Diffusion in Mixed Solvents

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Despite the considerable theoretical and experimental interest in binary liquid diffusion little work has been reported on liquid diffusion in ternary mixtures. Gosting (*1*, *3*) and Miller (*7*) have investigated the effects of interacting flows in systems containing two diffusing solutes in a single solvent to verify the Onsager reciprocal relations. Bird and co-workers (*2*) at one time suggested that multicomponent liquid diffusion might be amenable to treatment by the Maxwell-Stefan equation normally reserved for gaseous diffusion.

The purpose of this study was to investigate the transport of a very dilute solute in solvents consisting of various admixtures of paraffin hydrocarbon pairs. For ease of analysis toluene was chosen as the solute. Three binary solvent mixtures were studied: *n*-hexane—*n*-tetradecane; *n*-hexane—cyclohexane; and cyclohexane—*n*-decane. The entire binary composition range in each of the solvents was covered. Experiments were performed in stirred vertical diaphragm cells at solute concentrations less than 0.005 mole/liter. At such high dilution the nonideality correction ($d\ln a/d\ln x$) is unity.

The analysis of the experimental data is based upon the assumption that the ternary system behaves as a pseudobinary, or that the diffusing solute effectively sees a single component with properties consisting of appropriately weighted averages of the two constituents. The assumption that solute transfer does not effect a separation of the counterdiffusing solvent mixture appears to be reasonable for the extremely low fluxes associated with the small driving force employed in the experiments. In the terminology of the phenomenological approach of Miller (*7*) and other (*1*, *3*) the cross-diffusion coefficients are assumed negligible.

EXPERIMENTAL

Apparatus

The cell used in these studies is described in detail elsewhere (*5*). The diaphragms were normal pore diameter of 3 to 8μ, 5 cm. in diameter, and 0.5 cm. thick. Each compartment was 125 cc. in volume and was stirred by 1-in. covered magnetic stirrer bars. The experimental data were analyzed by the usual equation (*4*):

$$\log_{10}\left[\frac{\Delta C_i}{\Delta C_f}\right] = \beta Dt \qquad (1)$$

The cell constants were obtained by calibration with 0.2 N hydrochloric acid and the diffusivity data of Stokes (*11*). The effect of stirring speed on β is discussed elsewhere (*5*); it had no effect on the measurements reported here. The prerun suggested by Gordon (*4*) was found on theoretical grounds to be of negligible consequence and was therefore eliminated (*5*).

Densities were measured to ±0.2% with a balance. Viscosities reproducible to ±0.5% were determined with a viscosimeter calibrated with distilled water. All data were taken at 25 ± 0.1°C. at a stirring speed of 350 rev./min.

Procedure

One compartment was filled with pure solvent and forced through the diaphragm by pressure to purge all air from the pores. The other compartment was washed and filled with the concentrated solution. The experiments were allowed to proceed until the concentration difference ratio of Equation (1) was about 2 (this took from 3 to 10 days), at which time the cell contents were sampled and analyzed. Because of the low solute concentration the integral diffusion coefficients obtained are essentially equal to the differential coefficients at infinite dilution.

Solvents

The pure grade *n*-hexane and *n*-decane and spectro grade cyclohexane were used. The *n*-tetradecane had a melting point range of 4° to 6°C. The toluene was reagent grade. The solvents were first dried by contacting with silica gel, then batch distilled. The fraction within ±0.5°C. of the boiling point was used. The tetradecane was vacuum distilled, and the cut with a melting point of 5.4° to 5.6°C. was employed. Owing to the difficulty in removing toluene from the mixtures fresh solvents were made up for each experiment.

Analyses

Hydrochloric acid concentrations were determined to ±0.0005 N by titration with 0.1 N sodium hydroxide to a phenolphthalein end point. With an estimated ±0.1% sampling error the precision of the cell constant should have been ~ ±2.2%. Unless three cell-constant calibrations were within this figure, the cell was discarded. Toluene concentrations were measured with a spectrophotometer at 2620Å. Since the optical density was not exactly linear in toluene concentration, calibration curves were prepared for each of the solvent mixtures studied. The precision of the toluene determinations was ±1.0 to 1.5%, and the corresponding error of the diffusion coefficient was ±6%. In most cases the actual data were reproducible to within 5%, and at least two determinations were made for each system.

Results

The experimental diffusivity, viscosity, and density data for the systems investigated are presented in Table 1. The binary diffusivity data are between 5 to 9% higher than those reported by Chang and Wilke (*9*) either because of differences in solvent purity or possibly because of Chang's utilization of Beer's law in the spectrophotometric analyses.

DISCUSSION

If the solvent mixture is considered effectively stationary, the Maxwell-Stefan gas diffusion equations predict for these systems that the measured diffusivity and the individual binary diffusion coefficient should be related by (*2*):

$$D = \frac{1}{x_A/D_{SA} + x_B/D_{SB}} \qquad (2)$$

This relation reproduces the diffusion coefficients in the *n*-hexane—*n*-tetradecane and cyclohexane—*n*-decane solvents reasonably well (to within 10%) but is in error by 30% for the *n*-hexane—cyclohexane system. Since the variations of mixture viscosity are ignored, Equation (2) is probably not a reliable method for interpreting multicomponent liquid diffusion data.

If the mole fraction-average molecular weight of the solvent is used, and the molar volume of the solute toluene is taken as 118, the Wilke-Chang empirical correlation (*12*) becomes

$$\frac{D\mu}{T} \times 10^{10} = 0.422 \quad \overline{\overline{M}} \qquad (3)$$

Figure 1 compares the experimental data with Equation (3). It can be seen that, although the correlation is approximately 17% low, the trends with $\overline{M}$ are closely parallel. This may be the result of an overestimate of the molar volume of toluene; if the actual molar volume of toluene were ~100, the two lines of Figure 1 would have been practically coincident.

The most significant result which can be extracted from Figure 1 is the equivalence of the binary and ternary systems. All of the ternary data show

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TABLE 1. DIFFUSIVITY OF TOLUENE IN VARIOUS SOLVENTS AT 25°C.

Solvent	Mole fraction of light component	$\bar{M}$	ρ, (g./cc.)	$\mu \times 10^2$, (poises)	$D \times 10^5$, (sq. cm./sec.)	$D\mu/T \times 10^{10}$
n-tetradecane	—	198	0.750	2.035	1.08	7.38
n-hexane—n-tetradecane	0.197	177	0.749	1.504	1.37	6.91
n-hexane—n-tetradecane	0.328	162	0.740	1.254	1.58	6.65
n-hexane—n-tetradecane	0.499	144	0.727	0.957	1.92	6.17
n-hexane—n-tetradecane	0.664	126	0.710	0.695	2.38	5.55
n-hexane—n-tetradecane	0.785	112	0.694	0.529	2.90	5.15
n-hexane—n-tetradecane	0.887	101	0.676	0.411	3.57	4.92
n-hexane	—	86	0.655	0.308	4.62	4.77
n-hexane—cyclohexane	0.786*	86	0.679	0.355	4.10	4.88
n-hexane—cyclohexane	0.452*	85	0.715	0.464	3.37	5.25
n-hexane—cyclohexane	0.262*	85	0.737	0.574	2.78	5.35
Cyclohexane	—	84	0.774	0.881	1.81	5.35
Cyclohexane—n-decane	0.754	99	0.754	0.813	1.87	5.10
Cyclohexane—n-decane	0.492	114	0.741	0.810	1.94	5.27
Cyclohexane—n-decane	0.241	128	0.732	0.820	2.00	5.50
n-decane	—	142	0.726	0.840	2.24	6.31

* Mole fraction of n-hexane.

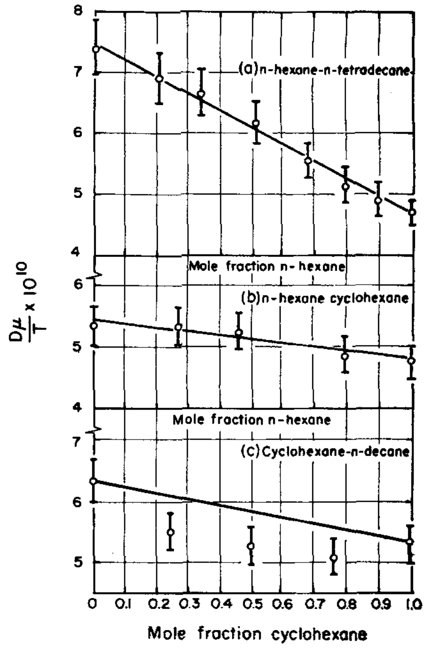

Fig. 2. Variation of $D\mu/T$ with composition of mixed solvents. Vertical bars correspond to ± 6% error.

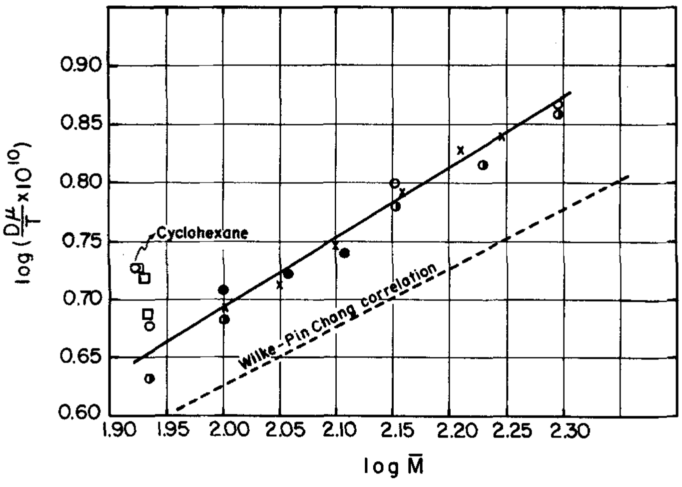

Fig. 1. Comparison of experimental $D\mu/T$ with the Wilke-Pin Chang correlation (12). Open circle, binary systems (this work), half open circle, binary systems [Pin Chang-Wilke (9)], X, n-hexane—n-tetradecane solvents, open square, n-hexane—cyclohexane solvents, closed circle, cyclohexane—n-decane solvents.

that the mixed solvent behaves as if it were a single solvent with a molecular weight or molar volume equivalent to the mole fraction average of its two components. The question of predicting diffusivities of dilute solutions in mixed solvents is thus reduced to the corresponding binary problem.

It is apparent from Figure 1 that the cyclo isomer behaves differently from the normal isomer. Again this phenomenon is not due to any effect of the mixed solvents because pure cyclohexane solvent shows the greatest deviation from the lines which represent the straight chain paraffins. It is possible that diffusion studies on cyclooctane, cyclodecane, etc. would yield results which fall in a line parallel to the normal isomer line but displaced above it by an amount equal to the distance between the measured cyclo- and n-hexane points. The discrepancy between the cyclic and normal isomers will be discussed later.

Many models of liquid diffusion suggest that for a binary the group $D\mu/T$ should be linear in mole fraction (6). With the mole fraction of one component of the mixed solvent chosen as the composition variable Figure 2 presents this treatment of the data for the three solvent systems considered. For the n-hexane—n-tetradecane and the n-hexane—cyclohexane solvents the plots are linear within the experimental precision. The cyclohexane—n-decane system however shows an unexplained deviation from linearity. This discrepancy cannot reasonably be attributed to extensive nonideality in the cyclohexane—n-decane system for the following reasons. A rough test of the interaction strength between two dissimilar species consists of plotting the logarithm of the mixture viscosity against mole fraction; for nearly ideal systems plots of this type are generally linear, while pronounced nonideality usually results in extensive curvature. When treated in this manner the viscosities of the three solvent pairs investigated in this study exhibited only mild deviations from linearity. In particular the extent of curvature of the cyclohexane—n-decane system was slightly less than in the other two mixtures. No suitable explanation for the discrepancy in Figure 2(c) can be offered.

Despite the minimum in the n-decane—cyclohexane plot a linear mole fraction average of $D\mu/T$ reproduces all of the data to within 10% over the entire range of composition. From a practical standpoint this appears to provide a satisfactory method of estimating diffusion coefficients in mixed binary solvents if the binary diffusion data are available.

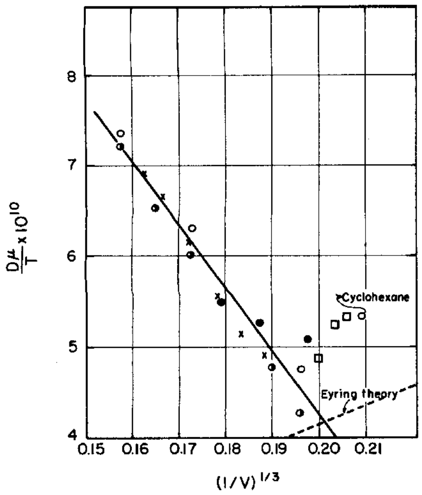

Fig. 3. Comparison of experimental $D\mu/T$ with Eyring's absolute rate theory—free energies of activation for viscosity and diffusion assumed equal. Open circle, binary systems (this work), half open circle, binary systems [Pin Chang-Wilke (9)], X, *n*-hexane—*n*-tetradecane solvents, open square, *n*-hexane—cyclohexane solvents, closed circle, cyclohexane—*n*-decane solvents.

For multicomponent solvents the results of Figure 1 suggest that an average value of $D\mu/T\overline{M}^{1/2}$, based on available binary diffusion data for the solute with respect to the solvent components, be used to predict values of D at other solvent compositions. In absence of any diffusion data use of the average molecular weight of the solvent in the Chang-Wilke correlation is recommended. Since these data represent hydrocarbon systems, it is not known how well the estimation procedures represented by Figures 1 and 2 will apply to other solvent mixtures.

Since Figure 1 strongly suggests that the ternary systems employed in this investigation behave as pseudobinaries, the experimental data should be amenable to interpretation in terms of a diffusion model such as that provided by absolute rate theory. In accordance with this formulation the group $(D\mu/T)$ is given by *(10)*

$$Y = \left(\frac{D\mu}{T}\right)\left(\frac{\xi}{k}\right)\left(\frac{V}{N_{AV}}\right)^{1/3} = \exp\left\{\frac{\Delta F_\mu{}^* - \Delta F_D{}^*}{RT}\right\} \quad (4)$$

where the factor ξ is approximately 5.6 and the molar volume is

$$V = \overline{M}/\rho \quad (5)$$

For self-diffusion the free energies of activation for viscosity and diffusion are equal, and the right-hand side of Equation (4) reduces to unity. Previous interpretations of mutual diffusion data in terms of absolute rate theory have, without justification, retained this assumption. A comparison of the experimental values of $D\mu/T$ from Table 1 and those predicted by Equation (4) (with $\Delta F_\mu{}^*$ assumed equal to $\Delta F_D{}^*$) is presented in Figure 3. Not only are the predicted values in error by as much as a factor of 2, but the experimental and theoretical variations with molar volume are in opposite directions.

Recently an approximate technique for evaluating the difference between the free energies of activation of the viscous and mutual diffusion processes in binary systems has been proposed *(8)*. The mechanism of viscosity is subdivided into volumetric or hole-forming and kinetic or bond-breaking contributions. In viscosity or self-diffusion both of these steps involve interactions between identical species because only one substance is present. In dilute mutual diffusion however only the hole-forming step involves solvent-solvent interactions. Since the solute is the species which is in motion, the kinetic or bond-breaking step must involve interactions between solute and solvent molecules, irrespective of the degree of dilution of the solute. On this basis the difference between the free energies of activation is estimated as

$$\frac{\Delta F_\mu{}^* - \Delta F_D{}^*}{RT} = f\delta \quad (6)$$

where

$$\delta = \left(\frac{\Delta F^*{}_{AA}}{RT}\right)\left\{1 - \left(\frac{\Delta F^*{}_{SS}}{F^*{}_{AA}}\right)^{1/2}\right\} \quad (7)$$

and $\Delta F^*{}_{AA}$ and $\Delta F^*{}_{SS}$ are the free energies of activation of the pure solvent and solute, respectively, evaluated from the viscosity and molar volumes by the definition

$$\frac{\Delta F^*}{RT} = \ln\left[\frac{\mu V}{hN_{AV}}\right] \quad (8)$$

The factor f in Equation (6) represents the fraction of the total free energy of activation of viscosity or self-diffusion which is due to the kinetic component of the overall process. By examination of thirty-six binary systems, f has been determined empirically to be ½. Previous interpretations of mutual diffusion data by absolute rate theory have assumed f (or the product $f\delta$) to be zero, which results in the erroneous prediction that Y of Equation (4) should be unity for dilute mutual diffusion in all systems.

The method of estimating $\Delta F_\mu{}^* - \Delta F_D{}^*$ for binary systems can be readily extended to include diffusion of dilute solutes in mixed solvents. If the solvent consists of a mixture of A and B, the parameter δ characteristic of the mixture is taken as the mole fraction average of δ_A and δ_B:

$$\delta = x_A\delta_A + x_B\delta_B \quad (9)$$

Since the solute is present in very low concentrations, $x_A + x_B \cong 1$. δ_A is given by Equation (7) and δ_B by the same relation with the subscripts A replaced by B.

A plot of the ternary diffusion data as suggested by Equations (4) and (6) is shown in Figure 4 along with the line for the binary systems taken from reference 8. The mixed solvent data tend to lie approximately 15% above the line, as do the four pure solvents which are also included in Figure 4. The comparison is a distinct improvement over that of Figure 3, for not only is the trend of the data paral-

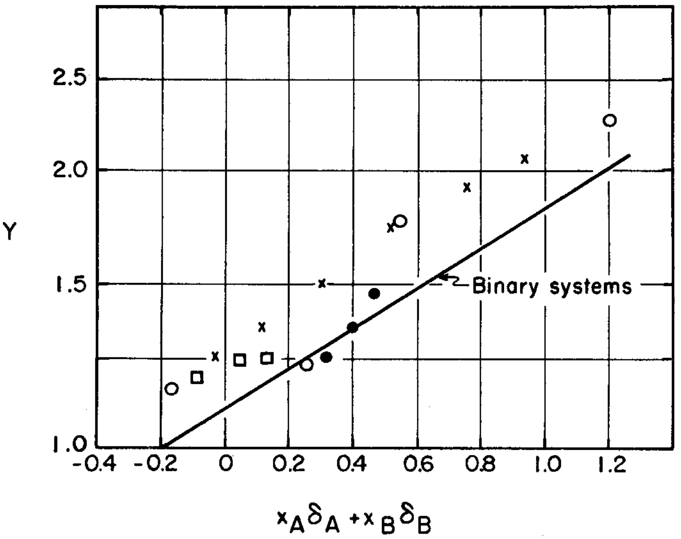

Fig. 4. Comparison of experimental $D\mu/T$ with modified absolute rate theory. Open circle, binary systems (this work), X, *n*-hexane—*n*-tetradecane solvents, open square, *n*-hexane—cyclohexane solvents, closed circle, cyclohexane—*n*-decane solvents.

leled by the modified absolute rate theory predictions, but the formulation of the latter gives some insight into reasons for the deviations of the cyclohexane-based solvents from the normal paraffin results. Equations (4) and (6) indicate that the deviations of the parameter Y from unity depend upon the value of f which characterizes the particular solute-solvent combination. The fraction f utilized in the line representing the binary data is an average value for a large number of systems but is not a true constant for all substances or mixtures. Values less than the average are expected for systems composed of spherical molecules (such as cyclohexane and toluene) because the enhanced ability of the solute molecule to move freely in its equilibrium position reduces the contribution of the kinetic step. By Equations (4) and (6) low values of f would tend to move the ordinates toward unity; the spherical shape of cyclohexane (compared with normal paraffins) is thus a reasonable explanation for its anomalous behavior relative to n-hexane, n-decane, and n-tetradecane.

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NOTATION

a = solute activity
ΔC_i = concentration difference between the two compartments of the diffusion cell at the beginning of an experiment, g.-moles/liter
ΔC_f = concentration difference between the two compartments of the diffusion cell at the end of an experiment, g.-moles/liter
D = diffusion coefficient, sq. cm./sec.
D_{SA}, D_{SB} = binary diffusivities of toluene (designated as S) in the components of the solvent mixture (designated by A and B), sq. cm./sec.
f = fraction of the total free energy of activation required for the kinetic or bond-breaking step
ΔF^* = free energy of activation, cal./mole
h = Planck's constant, 6.624×10^{-27} erg.-sec.
k = Boltzmann's constant, 1.38×10^{-16} erg./°K.
$\overline{M}$ = mole fraction-average molecular weight of solvent
N_{AV} = Avogadro's number, 6.023×10^{23}
t = time, sec.
T = temperature, °K.
V = molar volume of solution, cc./g.-mole
x = mole fraction
Y = defined by Equation (4)

Greek Letters

β = cell constant
δ = parameter defined by Equation (7)
ρ = solution density, g./cc.
μ = solution viscosity, poise
ξ = parameter in Eyring theory

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A Diffusion Model for Rinsing

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The removal, by immersion in water, of solute from a solution adhering to a 14.7-cm. wide flat plate has been experimentally investigated at about 80°F. over a 3.5 to 1,000 sec. range of contact time. Diffusivity was varied over a sixfold range (from 0.5 to 3.0 by 10^{-5} sq.cm./sec.) by the use of two dilute solutions, pontamine blue dye and 0.09 N nitric acid. Equations relating the effects of film thickness, contact time, and diffusivity on the mass fraction of solute which was not removed during rinsing were developed from a diffusion model, under the assumption that the adhering solution was present throughout as a stagnant film of uniform thickness.

The experimentally determined effects of time and diffusivity agreed with those indicated by the idealized model. The agreement of these effects and the magnitude of unremoved solute gave strong indication that diffusion may be considered the controlling mechanism. The experimental dip and rinse method used offers potential as a technique for studying natural convection at transient conditions in the region where diffusion is also important, because it offers the advantage of allowing independent selection of initial fluid densities.

It might be thought that the removal of a contaminant-containing solution from a solid body by dipping the solid in a tank of water is due to the agitation resulting from the dipping motion. It is the purpose of this paper to show that under certain conditions the effect of time and diffusivity on rinse removal is described by molecular diffusion.

The need to determine the controlling mechanism arose in the design of

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