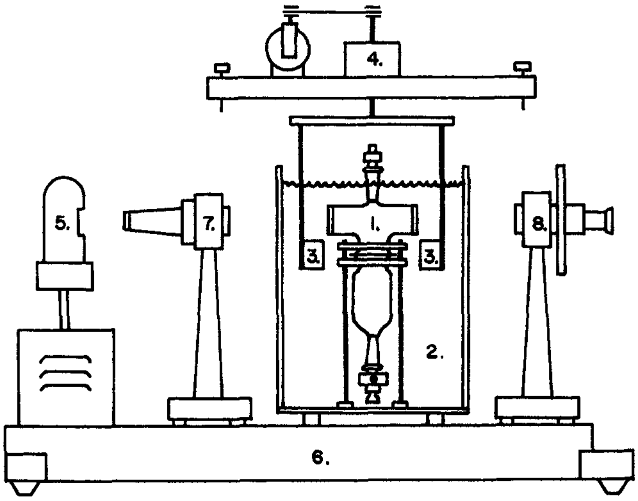

Fig. 1. Diaphragm cell apparatus.

Such an experiment tests the first condition which must be met by the theory and allows measurement of the eigenvalue σ_1. Similarly, when $\Delta C_{10} + \Delta C_{20} = 0$, Equations (8) and (9) become

$$\frac{\Delta C_1 - \Delta C_2}{\Delta C_{10} - \Delta C_{20}} = e^{-\sigma_2 \beta t} \qquad (16)$$

Since the polarimeter measures the concentration difference in the top compartment $(C_{1A} - C_{2A})$, $(\Delta C_1 - \Delta C_2)$ is known from a mass balance:

$$\Delta C_1 - \Delta C_2 = (\Delta C_{10} - \Delta C_{20}) - \left(1 + \frac{V_A}{V_B} \right) \cdot [(C_{1A0} - C_{2A0}) - (C_{1A} - C_{2A})] \qquad (17)$$

Once the two eigenvalues are known, the constants b_1 and b_2 are easily found from the difference of Equations (8) and (9) by trial and error. If either ΔC_1 or ΔC_2 is zero in the remaining experiments, the iteration is simplified. The values of the ternary diffusion coefficients are then found from

$$D_{11} = \frac{1}{2} [\sigma_1 + \sigma_2 + (\sigma_1 - \sigma_2) S] \qquad (18)$$

$$D_{12} = b_2\, (\sigma_1 - \sigma_2) \qquad (19)$$

$$D_{21} = b_1 (\sigma_2 - \sigma_1) \qquad (20)$$

$$D_{22} = \frac{1}{2} [\sigma_1 + \sigma_2 - (\sigma_1 - \sigma_2) S] \qquad (21)$$

where S is given by Equation (10).

RESULTS

Data for the binary diffusion experiments, including both individual isomers and the racemic mixture, are reported in Table 1. In this table, C_{A0} and C_{B0} refer to the initial concentrations in grams per cubic centimeters in the top and bottom compartments, respectively. The diffusion coefficients of sucrose and *d-l* glycerine are $0.51_4 \cdot 10^{-5}$ and $1.02 \cdot 10^{-5}$ sq.cm. /sec., respectively. These values, which agree with 2% of those in the literature (*25, 27*), show that the experimental technique is inter-

TABLE 1. BINARY DIFFUSION OF TARTARIC ACID AT 25.0°C.*

Expt.	Solute	C_{AO}	C_{BO}	$\beta t \cdot 10^{-5}$	$(C_A - C_B)_{\text{expt.}}$†	$(C_A - C_B)_{\text{calc.}}$**
17	Sucrose	0.034_2	0.000	1.417	0.016_6††	0.016_7***
18	Glycine	0.0075_1	0.000	0.932	0.029_0††	0.028_5***
2	*d* isomer	0.000	0.218	0.197	−0.176	−0.181
				0.432	−0.142	−0.145
				0.476	−0.135	−0.139
				0.652	−0.112	−0.117
				1.211	-0.070_4	-0.070_0
				1.825	-0.039_7	-0.039_4
13	*d* isomer	0.150	0.050	0.167	0.081_0	0.085_6
				0.377	0.068_8	0.070_1
				0.720	0.050_3	0.050_7
				1.246	0.029_8	0.031_0
14	*l* isomer	0.200	0.000	0.132	0.177	0.177
				0.220	0.162	0.163
				0.451	0.129	0.131
				0.665	0.107	0.107
				1.138	0.068_6	0.068_5
15	Racemic	0.150	0.050	1.150	0.033_9††	—

* Experiments numbered chronologically; units: C [=] g./cc., βt = sec./sq.cm., D [=] sq.cm./sec.

† Found by polarimetry, except where noted.

** Assuming $D = 0.94 \cdot 10^{-5}$ sq.cm./sec., except where noted.

†† Found by refractive index.

*** Calculated from literature values of $0.5096 \cdot 10^{-5}$ and 1.041 sq.cm./sec. for sucrose and glycine, respectively.

nally consistent. The average tartaric acid concentration in all experiments was approximately 0.10 g./cc. The most accurate value for the diffusion coefficient is that for the racemate, since this was measured by differential refractometry, a more accurate technique than optical rotation. Because of this accuracy, the coefficient in this experiment is taken as equal to σ_1, as shown in Table 3. However, this value is about 12% higher than the value reported previously (*28*). (This literature value was extrapolated from 18°C. by assuming that $D\mu/kT$ was constant, where μ is the viscosity, k is Boltzman's constant, and T is the temperature.) The reason for this disagreement is not known.

The other binary experiments give concentration vs. time curves predicted within an average of ±2% by the diffusion coefficient of the racemate. This accuracy is a consequence of the compromise between cell stirring and polarimeter cell length, which is discussed above. The diffusion coefficients of the isomers are equal. Moreover, the diffusion of *d* tartaric acid is seen to be independent both of the magnitude and of the sign of the initial concentration difference. The former fact proves that the concentration dependence of the diffusion coefficient is negligible within the accuracy of the experiment; the latter fact suggests that the precaution of inverting the cell so that the denser solution was on top was unnecessary. The close agreement of these experiments is consistent with the postulate that in an optically inactive solvent, a racemate diffuses as a binary. Much more accurate verification of this postulate is available elsewhere (*27*).

TABLE 2. TERNARY DIFFUSION DATA OF TARTARIC ACID AT 25°C.*

Expt.	ΔC_1†	ΔC_2†	$\beta t \cdot 10^{-5}$	$(\Delta C_1 - \Delta C_2)_{\text{expt.}}$	$(\Delta C_1 - \Delta C_2)_{\text{calc.}}$
8	0.100	−0.100	0.119	0.183	0.182
			0.210	0.172	0.169
			0.525	0.134	0.132
			0.830	0.103	0.104
			1.212	0.077_5	0.076_8
			1.672	0.053_2	0.053_3
6	−0.100	0.000	0.294	−0.0796	-0.079_3
			0.655	−0.0579	-0.059_8
			1.068	−0.0413	-0.043_2
9	0.100	0.000	0.306	0.078_3	0.0746
			0.630	0.061_7	0.0608
			0.881	0.050_3	0.049_9
			1.311	0.036_2	0.035_6
10	0.000	0.100	0.288	-0.078_3	-0.079_7
			0.556	-0.063_0	-0.064_5
			0.970	-0.047_7	-0.046_6
			1.388	-0.034_9	-0.033_4

* 1 = *d* tartaric acid; 2 = *l* tartaric acid; $\overline{C}_1$ = 0.050 g./cc.; $\overline{C}_2$ = 0.050 g./cc.; T = 25.0°C.

† ΔC_i is top compartment concentration minus bottom compartment concentration.

Ternary results with *d* and *l* tartaric acid are reported in Table 2. In each of these experiments, the average concentration of *d* tartaric acid and of *l* tartaric acid is 0.050 g./cc. Since the total acid concentration is thus 0.100 g./cc., these experiments compare directly with the binaries above. When $\Delta C_{10} + \Delta C_{20} = 0$, the results are seen to follow Equation (16), with the value of σ_2 found by least squares given in Table 3. The values of $\Delta C_1 - \Delta C_2$ calculated from σ_2 again agree within an average of ±2% with those observed experimentally. This agreement gives an independent verification of the second condition of the theory, that the system behaves as a binary when $\Delta C_{10} + \Delta C_{20} = 0$. This verification is quite different from that found in the usual tracer diffusion experiments, when one species is present only in vanishingly small concentration. Values of b_1 and b_2 found from the remaining experiments in Table 2 by the iteration described above are also reported in Table 3.

The four ternary diffusion coefficients calculated from Equations (19) to (22) are given in Table 3. Within the estimated experimental error, D_{11} equals D_{22} and D_{12} equals D_{21}, as required by the theory. The estimated error given here is subjective and optimistic. As $\sigma_1 - \sigma_2$ goes to zero, the accuracy with which the cross terms D_{12} and D_{21} (or b_1 and b_2) can be measured decreases sharply; this error affects all four diffusion coefficients drastically. A more satisfactory test of this third requirement of the theory is to assume that $b_1 = -1/2$, and $b_2 = +1/2$

Table 3. Ternary Diffusion Coefficients for Tartaric Acid at 25°C.

$1 = d$ tartaric acid $\qquad$ $2 = l$ tartaric acid

(Theoretical values in parentheses)

$$D \cdot 10^5 = \sigma_1 \cdot 10^5 = 0.94 \pm 0.03 \qquad b_1 = 0.6 \pm 0.3 \; (-0.50)$$

$$D^\dagger \cdot 10^5 = \sigma_2 \cdot 10^5 = 0.79 \pm 0.03 \qquad b_2 = \pm 0.4 \pm 0.3 \; (+0.50)$$

$$D_{11} \cdot 10^5 = 0.89_5 \pm 0.08 = (0.87_5 + 0.03) \qquad D_{12} \cdot 10^5 = (0.06 \pm 0.08) = (0.07_5 + 0.03)$$

$$D_{21} \cdot 10^5 = 0.09 \pm 0.08 = (0.07_5 \pm 0.03) \qquad D_{22} \cdot 10^5 = 0.83_5 \pm 0.08 = (0.87_5 \pm 0.03)$$

as required by Equations (2) and (11) to (14) and then to calculate $(\Delta C_1 - \Delta C_2)$. A comparison of these calculations with experimental values in Table 2 again shows an average deviation of ±2% consistent with earlier work. The isomers behave as diffusionally equivalent and agree with the predictions of Equation (2).

DISCUSSION

The relationship between the binary and ternary behavior of a system such as that considered here may be greatly clarified by writing Equations (8) and (9) for the specific values of b_1 and b_2 predicted by the theory:

$$\Delta C_1 = \left(\frac{C_1}{C_1 + C_2}\right)(\Delta C_{10} + \Delta C_{20})\, e^{-D\beta t} + \left(\frac{C_2}{C_1 - C_2}\Delta C_{10} - \frac{C_1}{C_1 + C_2}\Delta C_{20}\right) e^{-D^\dagger \beta t} \tag{22}$$

$$\Delta C_2 = \left(\frac{C_2}{C_1 + C_2}\right)(\Delta C_{10} + \Delta C_{20})\, e^{-D\beta t} + \left(-\frac{C_2}{C_1 + C_2}\Delta C_{10} + \frac{C_1}{C_1 + C_2}\Delta C_{20}\right) e^{-D^\dagger \beta t} \tag{23}$$

Obviously, this is in general a ternary equation, since the flux of species 1 is a function of the concentration gradients of both solute species. Furthermore, a gradient of species 2 will lead to a gradient of species 1, even if there is initially no gradient in species 1. But if, as in these experiments, we do not measure the concentration of an individual species but rather determine the difference between two concentrations, then Equations (22) and (23) collapse into Equation (16). The difference of the concentrations behaves as a binary with a single intradiffusion coefficient. If, on the other hand, we choose to measure the refractive index in our experiments, that is, we choose to measure the sum of the solute concentrations, then Equations (22) and (23) collapse into Equation (3) or Equation (15). The sum of the concentrations behaves as a binary with the mutual diffusion coefficient. The collapse of these equations, implicitly occasioned by the casual choice of an experimental method, is true even though the flux of a single component is given by the ternary equation.

The practical application of this work is found in the separation of two very similar species which are both dissolved in a third. A good example is the separation by distillation of two C_4 hydrocarbons dissolved in furfural (29). In this example, a distillation is assumed to be controlled by liquid phase mass transfer, but the extension to vapor phase controlled mass transfer or to other multicomponent separations is completely straightforward. Expressions for most separations of this type have been developed by Toor (*3*, *30*). Unfortunately, however, the matrices which appear in Toor's work can be calculated a priori only for the case of dilute gases. This work allows this calculation for the ternary liquid case of two similar species. The point multicomponent tray efficiencies $E^{(i)}$ may be defined as

$$E^{(i)} = \frac{(C_{i,n} - C_{i,n-1})}{(C^*_{i,n} - C_{i,n-1})} \tag{24}$$

where the numerator represents the actual concentration difference of species i between stages n and $(n - 1)$, and the denominator is the corresponding concentration difference if stage n is at equilibrium. The efficiencies are most conveniently calculated from

$$E^{(i)} = \sum_{j=1}^{2} E_{ij} \frac{C^*_{j,n} - C_{j,n-1}}{C^*_{i,n} - C_{i,n-1}} \tag{25}$$

where the E_{ij} are given by

$$E_{ij} = \sum_{k=1}^{2} P_{ik} E(\sigma_k) P_{kj}^{-1} \tag{26}$$

This equation, analogous to Equations (27) and (30) of Toor's development (*30*), is written in terms of the modal matrix $\mathbf{P}$, defined by

$$\sum_{j=1}^{2} \sum_{k=1}^{2} P_{ij}^{-1} D_{jk} P_{kl} = \delta_{il}\sigma_l \tag{27}$$

and in terms of the quantity $E(\sigma_k)$, which represents a known binary correlation for tray efficiency, in which the eigenvalue σ_k should be substituted for the binary diffusion coefficient.

For the special case treated in this paper, where the diffusion coefficients are given by Equation (2), the modal matrix $\mathbf{P}$ is

$$\mathbf{P} = \begin{bmatrix} 1 & -1 \\ \dfrac{C_2}{C_1} & 1 \end{bmatrix} \tag{28}$$

Thus, the four E_{ij} are

$$\begin{aligned} E_{11} &= [C_1 E(D) + C_2 E(D^\dagger)]/(C_1 + C_2) \\ E_{12} &= C_1 [E(D) - E(D^\dagger)]/(C_1 + C_2) \\ E_{21} &= C_2 [E(D) - E(D^\dagger)]/(C_1 + C_2) \\ E_{22} &= [C_1 E(D^\dagger) + C_2 E(D)]/(C_1 + C_2) \end{aligned} \tag{29}$$

and the ternary efficiencies are easily calculated from Equation (25). An interesting case occurs when $C_2 >> C_1$. Then the tray efficiency for component 1 is $E(D^\dagger)$, rather than $E(D)$. The difference between these results will be largest if the third species is present only in small concentration. The utility of these equations and of the analogous relations for mass transfer can only be tested experimentally. Unfortunately, such tests will be hampered by the paucity of intradiffusion data, although it may be possible to use existing empirical relations giving $D = D(D^\dagger)$ to approximate $D^\dagger$.

NOTATION

b_i = constant, function of D_{ij}

C_j = concentration of species j, g./cc. or mole/cc.

D = mutual diffusion coefficients, sq.cm./sec.

$D^\dagger$ = intradiffusion coefficient, sq.cm./sec.

D_{ij} = ternary diffusion coefficient relative to volume

average velocity, sq.cm./sec.
$\mathcal{D}$ = mutual diffusion coefficient of dilute gas, sq.cm./sec.
$\mathcal{D}_{12}$ = intradiffusion coefficient of dilute gas, sq.cm./sec.
$E(\sigma_k)$ = binary correlation of tray efficiency
$E^{(i)}$ = multicomponent tray efficiency
E_{ij} = constant
j_i = mass or mole flux relative to volume average velocity, g./(sq.cm. sec.) or mole/ (sq.cm./sec.)
P_{ij} = element of modal matrix of diffusion coefficients
S = constant, function of D_{ij}
t = time, sec.
V_i = volume of diaphragm cell compartment, cc.
x_i = mole fraction of species i
β = calibration constant of diaphragm cell, cm.$^{-2}$
ΔC_i = concentration difference in top, bottom diaphragm compartments
σ_i = eigenvalue of diffusion coefficients, sq.cm./sec.

Subscripts

A = top compartment of diaphragm cell
B = bottom compartment
0 = value at zero time
1, 2 = solute species
3 = solvent species

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Calculation of Solubility Parameters of Polar Compounds

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A graphical method is presented for calculating solubility parameters and molar volumes of functional groups, as well as for calculating solubility parameters of high molecular weight members of a homologous series from data on low molecular weight members. These functional group solubility parameters and molar volumes have been used to extend the values of $\sqrt{EV}$ presented earlier by Small. Finally, it is shown that the use of group contributions to calculate cohesive energy is limited by the lack of information available on the intramolecular energies of interaction of functional groups on the same molecule.

In order to study the behavior of components in mixtures of nonelectrolytes, it is necessary to estimate the interaction energies between molecules in solution. Hildebrand (*1*) and Scatchard (*2*), in laying the groundwork for what is called *regular solution theory*, suggested that these interaction energies could be calculated from what they called *solubility parameters*. These solubility parameters are the square root of the cohesive energy density (that is, the cohesive energy per cubic centimeter of liquid) for the pure components. If one assumes that, in the gas phase, the compound for which the solubility parameter is to be calculated forms a perfect gas with no interactions between the molecules, the solubility parameters (δ) can be calculated directly from heat of vaporization data by Equation (1):

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