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Binary Mutual Diffusion Coefficients of Aqueous Cyclic Ethers at 25 °C. Tetrahydrofuran, 1,3-Dioxolane, 1,4-Dioxane, 1,3-Dioxane, Tetrahydropyran, and Trioxane

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Taylor dispersion and differential refractometry are used to measure mutual diffusion coefficients (D) for the binary mixtures 1,4-dioxane + water, 1,3-dioxolane + water, and tetrahydrofuran + water at 25 °C. For each of these systems the plot of D against composition shows a pronounced minimum. Activity and viscosity data for aqueous 1,4-dioxane are used to discuss the strong composition dependence of D in terms of changes in the mobilities and thermodynamic driving forces. Diffusion coefficients are also reported for dilute aqueous solutions of 1,3-dioxane, tetrahydropyran, and trioxane. The limiting diffusion coefficients of the infinitely dilute aqueous ethers are discussed in terms of ring size, number and relative location of the oxygens, and the ether partial molar volume. A second or a third oxygen in the five- or six-membered rings reduces the ether partial molar volumes by about 10 cm^3·mol^{-1} and increases the limiting diffusion coefficients by (0.14 to 0.21) × 10^{-5} cm^2·s^{-1}.

Introduction

Aqueous 1,4-dioxane is an important mixed solvent for a number of separation processes and solution studies (Havenga and Leaist, 1998) because of its wide-ranging relative permittivity (2.2 to 78.3 at 25 °C). The properties of aqueous 1,4-dioxane mixtures have therefore been studied extensively. For example, densities (Hovorka et al., 1936), refractive indexes (Hovorka et al., 1936), surface tensions (Hovorka et al., 1936), vapor pressures (Bacarella et al., 1956; Vierk, 1950), enthalpies of mixing (Malcolm and Rowlinson, 1957; Vierk, 1950), and viscosities (Geddes, 1933) have been measured. In this paper mutual diffusion coefficients are reported for aqueous 1,4-dioxane mixtures. This system narrowly avoids a critical solution point (Malcolm and Rowlinson, 1957). Consequently, the diffusion coefficients and thermodynamic driving forces are strongly composition-dependent.

To provide additional transport data for aqueous cyclic ethers, binary mutual diffusion coefficients are also reported here for tetrahydrofuran + water and 1,3-dioxolane + water mixtures, and for dilute aqueous solutions of 1,3-dioxane, tetrahydropyran, and trioxane. The diffusion results and density measurements are used to discuss the limiting mobilities of cyclic ethers in terms of ring size, number and placement of the oxygens, and the ether partial molar volume.

Experimental Section

Solutions were prepared by mixing weighed amounts of distilled, deionized water and tetrahydrofuran (EM Science, purity >99.8%), 1,3-dioxolane (Fluka, >99%), tetrahydropyran (Aldrich, >99%), 1,4-dioxane (Caledon, >99.7%), 1,3-dioxane (Aldrich, >98%), or trioxane (Aldrich, >99%).

The binary mutual diffusion coefficients of the solutions were measured using the Taylor dispersion (peak-broadening) method (Erkey and Akgerman, 1991; Leaist, 1990; Tyrrell and Harris, 1984). A dual-piston liquid-chromatography pump (Waters model 501) maintained a steady laminar flow of solution through a Teflon dispersion tube (length 3524 cm, internal radius $r = 0.0473_8$ cm) which was coiled in the form of a 70-cm-diameter helix and held at (25.00 ± 0.05) °C in a thermostat. A Teflon injection valve (Rheodyne model 50) was used to introduce 20 mm^3 solution samples of slightly different composition into each carrier stream. The broadened distribution of the eluted samples was monitored by a flow-through differential refractometer (Gilson model 131, sensitivity 1 × 10^{-8} refractive-index units) at the tube outlet. The refractometer voltage was measured at 5-s intervals by a digital voltmeter (Hewlett-Packard model 3478A).

The dispersion profiles were analyzed by fitting the equation (Erkey and Akgerman, 1991)

$$v(t) = A_0 + A_1 t + A_2 (A_3/t)^{1/2} \exp[-A_4 (t - A_3)^2/t] \quad (1)$$

to the measured refractometer voltages, $v(t)$. A_3 is the retention time (≈8000 s) and A_2 is the peak height relative to the linear baseline voltage $A_0 + A_1 t$. Diffusion coefficients were evaluated using the relation $D = A_4 r^2/12$. Four to six replicate injections into each carrier stream indicated that the diffusion coefficients were reproducible within ±1% or better. The mole fractions of ether in the carrier and injected solutions differed by 0.03 or less. Within this range the calculated D values were independent of the initial composition differences.

The densities of dilute solutions of each ether (<0.6 mol dm^{-3}) were measured with a vibrating-tube density meter (Anton-Paar model DMA58, accuracy ±0.00001 g·cm^{-3}). Partial molar volumes of the infinitely dilute ethers (V_1^∞) were evaluated from the limiting slopes dρ/dc_1 of density ρ against ether concentration c_1 (Dunlop and Gosting, 1959):

$$V_1^\infty = (M_1 - \mathrm{d}\rho/\mathrm{d}c_1)/\rho_2^* \quad (2)$$

M_1 is the ether molar mass and ρ_2^* is the density of pure water (0.997044 g·cm^{-3} at 25 °C; Kell, 1975).

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Table 1. Mutual Diffusion Coefficients of Binary Ether(1) + Water(2) Mixtures at 25 °C

x_1	$D/10^{-5}$ cm^2·s^{-1}	x_1	$D/10^{-5}$ cm^2·s^{-1}
	Tetrahydrofuran(1) + Water(2)		
0.00182	1.08	0.369	0.28
0.00511	1.02	0.489	0.43
0.0137	0.93	0.690	0.85
0.0270	0.84	0.822	1.46
0.0585	0.56	0.896	2.20
0.0967	0.35	0.953	3.05
0.199	0.21	0.982	4.18
0.273	0.23		
	1,3-Dioxolane(1) + Water(2)		
0.00500	1.28	0.499	0.38
0.0100	1.26	0.600	0.54
0.0500	1.07	0.698	0.80
0.101	0.82	0.794	1.29
0.200	0.48	0.900	2.30
0.299	0.33	0.947	2.97
0.400	0.31	0.990	3.59
	Tetrahydropyran(1) + Water(2)		
0.00252	0.92	0.00753	0.82
0.00501	0.88	0.00756	0.82
0.00611	0.85	0.00991	0.80
	1,4-Dioxane(1) + Water(2)		
0.000180	1.10	0.234	0.42
0.000905	1.10	0.323	0.34
0.00183	1.09	0.449	0.32
0.00508	1.06	0.449	0.32
0.0222	0.95	0.644	0.47
0.0407	0.82	0.798	0.85
0.0806	0.71	0.901	1.41
0.120	0.59	0.950	1.92
0.170	0.52	0.988	2.38
	1,3-Dioxane(1) + Water(2)		
0.00188	1.11	0.00112	1.12
	Trioxane(1) + Water(2)		
0.00199	1.28	0.00992	1.22
0.00500	1.25	0.0196	1.14
0.00988	1.22		

Results and Discussion

Table 1 gives the ether mole fraction (x_1) and the average diffusion coefficient determined for each carrier solution. The tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane results cover essentially the complete composition range, from dilute ether to dilute water solutions. The results for the other systems were limited to relatively low ether mole fractions by the solubilities of tetrahydropyran and trioxane and by the high cost of 1,3-dioxane. The estimated accuracy of the reported D values is ±1%.

Limiting Ether Diffusion Coefficients. Limiting diffusion coefficients for the infinitely dilute ethers in water (D_1^∞) were evaluated by short ($x_1 < 0.10$) linear extrapolations of the measured D values. Equation 2 and the density data plotted in Figure 1 were used to calculate the ether partial molar volumes. Figure 2 gives the chemical structure of each ether and the values of D_1^∞ and V_1^∞.

Increasing the number of oxygens in an ether molecule might be expected to enhance the association with water, thereby reducing the diffusion rate of the aqueous ether. In fact, the opposite trend is observed. In the tetrahydropyran–dioxane–trioxane series, the number of oxygens per ether molecule increases from one to three. A second or a third oxygen in these six-membered rings produces a (0.15 ± 0.01) × 10^{-5} cm^2·s^{-1} increase in D_1^∞. A similar result is obtained for the five-membered cyclic ethers: the limiting diffusion coefficient of 1,3-dioxolane (two oxygens) is 0.21 × 10^{-5} cm^2·s^{-1} larger than that for tetrahydrofuran (one oxygen).

Figure 2 shows that each additional oxygen in these five- or six-membered rings reduces the ether partial molar volume by (10 ± 1) cm^3·mol^{-1}. The increase in D_1^∞ with increasing number of oxygens may simply reflect the more compact structures and hence lower frictional coefficients for these molecules. This explanation is consistent with the result that the five-membered cyclic ethers have smaller molar volumes and larger limiting diffusion coefficients

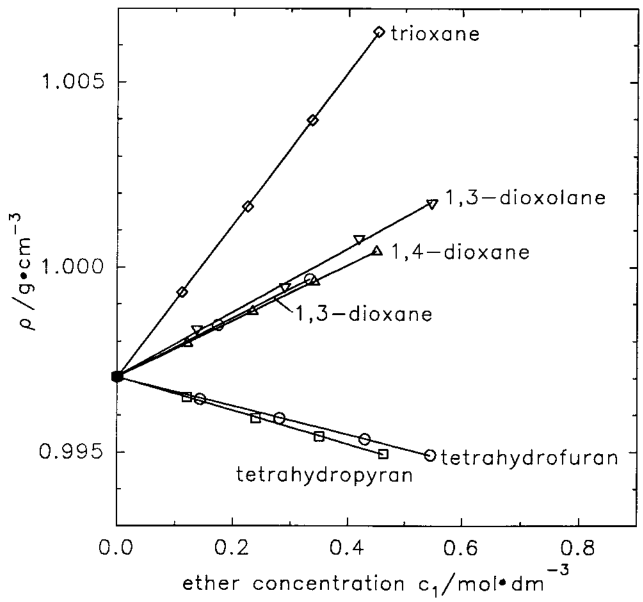

Figure 1. Densities of dilute aqueous ether solutions at 25 °C plotted against the ether concentration.

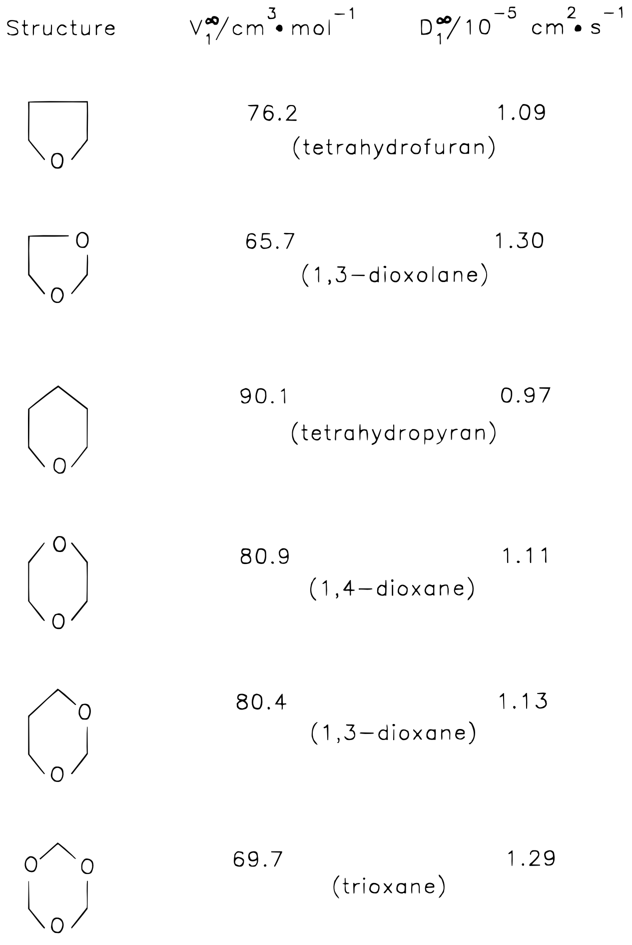

Figure 2. Chemical structures, limiting diffusion coefficients, and limiting partial molar volumes of aqueous cyclic ethers at 25 °C.

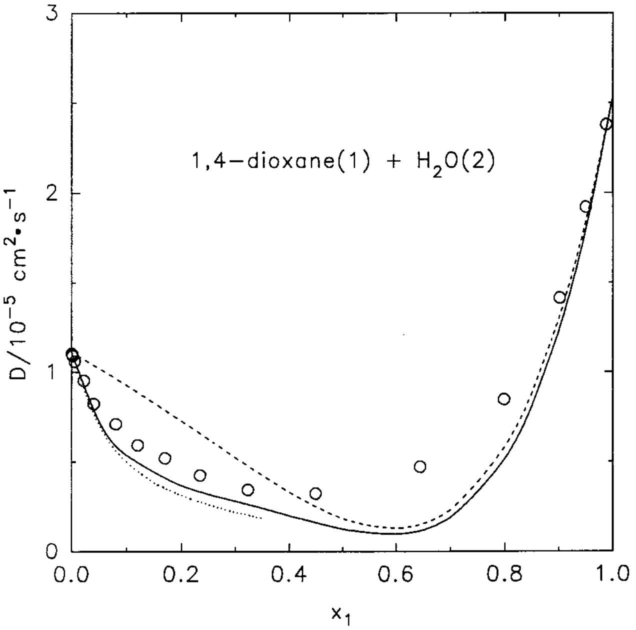

Figure 3. Binary mutual diffusion coefficient of 1,4-dioxane(1) + water(2) mixtures plotted against the 1,4-dioxane mole fraction. Measured values: ○. Predicted values (eq 3): —, using the activity data of Vierk; ·············, using the activity data of Bacarella et al.; - - - - - - -, using the activity data of Vierk with the viscosity factors omitted. The limiting diffusion coefficients $D_1^\infty = 1.13 \times 10^{-5}$ $cm^2 \cdot s^{-1}$ and $D_2^\infty = 2.53 \times 10^{-5}$ $cm^2 \cdot s^{-1}$ used in the calculations were obtained by extrapolation.

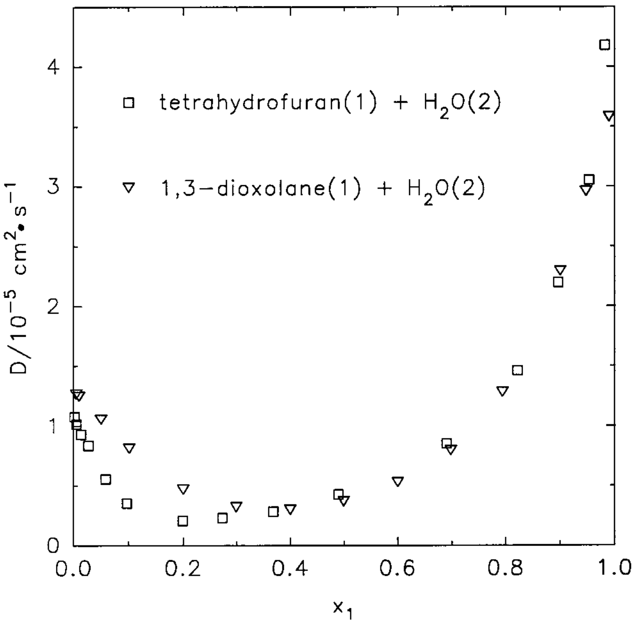

Figure 4. Binary mutual diffusion coefficients of tetrahydrofuran(1) + water(2) and 1,3-dioxolane(1) + water(2) mixtures at 25 °C plotted against the ether mole fraction.

than the six-membered ethers with the same number of oxygens. Also, the partial molar volume and limiting diffusion coefficient of 1,4-dioxane are almost identical to the corresponding quantities for the 1,3-dioxane isomer. The number of ether oxygens for a given ring size is evidently more important than the relative location of the oxygens.

Concentration Dependence of the Mutual Diffusion Coefficients. Figures 3 and 4 illustrate the strong composition dependence of the mutual diffusion coefficients for the completely miscible aqueous tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane systems. Previous work has shown that the diffusivities of aqueous acetone (Anderson et al., 1958), ethanol (Hammond and Stokes, 1953; Harris et al., 1993), and propanol isomers (Harris et al., 1993; Pratt and Wakeham, 1975) show similar deep minima.

Quantitative theories of diffusion in associated liquid mixtures are still under development. A qualitative interpretation of the composition dependence of D can, however, be attempted by using viscosity and activity data to estimate the changes in the mobilities and thermodynamic driving forces for diffusion (Hartley and Crank, 1949; Robinson and Stokes, 1959; Tyrrell and Harris, 1984). This approach gives (Carman and Stein, 1956)

$$D = \left(\frac{x_2 D_1^\infty}{\eta_{r1}} + \frac{x_1 D_2^\infty}{\eta_{r1}}\right)\left(1 + \frac{\mathrm{d}\ln \gamma_1}{\mathrm{d}\ln x_1}\right) \qquad (3)$$

for the predicted concentration dependence of D for ether(1) + water(2) mixtures. γ_1 is the activity coefficient of the ether and D_i^∞ is the limiting diffusion coefficient for infinitely dilute component i. η_{r1} and η_{r2} are the viscosities relative to the pure ether and pure water, η/η_1^* and η/η_2^*, respectively.

In Figure 3 the measured diffusion coefficients for aqueous 1,4-dioxane are compared with the values predicted by eq 3 using available viscosity (Geddes, 1933) and activity data (Vierk, 1950). To indicate the relative importance of the viscosity and thermodynamic contributions, the dashed curve gives the predicted D values with the viscosity terms omitted (relative viscosities set equal to one). The predictions given by the solid curve include both viscosity and thermodynamic terms. In this case both thermodynamic and viscosity contributions are significant. The mutual diffusion coefficients for the aqueous 1,4-dioxane system are clearly too low in the range $0.4 < x_1 < 0.9$. However, reasonable qualitative agreement is obtained.

The thermodynamic term in eq 3 is proportional to the second composition derivative of the excess Gibbs function, $\mathrm{d}\ln \gamma_1/\mathrm{d}\ln x_1 = x_1 x_2 RT \partial^2 G_m^E/\partial x_1^2$. Thus, small experimental errors in the activity data can produce significant uncertainties in the predicted diffusion coefficients (Harris et al., 1993). This point is illustrated by the dotted curve in Figure 3 which gives the D values predicted by using the activity data of Bacarella et al. (1956) (available for $x_1 < 0.3$) instead of the activities reported by Vierk (1950). At 1,4-dioxane mole fraction 0.30, the former activities give predicted D values that are 20% lower.

Conclusions

Binary mutual diffusion coefficients have been measured for aqueous cyclic ethers with five- or six-membered rings. The diffusion coefficients for the completely miscible systems are strongly composition-dependent and show deep minima. Each additional oxygen in the five- or six-membered rings produces a (0.14 to 0.21) × 10^{-5} $cm^2 \cdot s^{-1}$ increase in the limiting diffusion coefficients of the infinitely dilute ethers and a (10 ± 1) $cm^3 \cdot mol^{-1}$ decrease in the limiting ether partial molar volume.

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