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Tracer Diffusion of Water in Organic Liquids

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The tracer diffusion coefficient, D_w, for water (as HTO) in 28 organic solvents, including 13 esters, benzene, and 7 substituted benzenes, has been determined at 298.15 K using the diaphragm cell technique. The variation of the water diffusion coefficient with solvent viscosity (η) is significantly different for the hydrophobic solvents (benzene and substituted benzenes, cyclohexane, hexane, and tetrachloromethane) in comparison with the other solvents, in that the $D_w\eta$ product is significantly larger (average value 3.68 $\times 10^{-12}$ N compared to 1.60 $\times 10^{-12}$ N). The apparent hydrodynamic radius derived from the Stokes−Einstein equation is about half the molecular radius for water diffusing in the hydrophobic solvents, and 1−1.5 times the molecular radius for diffusion in the other solvents.

Introduction

Tracer diffusion coefficients (D) for solutes at low concentrations in various solvents have been determined experimentally for a wide variety of solutes and solvents. In addition, several empirical correlations of solute diffusion coefficients with solvent properties have been proposed; these approaches have been discussed at length by Reid *et al.* (1977). Although some of the empirical correlations provide reasonably accurate predictions of diffusion coefficients in general, in the particular case of water as solute, diffusing (with diffusion coefficient D_w) in organic liquid solvents, no single empirical correlation has been particularly successful as a basis for prediction.

The data base for diffusion of water in organic liquids is relatively small, although Sarram (1971) and Lees and Sarram (1971) reported measurements on a fairly wide range of solvents. However, there are very few data for water diffusion in groups of structurally related compounds except for straight chain alcohols, so that using existing data, it is difficult to identify trends in D_w within, for example, homologous series of compounds as solvents.

The primary objective of the present work was to extend the range of water diffusion data by measuring the tracer diffusion coefficient of water in groups of structurally similar compounds. All of the measurements were done at 298.15 K, and for the most part the solvents were groups of related compounds, with particular attention paid to esters and to substituted benzenes in an attempt to identify constitutional isomer and substituent effects. Furthermore, the application of the Stokes−Einstein equation to the case of a small solute diffusing in a solvent with larger molecular size was of interest.

Experimental Section

Tracer diffusion coefficients of water (as HTO, supplied by Amersham Radiochemicals) in solvents with nonexchangeable protons were determined at (298.15 ± 0.02) K using diaphragm cells with sintered glass diaphragms, and the associated cell calibration and other standard procedures described by Mills and Woolf (1968). Organic liquids of AnalaR (or equivalent) quality were used without further purification. Solvents of lesser purity were fractionally distilled, and the fractions with boiling point in accordance with accepted values (Riddick *et al.*, 1986) used for the measurements. Some of the esters used were synthesized and purified using the procedures recommended by Vogel (1966).

Since water is only very slightly soluble in many of the solvents that were used, a variation on the normal procedure for starting diffusion experiments (that is, injecting an appropriate volume of tracer into the liquid in the top compartment of the diaphragm cell) was needed for those (low solute solubility) cases. In a typical experiment, a suitable volume (5−50 μL) of HTO was dissolved in about 20 mL of organic solvent to make a tracer solution. The HTO/solvent tracer solution was then equilibrated, together with the diaphragm cell about 80% filled with solvent, at 298.15 K. After equilibration, the experiment was started by rapidly transferring the tracer solution to the top compartment of the diaphragm cell, topping the cell with pure solvent and inserting the top plug. The diaphragm cells used had total volumes on the order of 100 mL, so the average concentration of HTO in the organic solvent was about 0.005−0.05% by volume. There is no reason to expect that the tracer diffusion coefficient of water will be measurably concentration dependent, at these concentrations.

The standard radiochemical procedures described by Mills and Woolf (1968) utilizing liquid scintillation counting were used to analyze top and bottom cell compartment solutions after diffusion for times that were generally within 10% of the optimum time: at least 10^6 counts were accumulated for each solution. For a few randomly selected solvents, replicated experiments were done using two independently calibrated diaphragm cells, as a check on the accuracy of the overall procedure. The maximum difference in replicated values of D_w was about 0.5% and the overall accuracy of the tracer diffusion coefficients is estimated to be within ±1%.

For solvents for which viscosity data were not readily available, viscosities were measured using a capillary viscometer that had been calibrated using water and several organic liquids with accurately known viscosity. Efflux times were at least 200 s and were determined with reproducibility ±0.05 s. The accuracy of the measured viscosities is estimated to be within ±0.5%.

Results and Discussion

The measured values of D_w are listed in Table 1, together with water diffusion coefficients (for 298.15 K only) from the literature, solvent viscosity (η) which was either

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Table 1. Water Diffusion Coefficients at 298.15 K

solvent	$10^3\eta$/Pa s	10^9D_w/m^2 s^{-1}	ref	$10^{12}D_w\eta$/N
ethyl formate	0.379	3.71_1	*a*	1.41
methyl acetate	0.364	3.57_4	*a*	1.30
ethyl acetate	0.426	4.25_0	*a*	1.81
propyl acetate	0.551	3.12_8	*a*	1.72
1-methylethyl acetate	0.52	3.09_1	*a*	1.61
ethyl propionate	0.501	3.72_5	*a*	1.87
butyl acetate	0.686	2.92_3	*a*	2.01
		2.87	*b*	1.97
2-methylpropyl acetate	0.651	3.10_8	*a*	2.02
1-methylpropyl acetate	0.65	2.64_0	*a*	1.72
1,1-dimethylethyl acetate	0.679	1.92_3	*a*	1.31
ethyl butyrate	0.613	2.13_2	*a*	1.31
pentyl acetate	0.862	2.13_7	*a*	1.84
2-methylbutyl acetate	0.790	2.09_8	*a*	1.66
benzene	0.603	6.31	*a*	3.80
toluene	0.553	6.07	*a*	3.36
		6.12	*b*	3.38
o-xylene	0.756	4.37_9	*a*	3.31
m-xylene	0.581	5.53	*a*	3.21
p-xylene	0.605	5.62	*a*	3.40
1,3,5-trimethylbenzene	1.039	4.33_6	*a*	4.51
2-phenylpropane	0.739	4.89_5	*a*	3.62
nitrobenzene	1.778	2.80	*b*	4.98
-dichlorobenzene	1.324	3.33_4	*a*	4.41
formamide	3.302	0.476	*a*	1.57
-methylformamide	1.65	0.839	*a*	1.38
-dimethylformamide	0.802	1.81_7	*a*	1.46
acetonitrile	0.341	5.78	*c*	1.97
propionitrile	0.409	4.66_6	*a*	1.91
methanol	0.551	2.190	*d*	1.21
ethanol	1.083	1.132	*e*	1.23
		1.220	*f*	1.32
		1.18	*g*	1.28
1-propanol	1.943	0.4_8	*h*	0.93
acetone	0.303	5.26_7	*i*	1.60
dimethyl sulfoxide	1.991	0.899	*a*	1.79
cyclohexane	0.898	3.40_4	*a*	3.06
hexane	0.294	9.5_3	*a*	2.80
tetrachloromethane	0.900	4.115	*j*	3.70
-methylpyrrolidone	1.666	1.003	*k*	1.67

This work. [b] Lees and Sarram (1971). [c] Easteal (1980). [d] Deret *al.* (1985). [e] Hammond and Stokes (1953). [f] Dullien and Shemilt (1961). [g] Tominaga and Matsumoto (1990). [h] Hawlicka and Grabowski (1992). [i] Mills and Hertz (1980). [j] Weingartner (1985). [k] te Riele *et al.* (1995).

measured or taken from the compilation by Riddick *et al.* (1986), and the $D_w\eta$ product. Table 1 includes data from the literature in the case of solvents which provide a useful comparison with solvents that have been investigated in the present work. The data for the alcohols have been included for that reason, for comparison with acetonitrile and propionitrile specifically, but the table is not a comprehensive compilation of tracer diffusion coefficients for water in nonaqueous solvents. It should be noted that, for example, diffusion coefficients for water in acetone, tetrahydrofuran, and pyridine have been reported by von Goldammer and Zeidler (1969), but the accuracy of those data is relatively low and for that reason they have not been included in the table.

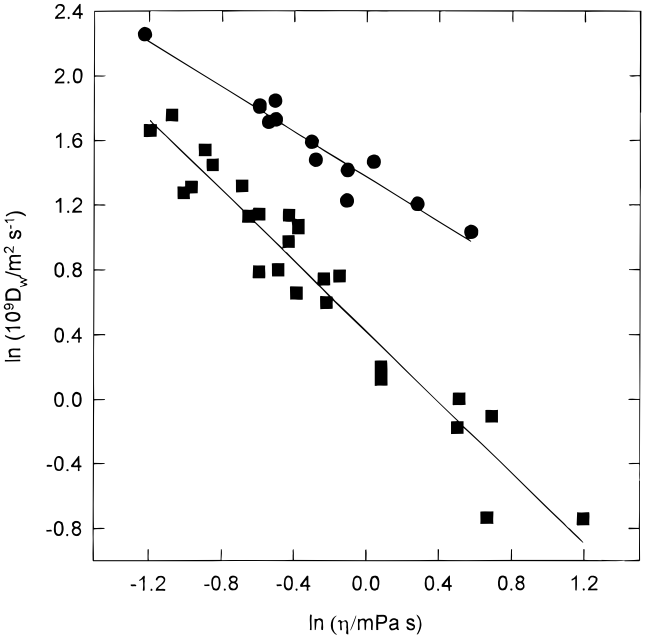

Figure 1. Dependence of the water diffusion coefficient on solvent viscosity: (●) hydrophobic solvents (see text); (■) other solvents. The lines drawn are best-fit lines calculated by the method of least squares.

The values reported by Mills (1973) for the tracer diffusion coefficient for HTO in normal water are about 3% smaller than self-diffusion data (i.e. the diffusion coefficient for $H_2{}^{16}O$) determined by Harris and Woolf (1980). It should be noted, however, that this difference is only partly a manifestation of an isotopic mass effect, because Easteal *et al.* (1984) found that the tracer diffusion coefficient for $H_2{}^{18}O$ in normal water is within approximately 1% of the self-diffusion coefficient. Consequently, most of the difference between the diffusion coefficients for HTO and $H_2{}^{16}O$ in water can be ascribed to stronger hydrogen bonding between T and oxygen from neighboring water molecules than between H and oxygen. A similar differential hydrogen bonding effect can be expected for HTO, compared to $H_2{}^{16}O$, in organic liquids which can form hydrogen bonds to water; that is the diffusion coefficient of HTO may be up to about 3% smaller than the diffusion coefficient for $H_2{}^{16}O$. On the other hand, for organic liquids which do not form hydrogen bonds to water the diffusion coefficient for HTO is likely to be within 1% of the value for $H_2{}^{16}O$. For example, Weingärtner (1985) found $D(\mathrm{HTO}) = 4.115 \times 10^{-9}$ m^2 s^{-1} and $D(\mathrm{H_2O}) = 4.07 \times 10^{-9}$ m^2 s^{-1} in tetrachloromethane at 25 °C.

In the few cases where a direct comparison with previous determinations of D_w is possible, the agreement with literature data is within the combined experimental uncertainties in the data. For example, for butyl acetate and toluene, the values of D_w obtained in the present work differ by about 1.5% and 0.8%, respectively, from the values reported by Lees and Sarram (1971). Most of the previously reported diffusion coefficients for water in organic solvents are for normal water rather than isotopically substituted water. However, as noted above the difference between $D(\mathrm{HTO})$ and $D(\mathrm{H_2O})$ in a particular solvent is not likely to exceed about 3%.

The $D_w\eta$ product for water in the hydrophobic solvents benzene and benzene derivatives, cyclohexane, hexane, and tetrachloromethane is up to about 400% larger than for the other solvents, including the esters in many of which water has a low solubility. (The term hydrophobic is used here to denote solvents for which water−solvent intermolecular interactions are primarily repulsive.) For the group of 12 hydrophobic solvents $D_w\eta$ is in the range 2.80×10^{-12} N (hexane) to 4.98×10^{-12} N (mesitylene), and the average value is 3.68×10^{-12} N (with standard deviation ±18%). The largest value of $D_w\eta$ for the remaining solvents is 45% smaller than the hydrophobic solvent average value. The different behavior of the hydrophobic and the remaining solvents is shown by Figure 1, which, notwithstanding the scatter of the points about the lines, suggests that the viscosity dependence of D_w is different for the two groups of solvents. That is, if the solute diffusion coefficient is assumed to be given by a relationship of the form

$$D_{\mathrm{w}} \propto 1/\eta^{\alpha} \qquad (1)$$

then for the hydrophobic solvents collectively $\alpha = 0.70$, which is close to the value found by Easteal (1990) for the tracer diffusion of several solutes in an aqueous sucrose solution. By contrast, for the group of other solvents $\alpha = 1.10$, which seems not to be a physically reasonable value because, to the author's knowledge, there are no other cases for which an exponent larger than unity has been found.

The data for the alcohols (methanol and ethanol in particular) provide an interesting contrast with the data for the similarly sized, but non-hydrogen bonding, acetonitrile and propionitrile. The $D_{\mathrm{w}}\eta$ product for the nitriles is 59% larger than for methanol and ethanol, and it seems reasonable to attribute this difference to direct or indirect effects of hydrogen bonding of water to the alcohol molecules. A similar explanation (invoking strong or weak intermolecular interactions) was advanced previously by Easteal and Woolf (1984) to account for the differing diffusivities of polar and apolar solutes in acetonitrile.

The data for water diffusing in esters as solvents show some trends that may be attributable to constitutional isomerism. In the first place, for the isomers ethyl formate and methyl acetate $D_{\mathrm{w}}\eta$ has the same value, to within a few percent. Similarly, for the 5-carbon atom isomers propyl acetate, 1-methylethyl acetate, and ethyl propionate is approximately constant, though the average value is about 28% larger than for the 3-carbon atom isomers. For the 6-carbon atom isomers, on the other hand, the situation is more complex. For example, butyl and 1-methylpropyl acetate have virtually the same viscosity, but the values of D_{w} differ by about 18%. This difference suggests that the structure of the larger hydrocarbon moiety of the solvent can affect the diffusive mobility of water even when the viscosity is unchanged. Also, D_{w} is 27% smaller for ethyl butyrate than for butyl acetate, while the viscosity is also smaller for ethyl butyrate. These data indicate that there may be a structural effect determined by the position of the carbonyl group in the ester molecule. For the esters collectively, the range of values of the $D_{\mathrm{w}}\eta$ product is surprisingly large (55% of the smallest value), and while it is tempting to suggest that the smaller values arise from relatively strong, specific solute–solvent interactions, it seems improbable that a group of solvents with such similar molecular structures would show significant differentiation on the basis of strong or weak interactions with water.

According to the Stokes–Einstein equation

$$D = kT/z\pi\eta r \qquad (2)$$

where k is the Boltzmann constant, T is temperature, r is the effective radius of the solute, and z is either 4 (the hydrodynamic slip condition) or 6 (stick condition); D should be inversely proportional to the solution (that is solvent, in the case of tracer diffusion) viscosity. The validity of the Stokes–Einstein equation for diffusion of relatively small solute molecules has been the subject of much discussion in the literature. One way in which eq 2 has been applied (Tyrrell and Harris, 1984) is to calculate a "Stokes–Einstein number" defined by

$$n = kT/D_{\mathrm{w}}\eta\pi r \qquad (3)$$

assuming a constant radius for the diffusing molecule. For this calculation the value of r for water was taken to be 169 pm, as estimated by Edward (1970) from Van der Waals increments of atoms. The values of n are in the approximate range 4–6 (corresponding to the "slip" and "stick" values for z in eq 2) for the nonhydrophobic solvents, and for the group of hydrophobic solvents n is approximately 2. As shown in Figure 2, n is almost independent of viscosity for the nonhydrophobic solvents (though there is considerable variation in n at constant viscosity).

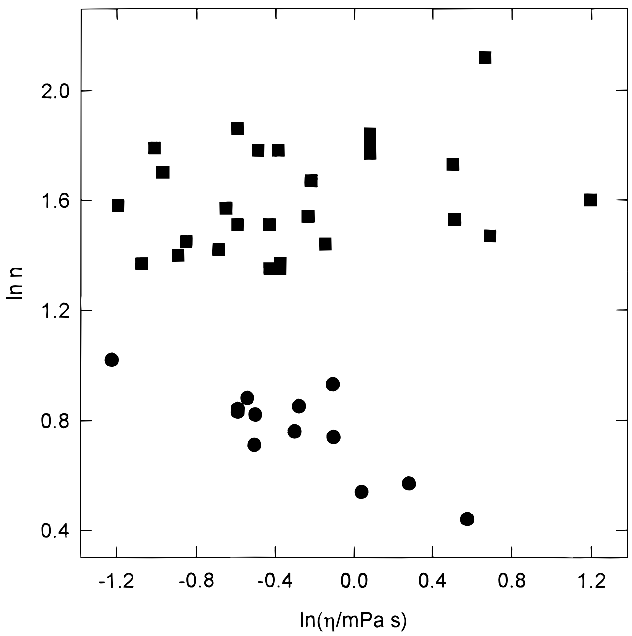

Figure 2. Dependence of the Stokes–Einstein number for water diffusion on solvent viscosity. (●) hydrophobic solvents (see text); (■) other solvents.

It has been shown by Pau *et al.* (1990), for diffusion of ions in aqueous solution, and by Balucani *et al.* (1990) that eq 2 with $z = 4$ is the most appropriate form for the Stokes–Einstein equation. Hawlicka and Grabowski (1992) concluded that for diffusion of water in 1-propanol + water solutions, departures from eq 2 with $z = 4$ can be ascribed to the hydrodynamic radius of the diffusing species being larger than the molecular radius. A hydrodynamic radius, r_{h}, for water as solute can be calculated from the equation

$$r_{\mathrm{h}} = kT/4\pi\eta D_{\mathrm{w}} \qquad (4)$$

It is convenient to calculate, instead of r_{h}, the radius ratio R_{h} defined by

$$R_{\mathrm{h}} = r_{\mathrm{h}}/r_{\mathrm{w}} \qquad (5)$$

where r_{w} (Edward's nomenclature) is the molecular radius of water, taken to be 169 pm. For the nonhydrophobic solvents in Table 1, the average value of R_{h} is 1.26 (standard deviation 0.26; range 0.96–2.08), and for all solvents except the alcohols R_{h} is less than 1.5. A possible interpretation of values of $R_{\mathrm{h}} > 1$ is that in those cases the diffusing unit is on average an aggregate of more than one molecule. A similar conclusion has been reached by Iwahashi *et al.* (1986, 1990) in relation to self-diffusion of alcohols and fatty acids; it was suggested that in both cases the diffusing unit is on average a dimer. However, for water diffusing as a tracer in the solvents studied in the present work, the R_{h} values greater than unity probably do not indicate that water is diffusing in part as dimers and in part as monomers, but rather that translational motion of the water molecule involves cooperative movement of one or more neighboring solvent molecules. Alternatively, $R_{\mathrm{h}} > 1$ may be a reflection of retardation of diffusive motions by strong specific interactions with neighboring solvent molecules. R_h values very close to unity for diffusion in the nitriles, compared to values above 1.5 for the alcohols, tend to support that argument.

R_h values for water diffusion in the hydrophobic solvents are almost all close to 0.5 (average value 0.54; standard deviation 0.08; range 0.39−0.69). In these cases the apparent hydrodynamic radius is about 40−70% of the molecular radius. The diffusive motions of the solute are evidently facilitated, perhaps by hydrophobic interaction of the solute molecules with nearest neighbor solvent molecules.

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