The Diffusivity of Water in Organic Solvents

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Despite the concerted efforts of a substantial number of workers, a successful theoretical interpretation of the phenomenon of liquid diffusion has yet to be uncovered. To date the most fruitful approach remains the twenty-year-old absolute reaction rate theory of Eyring (*2*). However its quantitative predictions are on the average 100% too high, discrepancies which would not satisfy even the most generous engineering approximation. To alleviate this unfortunate situation, a number of empirical correlations of liquid diffusivities have appeared (*3, 7, 9, 10*) which generally reproduce most of the available experimental data to within 10 to 15%. However for the diffusion of water into organic solvents these correlations are in error by factors ranging from 1½ to 2½.

To illustrate this deficiency, experimental diffusivities for solute water will be compared with the predictions of the Wilke–Pin Chang method (*10*). This particular correlation has been selected because it affords some insight into the peculiar behavior of water as a diffusing solute.*

The Wilke–Pin Chang expression is

$$D = 7.4 \times 10^{-8} \frac{\sqrt{xM}\,T}{\mu\,V^{0.6}} \tag{1}$$

Although twenty-five data points for the diffusion of various solutes into water were employed in the development of Equation (1), no data for water as a solute were included. The reliability of Equation (1) for this latter case was evaluated by a comparison of the experimental and predicted diffusivities for the meager amount of data which could be culled from the literature. These results are presented in Table 1. For comparison, the ability of Equation (1) to reproduce data for the diffusion of various organic solutes into solvent water is shown in Table 2. This latter compilation by no means exhausts the data available but serves to indicate that the correlation is sound for solvent water.

The experimental and calculated diffusivities of Tables 1 and 2 are presented graphically in Figure 1. The straight line representing the water-as-solute points indicates that the ratio of calculated-to-experimental diffusivities is essentially constant at a value of 2.3. Moreover this factor appears to be independent of solvent and temperature and extends to water concentrations as low as 0.5 volume %.

The associative behavior of pure water has been included in the Wilke-Pin Chang correlation via the association parameter. If the reliability of Equation (1) is assumed to extend to solute water systems as well, one must conclude that the molar volume of water as a diffusing species is much greater than that measured at its normal boiling point. Specifically the factor 2.3 mentioned above leads to a ratio of the molar volume of diffusing water to that suggested for use in Equation (1) of $2.3^{1.67}$ or 4.0. That this ratio is so close to an integer value immediately suggests this explanation: the species which actually transfers when water diffuses through an organic solvent is composed of four tightly bound single water molecules. If the polymerization reaction were represented by the equilibrium

$$4H_2O \rightleftarrows (H_2O)_4 \tag{2}$$

TABLE 1. DIFFUSIVITIES OF WATER AS THE SOLUTE

Solvent	Temperature, °C.	Volume %, water	Diffusion coefficient x 10^5 Experimental	Equation (1)	Reference
Acetone	25	0.8	4.56	8.70	*1*
Aniline	20	—	0.70	0.83	*5*
Ethyl acetate	20	—	3.20	7.52	*5*
Ethyl acetate	30	—	3.6	9.0	*5*
Ethyl alcohol	18	1.0	1.10	2.58	*4*
Ethyl alcohol	15	0.5	1.02	2.39	*4*
Ethylene chlorohydrin	21.5	80.0	0.46	1.20	*3*
Furfural	20	—	0.90	2.14	*5*
Furfural	30	—	1.69	2.69	*5*
Isobutanol	20	—	0.36	0.81	*5*
Isobutanol	18	7.5	0.22	0.75	*4*
Isobutanol	18	2.0	0.31	0.75	*4*
Isobutanol	15	0.5	0.30	0.67	*4*
Isopropanol	15	0.5	0.38	0.99	*4*
n-Butyl alcohol	30	3-17.5	1.24-0.27	1.43	*6*

TABLE 2. REPRESENTATIVE DIFFUSIVITIES IN SOLVENT WATER

Solute	Temperature, °C.	Volume %, water	Diffusion coefficient x 10^5 Experimental	Equation (1)	Reference
Acetone	25	0.2	1.28	1.28	*1*
Aniline	20	—	0.92	0.89	*5*
Ethyl acetate	20	—	1.00	0.88	*5*
Ethyl acetate	30	—	1.75	1.14	*5*
Furfural	20	—	1.04	0.99	*5*
Furfural	30	—	1.28	1.28	*5*
Isobutanol	20	—	0.84	0.92	*5*
Isobutanol	18	8.8	0.71	0.86	*4*
Isobutanol	18	1.0	0.85	0.86	*4*
Isobutanol	15	0.5	0.77	0.79	*4*
n-Butyl alcohol	15	0.5	0.77	0.79	*4*

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* Visual observation of the correlational plots presented by Othmer and Thakar (*9*) and Wilke and Pin Chang (*10*) indicates the latter to be a more effective representation of diffusion data in nonaqueous solvents. Furthermore Sherwood and Reid (*8*) have found that predictions by the Othmer-Thakar method of diffusivities in methanol (an oxygenated organic compound similar to the solvents considered here) were so much in error that comparison with experimental data was not warranted. Therefore the following discussion will be based solely upon the predictions of Equation (1).

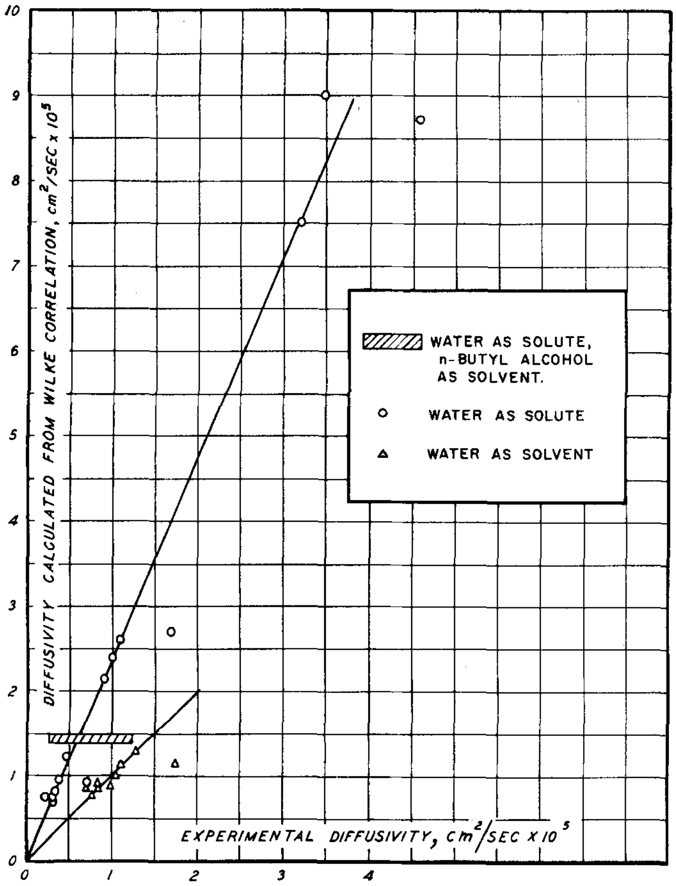

Fig. 1. Comparison of experimental and predicted diffusivities for water as solute and as solvent.

then the mass action constant for the reaction must be large to account for the invariance of polymer to monomer ratio with water concentration, as suggested by the constancy of the factor 2.3. However if diffusion experiments were conducted in sufficiently dilute water systems, then according to this explanation, the observed diffusion coefficients should approach those predicted by Equation (1).

It should be noted that the molar-volume ratio of four need not restrict the nature of the associated species to that indicated by Equation (2). It is more likely that there exist polymers containing a variable number of single molecules, with an average chain length of four units. In this case the near-integer value of the molar-volume ratio is fortuitous.

NOTATION

D = diffusion coefficient, sq. cm. sec.
M = molecular weight of solvent
T = temperature, °K.
V = molar volume of solute at its normal boiling point
x = association parameter for the solvent
μ = viscosity of the solution, centipoises

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The Ratio of Fluids to Solid Temperature and/or Concentration in Fixed-Bed Processes

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The following is a comment on the communication by H. E. Hoelscher (*1*).

The temperature difference in a bed initially at zero temperature and heated by a gas at unit inlet temperature is given by

$$T_f - T_s = e^{-x-y} I_0 \, (2\sqrt{xy})$$

where x and y are dimensionless place and time coordinates as defined by Hoelscher [see for instance (2), Equation (5)].

Or if use is made of a well-known expansion for the Bessel function I_0 [see for instance (2), Equation (17)]

$$T_f - T_s = \frac{e^{-(\sqrt{y}-\sqrt{x})^2}}{2\pi^{1/2}(xy)^{1/4}} \left(1 + \frac{1}{16\sqrt{xy}} + \frac{9}{512\,xy} + \ldots \right)$$

This function is very near maximum for $y = x$, at the mid-point of breakthrough, when

$$T_f - T_s = \frac{1}{2\sqrt{\pi x}} \left(1 + \frac{1}{16\,x} + \ldots . \right)$$

It is felt that the approach to the above problem via heat transfer theory (linear isotherms) is simpler than via adsorption theory (Langmuir isotherms). A survey of the heat transfer literature for the step-function input has been given by Klinkenberg (*2*), while Klinkenberg and Harmens (*3*) have recently dealt with the generalized problems of arbitrary initial solid and gas temperatures.

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