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Diffusion of Polar and Nonpolar Molecules in Water and Ethanol

Toshihiro TOMINAGA* and Shigetoshi MATSUMOTO
Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700

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Interdiffusion coefficients of 1,2-butanediol, 1,4-butanediol, *meso*-erythritol, xylitol, mannitol, and *myo*-inositol in water, and of 1-butanol, 1,2-ethanediol, 1,2-butanediol, 1,4-butanediol, 1,2,3-propanetriol, water, and benzene in ethanol have been measured at concentrations close to infinite dilution and temperatures between 278 and 373 K. In water, activation energies are not sensitive to the solutes, decrease with increasing temperature, and are close to that for the self-diffusion of pure water. In ethanol the activation energy is largest for water and smallest for benzene. The quantity $D\eta/T$ (D, η, and T are diffusivity, viscosity, and absolute temperature, respectively) is not sensitive to temperature in water, but shows strong dependence on the temperature for benzene and water in ethanol. Using the corrected Stokes–Einstein equation, the effective radii of the solutes were obtained in ethanol. Some differences in diffusion behavior in ethanol and water are discussed.

In previous studies, we examined the limiting interdiffusion coefficients of hydrophobic solutes such as aromatic hydrocarbons[1,2] and a neutral metal complex[3] in water. In particular, we tried to find out if there is any effect of "water-structure" itself or of the enhanced "water-structure" around solute molecules on the diffusion of hydrophobic molecules. We have also examined the diffusion in water of alcohols having one to four hydroxyl groups.[4] In two of the studies, we made measurements covering a wide temperature range, from the supercooled region to the region above the normal boiling point of water (265—433 K).[2,4] Activation energies for the diffusion were not sensitive to the solutes and were close to that for the self-diffusion of pure water. Over a wide temperature range of 278—433 K, the variation of the quantity, $D\eta/T$, was 12% or less, although for the whole temperature range (265—433 K) the variation was greater for some of the solutes. In ethanol, literature data show that the quantity, $D\eta/T$, is much more sensitive to the temperature and to the solute, e.g., 23% increase in $D\eta/T$ for ethanol (self-diffusion) from 280 to 338 K,[5] 12% increase for water from 298 to 338 K,[6] 22% decrease for trioxane from 298 to 353 K.[7]

This work was undertaken to study the difference in the diffusion behavior in the two hydrogen-bonding solvents, water and ethanol. We report here the diffusion coefficients of some alcohols, water, and benzene in ethanol from 278 to 373 K. The diffusion coefficients of polyols[8] and carbohydrates[9] have been studied in water at 298 K, but their temperature dependence has not been studied. We also report the diffusion coefficients of alcohols having two to six hydroxyl groups in water in the same temperature range. We will discuss some differences in diffusion behavior in the two solvents.

Experimental

1,2-Butanediol (1,2-BD), 1,4-butanediol (1,4-BD), xylitol, mannitol, *myo*-inositol (Tokyo Kasei Kogyo, guaranteed reagent); *meso*-erythritol (Merck, biochemistry grade); ethanol, 1-butanol, 1,2-ethanediol (1,2-ED), 1,2,3-propanetriol (1,2,3-PT), and benzene (Wako Pure Chemicals, special grade) were used as received. The density of ethanol was 0.78550—0.78557 g cm^{-3} at 298.2 K as compared with the literature value of 0.78509 g cm^{-3}.[10] The water was distilled twice. Diffusion coefficients were measured by the Taylor dispersion technique.[11] A spectrophotometric detector (Japan Spectroscopic Co., model UVIDEC 100-IV) or a differential refractometer (Waters Model R-401) was used for benzene and for the other solutes, respectively. At 373.2 K in water, and at 353.2 and 373.2 K in ethanol, slightly higher pressures (0.3—0.8 MPa) than the saturated vapor pressures were applied. Other details have been described elsewhere.[1,2]

Results and Discussion

Tables 1 and 2 show the diffusion coefficients in water and in ethanol, respectively. Each value is an average of at least four measurements. The solutions injected were 1 wt% or less in concentration, and they are diluted tenfold several times as they flowed through the capillary. Accordingly, the values can be considered as limiting interdiffusion coefficients.

Table 1. Limiting Interdiffusion Coefficients ($D/10^{-9}$ m^2 s^{-1}) in Water

T/K	1,2-Butanediol	1,4-Butanediol	*meso*-Erythritol	Xylitol	Mannitol	*myo*-Inositol
278.2	0.491±0.003	0.492±0.002	0.446±0.003	0.416±0.003	0.371±0.002	0.376±0.004
298.2	0.927±0.009	0.913±0.003	0.813±0.008	0.758±0.004	0.678±0.007	0.695±0.002
313.2	1.35 ±0.01	1.34 ±0.01	1.18 ±0.01	1.059±0.008	0.963±0.002	0.991±0.005
333.2	2.01 ±0.01	1.97 ±0.01	1.80 ±0.01	1.67 ±0.01	1.52 ±0.01	1.52 ±0.01
373.2	3.78 ±0.01	3.78 ±0.03	3.30 ±0.02	3.05 ±0.01	2.78 ±0.02	2.89 ±0.02

Table 2. Limiting Interdiffusion Coefficients ($D/10^{-9}$ m^2 s^{-1}) of Alcohols, Water, and Benzene in Ethanol

T/K	1-Butanol	1,2-Ethanediol	1,2-Butanediol	1,4-Butanediol	1,2,3-Propanetriol	Water	Benzene
278.2	0.611±0.004	0.536±0.007	0.493±0.003	0.433±0.002	0.431±0.002	0.690±0.006	1.26±0.01
298.2	0.927±0.009	0.808±0.008	0.778±0.011	0.662±0.003	0.686±0.009	1.18 ±0.01	1.86±0.01
333.2	1.84 ±0.01	1.75 ±0.04	1.64 ±0.01	1.40 ±0.02	1.48 ±0.03	2.65 ±0.05	3.33±0.01
353.2		2.52 ±0.04	2.38 ±0.06		2.12 ±0.03	3.82 ±0.04	4.35±0.03
373.2	3.38 ±0.10	3.33 ±0.02	3.25 ±0.02	2.83 ±0.03	3.08 ±0.05	5.56 ±0.03	5.57±0.02

Our values for *meso*-erythritol and mannitol at 298.2 K are in good agreement with those by Longsworth (0.805×10^{-9} m^2 s^{-1})[12] and Dunlop (0.666×10^{-9} m^2 s^{-1}),[13] respectively. The value for *myo*-inositol at 298.2 K is 8% higher than that by Sartorio et al. (0.641×10^{-9} m^2 s^{-1}).[8] The value for water in ethanol at 298.2 K may be compared with literature values of (1.08,[6] 1.13,[14] and 1.22[15])$\times10^{-9}$ m^2 s^{-1}. The values for benzene in ethanol at 298.2 and 373.2 K may be compared with (1.81[16] (298.3 K) and 5.60[17])$\times10^{-9}$ m^2 s^{-1}, respectively.

Figures 1 and 2 show Arrhenius plots in water and ethanol, respectively. Activation energies for the diffusion may be calculated from

$$E_\mathrm{D}=-R[\mathrm{d}\ln D/\mathrm{d}(1/T)]. \qquad (1)$$

In water, the slopes of the plots (Fig. 1), or the activation energies, are insensitive to the solutes and decrease with increasing temperature, as has been already noted.[2,4] Also shown in Fig. 1 are literature data for the self-diffusion of water.[18] We see that the activation energies (slopes of the curves) for the solute studied are very close to that for the self-diffusion of water. In ethanol, the plots are linear within experimental uncertainties (Fig. 2). Activation energies calculated from Eq. 1 are shown in Table 3. With the exception of water, there is a tendency for E_D to increase with decreasing diffusion coefficient, i.e., E_D decreases in the order, water >1,2,3-PT>1,2-BD, 1,4-BD, 1,2-ED>1-butanol>benzene. The E_D values for the hydroxylic compounds are larger than those for crown ethers[7] when compared at the same solute size.

Table 3. Activation Energies for the Diffusion in Ethanol (E_D/kJ mol^{-1})

1-Butanol	15.6
1,2-Ethanediol	17.0
1,2-Butanediol	17.3
1,4-Butanediol	17.2
1,2,3-Propanetriol	17.8
Water	18.9
Benzene	13.5

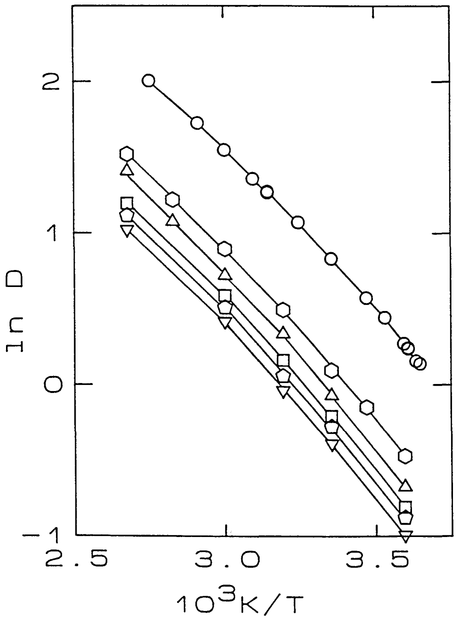

Fig. 1. Arrhenius plots for diffusion in water. ○, water (Ref. 18); ⬡, benzene (Ref. 2); △, 1-butanol (Ref. 4); □, *meso*-erythritol; ⬠, xylitol; ▽, mannitol.

The diffusion coefficient of a spherical solute of radius r in a continuum of viscosity η is given by the Stokes-Einstein equation

$$D=\frac{kT}{f\pi\eta r}, \qquad (2)$$

where k is Boltzmann's constant. The value of f is 4

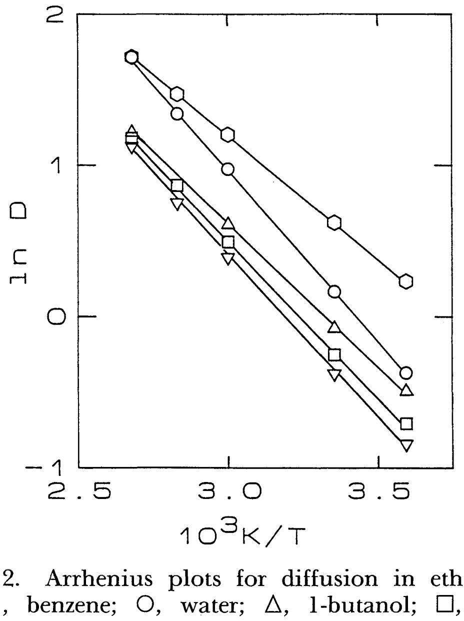

Fig. 2. Arrhenius plots for diffusion in ethanol. ⬡, benzene; ○, water; △, 1-butanol; □, 1,2-butanediol; ▽, 1,2,3-propanetriol. For clarity, data for 1,2-ethanediol and 1,4-butanediol are not shown.

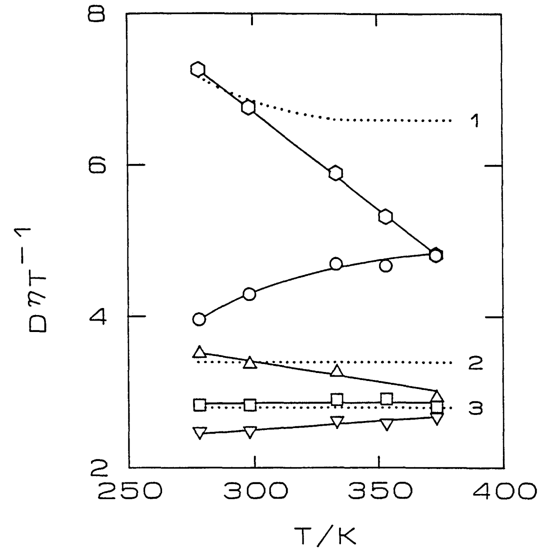

Fig. 3. The quantity $D\eta/T$ as a function of temperature. Symbols are the same as in Fig. 2. The units of $D\eta/T$ are 10^{-15} J m^{-1} K^{-1}. Dotted lines show the results for water (1); benzene (2); and 1,2,3-propanetriol (3) in water. The results for 1-butanol and 1,2-butanediol in water are close to the line for 1,2,3-propanetriol.

for the slip boundary condition and 6 for the stick boundary condition. If the Stokes-Einstein equation holds, the quantity $D\eta/T$ should be constant. If $D\eta/T$ varies from temperature to temperature or from solvent to solvent, it means either that the Stokes-Einstein law does not hold (in terms of Eq. 2, the coefficient f is varying), that the effective (solvated) radius is varying, or both of them. Plotted in Fig. 3 are $D\eta/T$ values in ethanol as a function of the temperature. Dotted lines show the results for three solutes, water (self-diffdision),[18] benzene,[1,2] and 1,2,3-PT,[4] in water. Viscosity values both for ethanol and water were taken from the literature.[19] For the three diols (only 1,2-BD is shown in Fig. 3) and 1,2,3-PT, the temperature dependence of $D\eta/T$ is not great. For benzene and water as solutes, $D\eta/T$ values are strong functions of the temperature and are very different in the two solvents. For benzene as a solute, $D\eta/T$ values in ethanol are much larger than those in water and decrease with increasing temperature. However, even at 373 K, $D\eta/T$ is still higher in ethanol. This tendency for the decrease of $D\eta/T$ with increasing temperature, or with decreasing viscosity, has been known for nonpolar solutes in polar and nonpolar organic solvents.[20–24] If we take the coefficient f to be constant, it means that the effective radius r is increasing with an increase in the temperature, which is physically unrealistic. This tendency is preferably attributed to the breakdown of the Stokes-Einstein law at the molecular level, i.e., the f value is smaller than 4 and is decreasing with a decrease in the temperature, as will be seen later. For water as a solute, the results are opposite from those for benzene, i.e., $D\eta/T$ values in ethanol are much smaller than those in water (self-diffusion), and increase with temperature. In this case, we can interpret the latter trend to mean that the effective radius is decreasing with increasing temperature. Note that $D\eta/T$, is still lower in ethanol even at 373 K, suggesting that the effective radius of water is larger in ethanol than in water.

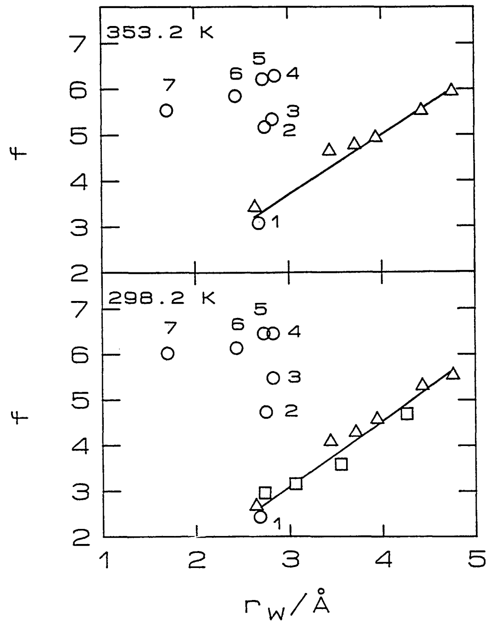

Fig. 4. The coefficient, f, of Eq. 2 as a function of the solute van der Waals radius in ethanol. 1, Benzene; 2, 1-butanol; 3, 1,2-BD; 4, 1,4-BD; 5, 1,2,3-PT; 6, 1,2-ED; 7, water. (The f values for 1-butanol and 1,4-BD at 353.2 K were obtained from the interpolated diffusion coefficients.) △, Crown ethers from Ref. 7; □, carbon tetrachloride and tetraalkyltins from Ref. 20.

Using the van der Waals radius, r_w, of the solute,[25] we can calculate the coefficient f of Eq. 2. For nonpolar solutes in various kinds of organic solvents, where solute-solvent interactions are weak and the solute radius is considered to be constant, the following have been shown: 1) for a fixed solute, the f value of Eq. 2 decreases with an increase in the solvent viscosity or a decrease in the temperature,[20–24] 2) for a fixed solvent, the f value decreases with a decrease in the solute size.[20] Using van der Waals radii (shown in the 2nd column of Table 4), f values were calculated, and the results at 298.2 and 353.2 K are shown in Fig. 4 together with literature values for nonpolar solutes, carbon tetrachloride,[20] tetraalkyltins,[20] and crown ethers.[7] (Unfortunately, data are not available for nonpolar solutes at the lowest and the highest temperatures we studied, i.e., 278.2 and 373.2 K.) For the hydroxylic solutes, the f values range from 4.6 (for 1-butanol at 278.2 K) to 6.3 (for 1,4-BD and 1,2,3-PT at 373.2 K), and in many cases they are within the Stokes-law limit, i.e., $4 \leq f \leq 6$. Slightly larger f values than 6 may be explained by the increase in the effective radius. Thus, for the hydroxylic solutes, the results are apparently understood in the framework of the Stokes-Einstein law without any correction. For benzene, however, the f values are 2.3—3.4 and are well below the Stokes-law limit. The f values smaller than 4 have no physical significance, and imply the breakdown of the Stokes-Einstein law. Robinson and Stokes calculated correction factors to the Stokes law for solutes of less than 5 Å radius in water, and estimated the radii of heavily hydrated ions from the limiting ionic mobilities.[26] We will take the similar procedure in ethanol, but we are in a better situation because we have experimental data for the diffusion of nonpolar solutes in ethanol, and the case must be simpler than that of the ionic mobility in water.

For the nonpolar solutes, over the range of r_w= 2.64—4.76 Å, f can be expressed by

$$f = -1.068 + 1.405 r_w \tag{3}$$

for 298.2 K and

$$f = -0.005 + 1.263 r_w \tag{4}$$

for 353.2 K, where r_w is in Å. Using Eqs. 2—4, we obtained the effective radii, r, and corresponding f values, which are listed in Table 4. The solutes of r_w=1.7—2.8 Å are seen to be diffusing with an effective radius of r=3.1—4.0 Å at 298.2 K. Even at 353.2 K (a little above the normal boiling point of the solvent), the effective radii are seen to be 22 to 61% larger than the van der Waals radii.

Plotted in Fig. 5 are f values in water including previous results of ours and others for hydroxylic compounds[4,18,27] and nonpolar molecules.[2,28,29] If we assume that the nonpolar molecules are not hydrated (effective radius is equal to r_w), we find the effective radii for the hydroxylic solutes (except water and methanol) to be 9±2% and 11±3% larger than the van der Waals radii at 298.2 and 373.2 K, respectively. These effective radii are much smaller than those in ethanol. This may be due in part to the fact that the nonpolar molecules are hydrated (hydrophobic hydration), which increases the effective radii of the nonpolar molecules themselves and also of the hydroxylic compounds. For the six hydroxylic solutes studied here, the f values decrease from 298 to 373 K, but only by 3 to 5% ($D\eta/T$ values increase by the same amount). For 1-butanol, 2-methyl-2-propanol, and butylbenzene, the f values decrease by 8 to 10% from 298 to 373 K, and for all the other solutes in Fig. 5, they vary no more than 5% over the same temperature range. In view of the fact that water is a more "structured" solvent than ethanol, it is worth noting that both the temperature dependence and the solute dependence of f (in other words, $D\eta/T$ or effective radius) are smaller in water than in ethanol.

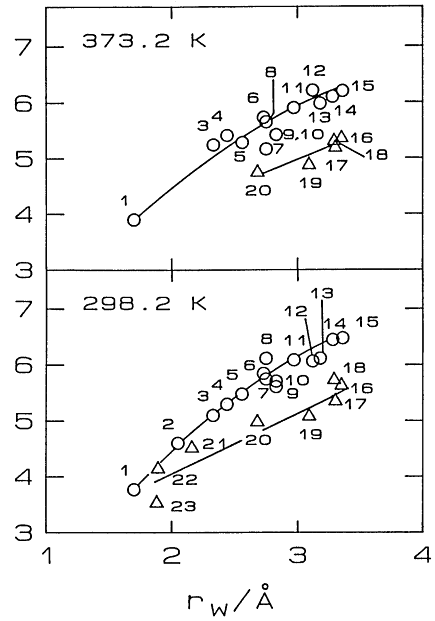

Fig. 5. The coefficient, f, Eq. 2, as a function of the solute van der Waals radius in water. 1, Water (Ref. 18); 2, methanol (Ref. 27); 3, ethanol (Ref. 4); 4, 1,2-ED (Ref. 4); 5, 1-propanol (Ref. 4); 6, 1,2,3-PT (Ref. 4); 7, 1-butanol (Ref. 4); 8, 2-methyl-2-propanol (Ref. 4); 9, 1,2-BD; 10, 1,4-BD; 11, *meso*-erythritol; 12, pentaerythritol (Ref. 4); 13, xylitol; 14, *myo*-inositol; 15, mannitol; 16, 1-ethylnaphthalene (Ref. 2); 17, biphenyl (Ref. 2); 18, butylbenzene (Ref. 2); 19, naphthalene (Ref. 2); 20, benzene (Ref. 2); 21, xenon (Ref. 29); 22, methane (Ref. 28); 23, argon (Ref. 28).

Table 4. The van der Waals Radius, r_w, the Effective Radius, r, and the Coefficient f of Eq. 2 in Ethanol

Solute	r_w/Å	298.2 K		353.2 K	
		r/Å	f	r/Å	f
1-Butanol	2.75	3.45	3.78	3.35[a]	4.23[a]
1,2-Ethanediol	2.44	3.67	4.09	3.36	4.24
1,2-Butanediol	2.83	3.73	4.17	3.46	4.37
1,4-Butanediol	2.83	4.01	4.57	3.75[a]	4.73[a]
1,2,3-Propanetriol	2.73	3.94	4.47	3.66	4.62
Water	1.70	3.11	3.30	2.73	3.44
Benzene	2.68	2.57	2.54	2.56	3.23

a) These values were obtained using interpolated diffusion coefficients.

Cyclic and open-chain hexahydroxylic molecules, *myo*-inositol and mannitol, were studied because *myo*-inositol has a large negative apparent molal compressibility,[30a] and the observed partial molar heat capacity relative to the calculated value by an additivity relation is larger for *myo*-inositol than for mannitol.[30b] Uedaira and Uedaira have found a good correlation between the diffusion coefficient and the number of equatorial OH groups for carbohydrates.[9] However, we do not observe any appreciable difference in the diffusion coefficients themselves and their temperature dependencies for *myo*-inositol and mannitol. Finally, the diffusion coefficients of the two butanediols in water and in ethanol are notable, i.e., they are essentially the same in water, but they are consistently smaller for 1,4-BD in ethanol. Our preliminary measurement shows that the partial molar volume of 1,4-BD is smaller than that for 1,2-BD in ethanol. This suggests more compact packing or stronger solute-solvent interactions between 1,4-BD and ethanol, and may explain the smaller diffusion coefficient for 1,4-BD than for 1,2-BD in ethanol. In water, the partial molar volume is found to be smaller for 1,2-BD than for 1,4-BD,[31)] but the diffusion coefficients are essentially the same. This is another example of the diffusion coefficient being more sensitive to the solute in ethanol than in water.

In summary, the diffusion behavior of nonelectrolytes is different in ethanol and in water. In ethanol, temperature dependence of the diffusion coefficient is very different between polar and nonpolar molecules. Further, the coefficient f of the Stokes-Einstein equation is less than four for nonpolar solutes of small size. In the framework of a corrected Stokes-Einstein law, we obtained effective radii for the hydroxylic molecules. In water, the difference in diffusion coefficients between polar and nonpolar molecules are much smaller than in ethanol when compared at the same molecular (van der Waals) radius. In contrast to the large difference in ethanol, there is much less difference in the temperature dependence of the diffusion coefficients between polar and nonpolar molecules in water. These results may be partly due to the fact that nonpolar molecules are hydrated in water while they are much less solvated in ethanol. In order to clarify this, further work is neccesary.

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