Diffusion in the Solvents Hexane and Carbon Tetrachloride

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Binary diffusion coefficients were measured for several solutes in very dilute solutions of hexane and carbon tetrachloride. When the product of diffusion coefficient and viscosity is correlated with mole fraction of the solute, the data for the two solvents are very nearly superimposed.

IN THE STUDY OF LIQUID DIFFUSION, it is often necessary to obtain values for the friction coefficients of molecules. For instance, the Hartley and Crank equation (13),

$$D_{AB} = \frac{kT}{\eta} \left[\frac{X_A}{f_B} + \frac{X_B}{f_A} \right] \frac{d \ln a_i}{d \ln X_i} \qquad (1)$$

predicts that the concentration dependence of the mutual diffusion coefficient is such that a plot of $D_{AB} \, \eta / (d \ln a)/ (d \ln X)$ is linear with mole fraction if the friction coefficients, f_A and f_B, are assumed constant. Several workers have shown that Equation 1 is not valid for associating systems where the diffusing species are not simply monomers but include hydrogen bonded complexes of two or more molecules (1, 3, 8, 11). However, for binary systems in which no association occurs, Equation 1 predicts the concentration dependence of the mutual diffusion coefficient with reasonable accuracy (4,5).

In the course of diffusion studies in this laboratory on a number of binary systems, the effects of size and shape of both the diffusing and solvent molecules on f_i were examined. It was of particular interest to eliminate any effect of hydrogen bonding on friction coefficients. Therefore, diffusivities were measured for a number of solutes in very dilute solutions of two solvents, hexane and carbon tetrachloride, chosen because they are inert and do not associate with the solute or self-associate. In addition, since the data are for very dilute solutions, solute-solute association is eliminated even though such interactions could occur at higher concentrations. Thus, all molecular association is eliminated.

EXPERIMENTAL

The diffusion coefficients were measured using a Mach-Zehnder diffusiometer constructed in this laboratory, similar to that used by Caldwell, Hall, and Babb (7). This diffusiometer measures refractive index gradients, which are proportional to concentration gradients over narrow concentration ranges, by means of interference fringes. A beam of light is split by half-silvered mirrors, and one half is passed through a cell containing a concentration gradient of the system under study. The two beams are then recombined, and the resulting fringes are recorded photographically. The diffusion coefficient may be calculated from the change in refractive index with time, as diffusion proceeds (4, 7). The instrument has been shown to be accurate

to within 0.5% for sucrose-water solutions. For the more volatile systems involved in this study, 1.0% is the estimated error. Viscosities were measured using a Cannon-Fenske viscometer and checked with literature values. Agreement was within 0.5%.

The organic chemicals were the purest grades commercially available, used without further purification.

DISCUSSION

At infinite dilution, the term $d \ln a/d \ln X$ in Equation 1 is unity. Thus if A is the solute and B the solvent,

$$D_{AB} \Big|_{X_A \to 0} = \frac{kT}{\eta_B f_A} \qquad (2)$$

If f_A is a function of the size and shape of the solvent and solute molecules, a plot of $D_{AB} \, \eta_B$ vs. molar volume of the solute should be worth examination. The Stokes-Einstein equation predicts that $f_A = 6\pi r_A$ and a log-log plot of $D_{AB} \, \eta_B$ would be a straight line slope 1/3. This, of course, is only a first approximation and experimental agreement is not expected, since the Stokes-Einstein equation assumes that the solvent is a continuous medium rather than particles of finite size.

Figure 1 shows the data for 18 solutes in the two solvents. The data are tabulated in Table I. Each reported diffusivity represents one measurement. The molar volumes were calculated from the density and molecular weight of the liquid
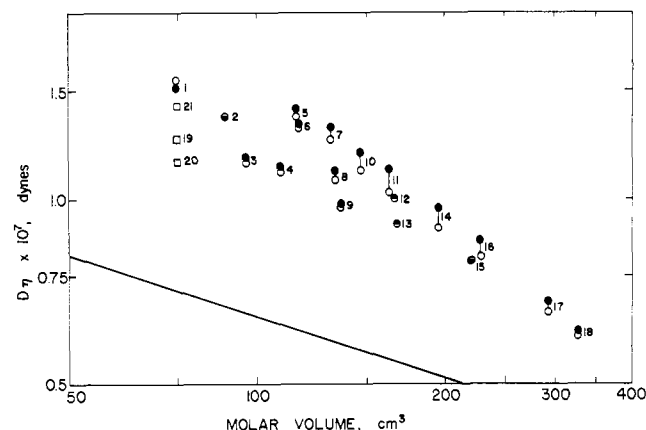

Figure 1. Diffusion of solutes at 25° C.
○ In hexane
● In carbon tetrachloride

Table I. Summary of Experimental Data for Diffusion of Solvents Hexane and Carbon Tetrachloride at 25° C.

$(\eta_{CCl_4} = 0.888, \eta_{C_6} = 0.2958)$

Solute	$D_{in\ CCl_4}$, Sq. Cm./Sec.	$D_{in\ C_6}$, Sq. Cm./Sec.	$D\eta_{CCl_4}$, Dynes	$D\eta_{C_6}$, Dynes	V_{solute}, Cc./G. Mole
Acetone	1.70 (2)	5.26	1.51	1.56	74.0
Benzene	1.54 (6)	4.64	1.37	1.37	89.4
CCl$_4$	1.32 (14)^a	3.86	1.17	1.14	97.1
Cyclohexane	1.27 (11)	3.77	1.13	1.12	109
$n - C_5H_{12}$	1.57 (9)	4.59	1.39	1.36	116
2-Methylbutane	1.49	4.40	1.32	1.30	117
$n - C_6H_{14}$	1.47	4.21 (10)^a	1.31	1.25	132
2,2-Dimethylbutane	1.25	3.63	1.11	1.07	134
Tetralin	1.10	3.27	0.977	0.976	137
$n - C_7H_{16}$	1.34 (9)	3.78	1.19	1.12	147
$n - C_8H_{18}$	1.26 (9)	3.47	1.12	1.03	164
2,2,4-Trimethylpentane	1.13	3.38	1.00	1.00	166
Phenanthrene	1.03	3.08	0.915	0.911	168
$n - C_{10}H_{22}$	1.09 (9)	3.02	0.968	0.907	196
2-Methylpropene (trimer)	0.884	2.68	0.785	0.793	222
$n - C_{12}H_{26}$	0.964 (9)	2.74	0.856	0.810	229
$n - C_{16}H_{34}$	0.765 (9)	2.21	0.679	0.654	294
$n - C_{18}H_{38}$	0.690 (9)	2.01	0.613	0.595	328
Acetone in chloroform	2.90 (3)				
Acetone in water	1.28 (3)				
Self diffusion of acetone	4.5 (12)				

^{a} Self-diffusion coefficients.

wherever possible but in some cases were estimated from the properties of the solid. The scatter in the data seems to be influenced mostly by the solute molecule, while the solvent has only a minor effect. Except for the normal hydrocarbon solutes, the data for the two solvents are very nearly superimposed.

The solid line is a plot of $D_{AB}\eta_B$ predicted by the Stokes-Einstein equation. The data tend to approach the line as a molar volume of the solute increases. This is to be expected, since for large solute molecules the surrounding fluid can be represented more accurately as a continuous medium.

The data indicate that, for these two solvents, the viscosity adequately accounts for the effect of the solvent on the diffusion coefficient of the solute. That is not surprising, however, since hexane and carbon tetrachloride do not differ greatly in size and shape. In addition, if the solute is capable of hydrogen bonding with the solvent, the diffusion coefficient even at infinite dilution is decreased. On Figure 1, the diffusion coefficients of acetone in water and chloroform and the self-diffusion coefficient are presented along with the values for acetone in hexane and carbon tetrachloride. Since acetone as a solute forms hydrogen bonds with water, chloroform, or acetone itself as solvents, the corresponding $D\eta$ products are considerably lower.

ACKNOWLEDGMENT

NOMENCLATURE

D_{AB} = mutual diffusion coefficient, sq. cm. sec.$^{-1}$
k = Boltzmann constant, erg ° K.$^{-1}$
T = absolute temperature, ° K.
a_i = activity of species i in solution, dimensionless
f_i = friction coefficient of species i, cm.
r_i = Stokes-Einstein radius of species i, cm.
V = solute molar volume, cc. g.-mole^{-1}
X_i = mole fraction of species i in solution, dimensionless
η = viscosity, g. cm.$^{-1}$ sec.$^{-1}$

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