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Infinite Dilution Binary Diffusion Coefficients of C_5-Monoalcohols in Water in the Temperature Range from 273.2 K to 353.2 K at 0.1 MPa

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Infinite dilution binary diffusion coefficients of C_5-monoalcohols in water were measured by the Taylor dispersion method at 273.2 K to 353.2 K and 0.1 MPa. At each temperature it was found that the D_{12} values for the isomers increase with the boiling point of the pure alcohols. The D_{12} values were correlated with temperature, water viscosity, and solute boiling point. The accuracy in the correlation was superior to the various correlations reported in the literature.

Introduction

Binary diffusion coefficients D_{12} for alcohols in water are of importance in the design of chemical reactors for aqueous systems, but accurate D_{12} data are limited. Alcohols and water show strong interactions such as hydrogen bonding, and the accurate prediction of the D_{12} values is difficult.

Recently, the Taylor dispersion method (Taylor, 1953; Aris, 1956), which is capable of measuring D_{12} with moderate accuracy (the intrinsic measurement error of ca. 1%, claimed by Wakeham et al., (1991)), has often been employed to measure D_{12} for alcohols in water (Pratt and Wakeham, 1974; Tominaga and Matsumoto, 1990; Harris et al., 1993; van Ven-Lucassen et al., 1995; Hao and Leaist, 1996). However, the D_{12} data have been measured for mainly alcohols having relatively lower molecular weights, and data for C_5-alcohols in water are extremely limited. In this study the D_{12} values of C_5-monoalcohols (eight isomers) in water at 0.1 MPa in the temperature range from 273.2 K to 353.2 K were measured by the Taylor dispersion method. The D_{12} data were correlated with temperature, water viscosity, and the solute boiling point, and the accuracies in the various correlations were examined.

Theory

The Taylor dispersion method is a dynamic technique for the measurement of diffusion coefficients from the dispersion of the species in a laminar flow in capillary tubing of circular cross section. This technique was first used by Taylor (1953) and developed by Aris (1956).

The theoretical background of this technique (e.g., Hunt, 1977; Alizadeh et al., 1980) and the design of the experimental apparatus (Erkey and Akgerman, 1991) have been described in detail. When a small amount of a solute species is injected at $z = 0$, the solute concentration C at distance $z = L$ downstream is given by eq 1.

$$C = \frac{m}{2\pi R^2\sqrt{\pi K t}} \exp\left[\frac{(L - ut)^2}{4Kt}\right] \tag{1}$$

where m is the amount of a solute injected, u is the average flow velocity,

$$K = D_{12} + \frac{u^2R^2}{48D_{12}} \tag{2}$$

and R is the inner radius of the dispersion tubing. The diffusion coefficient D_{12} is determined by the curve-fitting method (Funazukuri et al., 1994; Funazukuri and Nishimoto, 1996).

Experimental Apparatus and Procedures

While the constituents of the experimental apparatus are substantially identical to that described in a previous study (Funazukuri et al., 1994), some modifications were made and are described briefly below. The distilled and degassed water was supplied with a microfeeder pump (JEOL CAP G01, Japan) at flow rates of 80−150 μL/min. This tubing is made of an empty fused silica tubing (0.528 mm i.d. × 31.78 m, untreated, Supelco), coiled in a diameter of 0.25 m, and is installed horizontally in a temperature-controlled water bath, whose temperature variations are within ±0.1 K. The outlet of the diffusion column is connected directly to the detector inlet. The portion of the tubing between the water bath and the detector (0.15 m, this is counted in 31.78 m) is maintained at 308.2 K with a temperature-controlled ribbon heater. The detector cell block is also designed to be kept at 308.2 K. A tracer species, which was diluted with distilled water at 0.1 wt %, was injected into the diffusion tubing through an injector (Rheodyne 7520) with a 20-μL sampling loop. The sampling loop was also immersed in the water bath. The temperature of the tracer samples was kept at the same temperature as that of the water bath prior to each injection. The eluted tracer species was monitored with a refractive-index detector (model L-3300, Hitachi, Japan). Three to four measurements were carried out for each condition.

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Table 1. Comparison of D_{12} Values for Ethanol in Water at 298.2 K and 0.1 MPa

workers	$D_{12}/10^{-9}$ m^2 s^{-1}
Smith and Straw (1952)	1.13
Hammond and Stokes (1953)	1.24
Dullien and Shemilt (1961)	1.22
Gary-Bobo and Weber (1969)	1.26[a]
Pratt and Wakeham (1974)	1.23
Easteal and Woolf (1985)	1.22
Tominaga and Matsumoto (1990)	1.24
Harris et al. (1993)	1.23
van de Ven-Lucassen et al. (1995)	1.20
Hao and Leaist (1996)	1.23
present study	1.24

[a] 24.8 °C.

Water as a solvent was deionized, distilled, and then filtered with micropore membrane. 1-Pentanol (98+%), 2-pentanol (99%), 3-pentanol (98+%), (±)2-methyl-1-butanol (98+%), 2-methyl-2-butanol (98+%), and 2,2-dimethyl-1-propanol (98+%) were obtained from Wako Pure Chemical Ind. (Japan), and 3-methyl-1-butanol (98+%) and 3-methyl-2-butanol (97+%) from Kanto Chemicals (Japan). The figures shown in the parentheses are the purities, measured with GC, claimed by the suppliers. These reagents were used without further purification.

Results and Discussion

Comparison of the D_{12} Values of Aqueous Ethanol at 298.2 K. Table 1 compares the D_{12} values of ethanol in water at 298.2 K and atmospheric pressure with those in the literature. The present data, which is a mean value from five measurements with deviations within ±2%, is almost consistent with the recent data obtained mainly by the Taylor dispersion method (Pratt and Wakeham, 1974; Tominaga and Matsumoto, 1990; Harris et al., 1993; van Ven-Lucassen et al., 1995; Hao and Leaist, 1996).

Error Sources. (a) The Effect of the Secondary Flow Due to Coiled Diffusion Tubing. The D_{12} values obtained have been known to be higher than the intrinsic values owing to the secondary flow caused by coiled diffusion tubing when the solvent velocity is higher than a certain value. It was found that the determined D_{12} values of ethanol at 298.2 K were independent of water velocities in the range of 0.5×10^{-2} to 2×10^{-2} ms^{-1} for all the conditions. Furthermore, since the values of $De\ Sc^{1/2}$ were always lower than 8 for all solutes the criteria in eq 3 was fulfilled: Alizadeh et al. (1980) estimated that the error ascribed to the secondary flow on the D_{12} values was lower than 1% when $Q = 8$.

$$De\ Sc^{1/2} < Q \tag{3}$$

(b) The Effect of the Tracer Concentration. The effect of the tracer concentration on the D_{12} values was found to be negligible when the concentration of ethanol in the 20-μL aqueous solutions injected varied from 0.05 to 2 wt % at 298.2 K. In this range the peak areas were also found to be proportional to the tracer concentrations. Since the concentrations of the tracer species injected are 0.1 wt % for all the C_5-alcohol measurements, the conditions can be regarded as infinite dilution.

Correlation Development. Table 2 shows the measured binary diffusion coefficients D_{12} for the eight isomers, together with water viscosities (CRC Handbook, 1987) and the solute boiling points (Merck Index, 1996). The D_{12} values listed are the mean values of three to four measurements. These are quite reproducible (within ± 3%, mainly within ±2%) for all the conditions.

As mentioned in previous studies (Reid et al., 1987), the D_{12} values can be correlated accurately with the water viscosity. Funazukuri et al. (1996) also found that eq 4 with a single set of the constants α and β represented well the D_{12} data for benzene in supercritical carbon dioxide as well as in hexane, dodecane, and cyclohexane.

$$(D_{12}/m^2\ s^{-1})/(T/K) = \alpha(\eta/Pa\ s)^{\beta} \tag{4}$$

Table 3 lists the determined constants α and β in eq 4 and the average absolute deviation (%AAD) for each solute.

$$\%AAD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{D_{12,\mathrm{exp},i} - D_{12,\mathrm{crrl},i}}{D_{12,\mathrm{crrl},i}}\right| \tag{5}$$

where N is the number of data points and $D_{12,\mathrm{exp}}$ and $D_{12,\mathrm{crrl}}$ are binary diffusion coefficients obtained experimentally and predicted, respectively. It is found that the values of β are almost equal to -1, as listed in Table 3. Figure 1 is logarithmic plot of D_{12}/T vs water viscosity. One datum for D_{12} of 1-pentanol is available in the literature: the datum (0.88×10^{-9} m^2 s^{-1}) of Hao and Leaist (1996) at 298.2 K is slightly lower than ours (0.920×10^{-9} m^2 s^{-1}). Note that the solid straight line drawn in this figure was obtained by eq 4 with α and β values listed in Table 4, assuming no difference in the D_{12} values for the isomers. Equation 4 was found to represent the D_{12} values well (%AAD = 1.4%).

While various correlations for predicting D_{12} values have been proposed, most correlations cannot distinguish isomers: the solute properties are represented by the solute molar volume V_b at the normal boiling point, which can be calculated by the method of Le Bas (Wilke and Chang, 1955). These values predicted by this method are the same for the C_5-monoalcohols. We choose the solute boiling point as a reliable and convenient physical property to distinguish the different isomers. Figure 2 shows the D_{12} data vs the solute boiling point at each temperature. It is

Table 2. Measured Binary Diffusion Coefficients $D_{12}/10^{-9}$ m^2 s^{-1} of C_5-Monoalcohol Isomers in Water at 0.1 MPa in the Temperature Range from 273.2 K to 353.2 K

		temperature/K, viscosity/mPa s[a]					
solute	T_b/K[b]	273.2, 1.787	293.2, 1.002	298.2, 0.8905	313.2, 0.6530	333.2, 0.4666	353.2, 0.3548
1-pentanol	410.7	0.417	0.794	0.920	1.37	2.13	2.98
2-pentanol	392.5	0.402	0.816	0.911	1.34	2.04	2.89
3-pentanol	388.8	0.400	0.792	0.899	1.33	2.05	2.94
2-methyl-1-butanol	401.2	0.415	0.794	0.920	1.35	2.08	2.99
2-methyl-2-butanol	375.7[c]	0.386	0.759	0.873	1.30	2.01	2.87
3-methyl-1-butanol	403.7	0.407	0.784	0.903	1.33	2.05	2.89
3-methyl-2-butanol	386.7	0.403	0.798	0.899	1.34	2.06	2.96
2,2-dimethyl-1-propanol	387.2	0.403	0.789	0.920	1.34	2.06	2.91

[a] From CRC Handbook (1989). [b] From Merck Index (1996). [c] At 765 mmHg.

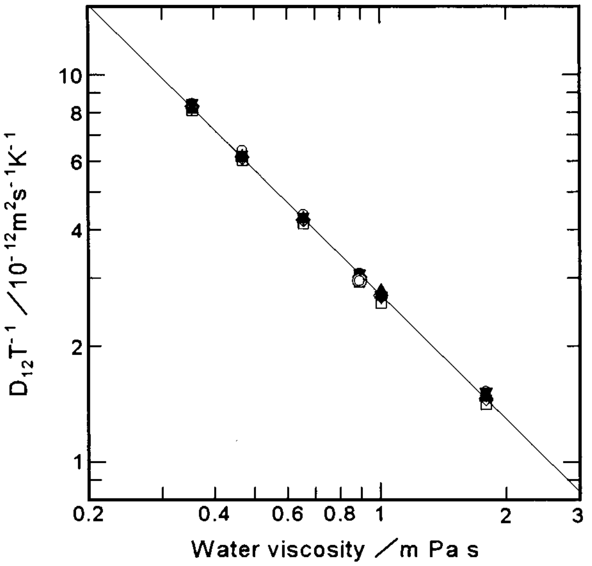

Figure 1. D_{12}/T vs water viscosity for (○) 1-pentanol, (▲) 2-pentanol, (◇) 3-pentanol, (△) 2-methyl-1-butanol, (+) 2-methyl-2-butanol, (▼) 3-methyl-1-butanol, (□) 3-methyl-2-butanol, (×) 2,2-dimethyl-1-propanol, and (○) 1-pentanol by Hao and Leaist (1996).

Table 3. Determined Coefficients in Eq 4 for Each Solute

solute	α	β	%AAD
1-pentanol	1.709×10^{-15}	−1.070	1.44
2-pentanol	1.830×10^{-15}	−1.058	0.670
3-pentanol	1.602×10^{-15}	−1.076	0.778
2-methyl-1-butanol	1.745×10^{-15}	−1.067	1.31
2-methyl-2-butanol	1.436×10^{-15}	−1.087	0.874
3-methyl-1-butanol	1.788×10^{-15}	−1.060	1.02
3-methyl-2-butanol	1.614×10^{-15}	−1.076	0.907
2,2-dimethyl-1-propanol	1.708×10^{-15}	−1.068	0.451

Table 4. Accuracy for Predicting D_{12} for Various Correlations for All C_5−Monoalcohols

	%AAD	max %AD	parameter values
Wilke and Chang (1955)	3.54	10.2	$\phi = 2.6$
	6.53	13.6	$\phi = 2.26$
Hayduk and Laudie (1974)	7.52	18.2	
Nakanishi (1978)	13.0	19.7	
Hayduk and Minhas (1982)	3.90	11.5	
Siddiqi and Lucas (1986)	23.2	27.7	
eq 4	1.41	4.89	$\alpha = 1.675 \times 10^{-15}$, $\beta = -1.070$
eq 6	1.31	3.09	$A = 3.721 \times 10^{-9}$ $m^2 s^{-1}$, $E = 20.21$ kJ mol^{-1}

interesting that the D_{12} values increase with boiling point of the pure alcohols, and the slope also increases with increasing temperature.

Table 4 compares the accuracy for the various correlations for the D_{12} data of the aqueous C_5-alcohols reported in the present study. Equation 4 is more accurate than those in the literature. Note that the association factor Φ in the original Wilke and Chang equation (Wilke and Chang, 1955) is 2.6 for water as the solvent, but Hayduk and Laudie (1974) claimed that Φ = 2.26 is better than Φ = 2.6. However, this modification does not improve the accuracy for the present C_5-monoalcohol + water systems.

While the difference in the D_{12} values for the eight isomers at each temperature is quite small, the values obviously increase with boiling points of the pure alcohols, as mentioned above. On the basis of 1-pentanol

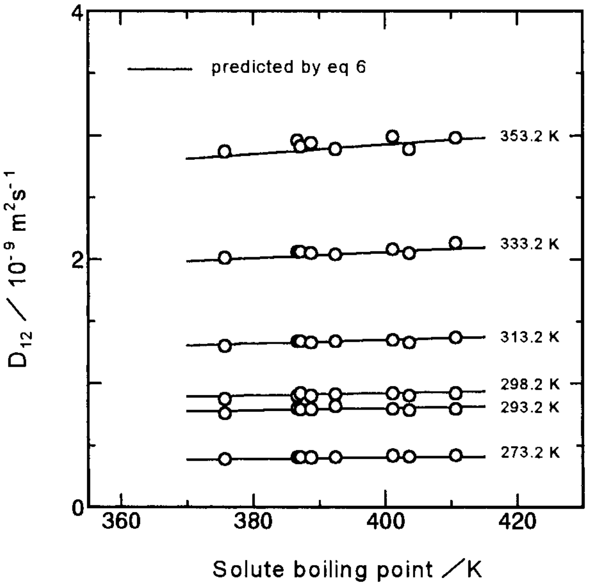

Figure 2. D_{12} values vs the solute boiling point at temperatures from 273.2 K to 353.2 K for all the solutes.

$$D_{12}/\mathrm{m}^2\,\mathrm{s}^{-1} = D_{12}^{\circ} + A\exp\left[\frac{-E}{R_g T}\right](T_b - T_b^{\circ}) \qquad (6)$$

where the superscript ° indicates the value for 1-pentanol, and $A = 3.721 \times 10^{-9}$ $m^2 s^{-1} K^{-1}$ and $E = 20.21$ kJ mol^{-1}, D_{12}° is obtained by eq 4 with the values of α and β for 1-pentanol listed in Table 3. It is found that %AAD of eq 6 is 1.31% (the maximum %AD = 3.1%) for all C_5-monoalcohols, and the accuracy has been improved.

Conclusions

Inifinite dilution binary diffusion coefficients for eight isomers of C_5-monoalcohols in water were measured by the Taylor dispersion method at 273.2 K to 353.2 K and 0.1 MPa. The measured D_{12} values were correlated with temperature, water viscosity, and solute boiling point, and the accuracy in the correlation was better than those in the literature.

Notation

%AD = absolute deviation
%AAD = average absolute deviation defined by eq 5
C = concentration of tracer species
De = Dean number = $(\rho u d_{tube}/\eta)(d_{tube}/d_{coil})^{1/2}$
D_{12} = binary diffusion coefficient at infinite dilution
d_{coil} = coil diameter
d_{tube} = diameter of diffusion tubing
E = activation energy
L = length of diffusion tubing
u = average velocity
R = radius of diffusion tubing
R_g = gas constant
r = radial distance
Sc = Schmidt number = $\eta/\rho D_{12}$
T = temperature
t = time
z = axial distance

Greek symbols

α = constant
β = constant

η = water viscosity
ρ = water density

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