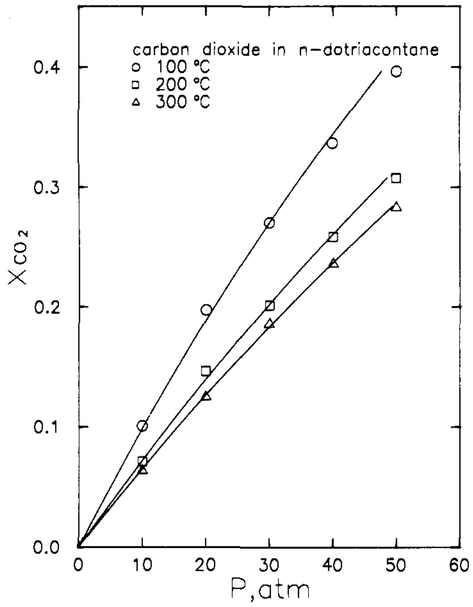

Figure 4. Comparison of calculated solubility of carbon dioxide in *n*-dotriacontane with experimental data.

and Robinson's correlation as described by Huang et al. (*7*). Values of normal boiling points needed in the calculations for T_c are taken from API-44 Tables (*11*).

The calculated results with the optimum values of k_{ij} for each isotherm are listed in Table IV. The average absolute deviations in P are not more than 4%. Figures 3 and 4 show the comparisons of calculated solubilities of carbon dioxide in n-$C_{24}H_{50}$ and in n-$C_{32}H_{66}$, respectively, with experimental data. It indicates that the modified Soave equation with one interaction parameter is adequate to correlate the solubility data.

Glossary

a,b	parameters in Soave equation of state
f	fugacity
k_{ij}	interaction parameters between components i and j in mixing rules for equation of state
K	vaporization equilibrium ratio, y/x
P	pressure
P_c	critical pressure
T	temperature
T_c	critical temperature
T_r	reduced temperature, T/T_c
v	molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	mole fraction (liquid or vapor phase)
ω	acentric factor

Registry No. CO_2, 124-38-9; *n*-tetracosane, 646-31-1; *n*-dotriacontane, 544-85-4.

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Limiting Interdiffusion Coefficients of Some Hydroxylic Compounds in Water from 265 to 433 K

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Interdiffusion coefficients of ethanol, 1-propanol, 1-butanol, 2-methyl-2-propanol, ethylene glycol, glycerol, and pentaerythritol have been measured in water at concentrations close to infinite dilution and temperatures between 265.2 and 433.2 K. Activation energies are not sensitive to the solutes, decrease with increasing temperature, and are close to that for the self-diffusion of pure water. At the lower temperatures, the quantity $D\eta/T$ decreases with decreasing temperature for 2-methyl-2-propanol. This effect is smaller for 1-butanol and 1-propanol. For ethanol and the polyols, the quantity $D\eta/T$ is insensitive to temperature.

Introduction

In earlier work, we determined the limiting interdiffusion coefficients of hydrophobic solutes such as aromatic hydrocarbons (*1*, *2*) and a neutral metal complex (*3*) in water. Because water is known to be a "structured" solvent (*4*), we attempted to discover if there is an effect of "water structure" itself, or of the enhanced water structure around hydrophobic solute molecules, on the diffusion of hydrophobic molecules. In one of these studies, we made measurements covering a wide temperature range—from the supercooled region to the region above the normal boiling point of water (*2*).

The present study was undertaken to make measurements on hydroxylic compounds over a wide temperature range and

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

T/K	ethanol	1-propanol	1-butanol	2-methyl-2-propanol	ethylene glycol	glycerol	pentaerythritol
265.2	0.386 ± 0.003	0.330 ± 0.003	0.297 ± 0.006	0.260 ± 0.009	0.384 ± 0.003	0.301 ± 0.002	0.256 ± 0.003
268.2	0.429 ± 0.008	0.365 ± 0.002	0.333 ± 0.003	0.301 ± 0.003	0.426 0.003	0.331 ± 0.003	0.278 ± 0.002
278.2	0.633 ± 0.010	0.564 ± 0.003	0.510 ± 0.004	0.468 ± 0.005	0.616 ± 0.002	0.506 ± 0.004	0.426 ± 0.004
298.2	1.24 ± 0.01	1.05 ± 0.02	0.933 ± 0.004	0.874 ± 0.002	1.14 ± 0.01	0.921 ± 0.020	0.779 ± 0.008
313.2	1.83 ± 0.09	1.54 ± 0.02	1.40 ± 0.01	1.29 ± 0.02	1.61 ± 0.01	1.32 ± 0.01	1.13 ± 0.02
333.2	2.62 ± 0.02	2.29 ± 0.02	2.06 ± 0.03	2.00 ± 0.01	2.36 ± 0.01	2.02 ± 0.01	1.64 ± 0.02
353.2	3.58 ± 0.10	3.19 ± 0.01	2.93 ± 0.02	2.82 ± 0.01	3.25 ± 0.04	2.77 ± 0.01	2.37 ± 0.06
373.2	4.75 ± 0.09	4.29 ± 0.02	4.09 ± 0.03	3.73 ± 0.04	4.39 ± 0.01	3.70 ± 0.02	3.00 ± 0.01
393.2	6.39 ± 0.07	5.77 ± 0.06	5.25 ± 0.06	5.15 ± 0.08	5.83 ± 0.08	4.91 ± 0.01	4.25 ± 0.04
413.2	7.75 ± 0.16	7.08 ± 0.16	6.38 ± 0.04	5.91 ± 0.13	6.98 ± 0.06	5.84 ± 0.05	5.16 ± 0.06
433.2	9.25 ± 0.11	8.25 ± 0.11	7.48 ± 0.18	7.13 ± 0.09	8.50 ± 0.04	6.90 ± 0.10	6.39 ± 0.07

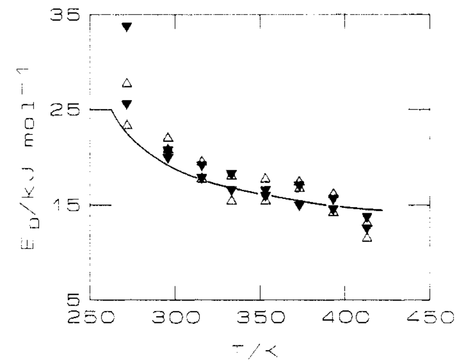

Figure 1. Activation energies for diffusion: △, hydroxylic compounds (this study); ▼, aromatic hydrocarbons (ref 2). For both cases, only the highest and the lowest values are shown. The solid line shows E_D for the self-diffusion of water (ref 14–17).

to determine if there is any difference between hydroxylic molecules and hydrophobic molecules in terms of their diffusion processes in water.

Experimental Section

Ethanol, 1-propanol, 1-butanol, 2-methyl-2-propanol, ethylene glycol, glycerol (all from Wako Pure Chemical Industries; special grade), and pentaerythritol (Tokyo Kasei Kogyo; guaranteed reagent) were used as received. Water was distilled twice. Diffusion coefficients were measured by the Taylor dispersion technique (*5*) with use of a differential refractometer (Waters Model R-401) as a detector. The concentrations of the injected solutions were 1% or less. Above 373 K, pressures slightly higher (0.5–2 MPa) than saturation vapor pressures were applied. Other experimental details have been described elsewhere (*2*).

Results and Discussion

Table I summarizes the measured diffusion coefficients. Each value is an average of five or more determinations. The solutions injected were dilute, and as the solutes disperse along the tube, they are diluted by up to 100 times. Thus, the diffusion coefficients obtained can be considered as limiting interdiffusion coefficients. The values for ethanol and 1-propanol are in fairly good agreement with those obtained by Pratt and Wakeham in the temperature range between 298 and 338 K (*6*, *7*). Values at 298.2 K may be compared with the literature values ($D/10^{-9}$ m^2 s^{-1}): 1.23 (*6*) and 1.22 (*8*) for ethanol; 1.02 (*7*) for 1-propanol; 0.972 (*9*) for 1-butanol; 0.98 (*10*) (298.0 K) for 2-methyl-2-propanol; 1.153 (*11*) for ethylene glycol; 0.938 (*11*) for glycerol; and 0.762 (*12*) for pentaerythritol. Our value for ethanol at 278.2 K (0.63 × 10^{-9} m^2 s^{-1}) is higher than that reported by Easteal and Woolf (0.53 × 10^{-9} m^2 s^{-1}) (*8*), but their value was too low (*13*).

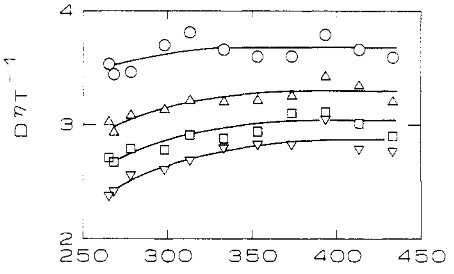

Figure 2. Quantity $D\eta/T$ vs temperature: ○, ethanol; △, 1-propanol; □, 1-butanol; ▽, 2-methyl-2-propanol. The units of $D\eta/T$ are 10^{-15} J m^{-1} K^{-1}.

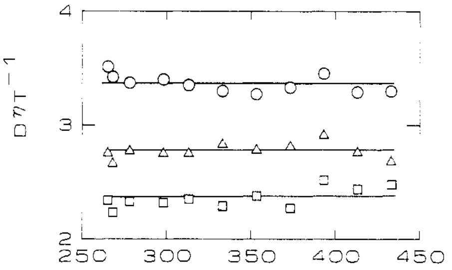

Figure 3. Quantity $D\eta/T$ vs temperature: ○, ethylene glycol; △, glycerol; □, pentaerythritol. The units of $D\eta/T$ are 10^{-15} J m^{-1} K^{-1}.

Figure 1 shows activation energies calculated from

$$E_D = -R[d \ln D/d(1/T)] \qquad (1)$$

where R is the gas constant. The activation energies were calculated from pairs of data at 30–40 K intervals with an exception at the lowest temperature where they were calculated from data at 13 K intervals. Within experimental uncertainties, no systematic dependence on the solute was observed, i.e., with respect to the solute size or the number of hydroxyl groups. The activation energies decrease with increasing temperature, and they are close to those for the self-diffusion of pure water (*14*–*17*). Furthermore, we do not observe any systematic difference in E_D values between hydroxylic compounds and aromatic hydrocarbons except at the lowest temperature (Figure 1). In ethanol, however, in another study we found differences in activation energies between benzene and alcohols as solutes (*18*).

Figures 2 and 3 show the quantity $D\eta/T$ vs temperature. Viscosity values, η, were taken from the literature (*19*). For 2-methyl-2-propanol, we observe a tendency for $D\eta/T$ to decrease with decreasing temperature. This tendency becomes less pronounced with a decreasing number of carbon atoms of the alkanols. For ethanol and the solutes having more than two hydroxyl groups, the quantity $D\eta/T$ is essentially temperature-independent. This is in contrast to results obtained for nonpolar solutes in organic solvents where $D\eta/T$ tends to increase with increasing viscosity of the solvent or with decreasing temperature (*18*, *20–22*). In view of the smaller variation of $D\eta/T$ in water, the diffusion coefficients of nonelectrolytes in water may be estimated with greater certainty than in organic solvents.

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Excess Volume, Isothermal Compressibility, and Excess Enthalpy of the Binary Liquid System 2,2,2-Trifluoroethanol + 2,5,8,11,14-Pentaoxapentadecane

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Molar excess volumes of the binary liquid mixtures of 2,2,2-trifluoroethanol + 2,5,8,11,14-pentaoxapentadecane (tetraethylene glycol dimethyl ether) have been determined from density measurements at atmospheric pressure and 293.15 and 313.15 K, the isothermal compressibilities were determined from density measurements at 0.1–10 MPa and 293.15 K, and the molar excess enthalpy has been measured by a Picker calorimeter at atmospheric pressure and 293.15 K. The data were needed for a possible application of the mixture as the working fluid in heat transformers.

Introduction

Thermodynamic property data on 2,2,2-trifluoroethanol (TFE) + 2,5,8,11,14-pentaoxapentadecane (E 181) mixtures are scarce, although these mixtures have been suggested as working fluids in heat transformers (*1*). In this paper we report excess enthalpy data that are especially needed in the design of transformers providing heat at high temperatures (*2*). Additionally, we measured the excess volumes necessary to calculate the molar excess enthalpy data obtained by means of a Picker flow calorimeter. Also, isothermal compressibilities were determined for future theoretical studies of a recently developed equation of state that incorporates information on molecular shape (*3*).

Experimental Section

TFE (p. synth.; Merck, West Germany; stated purity 98%), with a purity of 99.8% checked by GLC, was not further purified. It was degassed by several pump–thaw cycles until the density remained constant and was stored over molecular sieve 3A in contact with the gas phase. E 181 (p. synth.; Merck, West Germany; stated purity 98%), with a purity of 99.5% determined by GLC, was treated similarly. However, degassing to constant density had to be performed by continuous pumping of the hot liquid to reduce its viscosity, which otherwise would have impeded the diffusion of gases.

Table I. Measured Densities ρ and Calculated Molar Excess Volumes V^E of the Liquid System TFE (1) + E 181 (2) at 293.15 or 313.15 K and Atmospheric Pressure

	T = 293.15 K		T = 313.15 K	
x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
0.000 00	1.011 26	0.000	0.992 74	0.000
0.025 80	1.014 54	0.002		
0.057 61	1.018 73	0.000	0.999 97	−0.004
0.093 85			1.004 84	−0.015
0.143 16	1.030 99	−0.004		
0.181 66	1.037 02	−0.003	1.017 66	−0.021
0.293 35	1.056 74	−0.007	1.036 72	−0.035
0.395 49	1.078 28	−0.006	1.057 52	−0.042
0.487 05	1.101 32	−0.007	1.079 77	−0.055
0.588 18	1.132 27	−0.009	1.109 61	−0.065
0.692 38	1.172 50	−0.020	1.148 36	−0.083
0.801 49	1.228 13	−0.061	1.201 82	−0.130
0.851 42	1.260 08	−0.088	1.232 40	−0.151
0.900 85	1.297 41	−0.134	1.267 96	−0.185
0.919 90	1.313 38	−0.141	1.283 15	−0.186
0.949 43	1.340 13	−0.136		
0.950 67			1.309 68	−0.172
0.970 74	1.360 70	−0.098	1.328 12	−0.130
1.000 00	1.390 99	0.000	1.356 45	0.000

The densities of the pure compounds at atmospheric pressure can be found in Table I. Recently, molar volumes of TFE of 72.25 (*4*) and 72.4 cm^3 mol^{-1} (*5*) and a density of E 181 of 1.006 51 g cm^{-3} (*6*), all at 298.15 K, have been published. The