(15) Carnahan, B.; Luther, H. A.; Wilkes, J. O. *Applied Numerical Methods*; Wiley: New York, 1969; Chapter I.
(16) Gottfried, B. S.; Weismann, J. *Introduction to Optimization Theory*; Prentice-Hall: Englewood, NJ, 1973; Chapter 2.
(17) Ried, C. E.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; Chapter 6.
(18) Riedel, L. *Chem.-Ing.-Tech.* **1954**, *26*, 83.
(19) Gültekin, N. *J. Karadeniz, Univ. Faculty Arts Sci. Chem. Biol. (Trabzon, Turkey)* **1985**, *1*, 25.
(20) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*: CRC: Cleveland, OH, 1976; p C-57.

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Infinite Dilution Diffusion Coefficients of Several Alcohols in Water

Sam F. Y. Li* and Hui M. Ong

Department of Chemistry, National University of Singapore, Singapore 0511

A Taylor dispersion instrument was used to measure the diffusion coefficients of methanol, ethanol, and 1-butanol in water. A correlation scheme based on a free-volume-type expression could be used to represent the experimental data to within experimental uncertainty.

Introduction

Diffusion coefficient measurements are required in a number of engineering applications, in the study of mass-transfer processes and in evaluating theories of diffusion and the liquid state. The Taylor dispersion technique (*1*–*5*) has in recent years been established as a rapid and accurate method for measuring the diffusion coefficients of liquids. In previous publications (*6*, *7*), we have reported diffusion data for mixtures of alkanes obtained using an instrument based on this technique. In this work, the same instrument was used to measure the diffusion coefficients of a series of alcohols in water at infinite dilution.

The rough hard-sphere theory (*8*–*10*) has been used extensively for the correlation of diffusion coefficient data for alkane mixtures (*11*–*14*). In particular, it has been shown that a free-volume-type expression (*11*) derived from the rough hard-sphere theory can be used for correlating and predicting diffusion coefficients of *n*-alkanes. However, the application of this theory to water/alcohol systems has not been examined. It is therefore one of the objectives in this paper to examine the applicability of this theory to these latter systems.

Experimental Techniques

The Taylor dispersion technique is based on the dispersion of a pulse of an injected mixture in a laminar flowing stream of slightly different composition. The ideal model to measure liquid diffusivities consists of an infinitely long straight tube of uniform, circular cross section, radius a_0, through which flows a fluid or a mixture of fluids with physical properties independent of composition, at a mean velocity u_0. Following the injection of a δ-function of another fluid of a different composition at a particular axial location in the tube, the combined action of the parabolic velocity profile and molecular diffusion causes dispersion of the injected material. Under suitable conditions, the measurements of the first two temporal amounts of the distribution of the concentration perturbation a distance L downstream from the point of injection allows the mutual diffusion coefficients of the binary fluid mixture, D_{12}, to be determined according to the following equation (*2*):

$$D_{12} = \frac{A_0}{24\pi\bar{t}_{id}}\left(\frac{[1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 3}{[1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 2\sigma_{id}^2/\bar{t}_{id} - 1}\right)\times \{1/2 + 1/2(1 - \zeta_a)^{1/2}\} \quad (1)$$

Table I. Infinite Dilution Diffusion Coefficients of Methanol, Ethanol, and 1-Butanol in Water

T, °C	$10^9 D_{12}$, m^2 s^{-1} methanol	ethanol	1-butanol
35	1.88	1.53	1.18
40	2.10, 2.19,[a] 2.42[b]	1.69	1.34
45	2.35	1.91	1.47

[a] Easteal and Woolf (*15*). [b] Extrapolated from Matthews and Akgerman (*13*).

Here $A_0 = \pi a_0^2$ is the cross-sectional area of the tube. $\bar{t}_{id}$ denotes the first raw moment of the distribution and σ_{id}^2 its second central moment. In addition

$$\delta_a = 12.7997\zeta_0 \quad (2)$$

with

$$\zeta_0 = \frac{\bar{u}_0 a_0^2}{48LD_{12}} \quad (3)$$

Diffusion times of the order of 1–2 h were used in the measurements to ensure that the effects due to secondary flow in the diffusion tubes were negligible (*1*, *2*). The injected samples contained less than 0.1 mole fraction of the alcohols as it has been found that, below this concentration, the diffusion coefficients were independent of the concentration of the sample injected.

Results and Discussion

Table I displays the results obtained for the diffusion coefficients of methanol, ethanol, and 1-butanol in water at temperatures 35, 40, and 45 °C. For methanol, previous measurements by Akgerman (*13*) and Easteal and Woolf (*15*) were available for comparison with the present data. The agreement with the data of Easteal and Woolf is within mutual experimental uncertainties whereas the extrapolated data of Matthews and Agkerman were found to be higher than the present data.

Dymond (*16*) has shown that a free-volume-type equation can be used to represent computer calculations for self-diffusivity of rough hard-sphere molecules. Chen et al. (*17*) developed an analogous expression for mutual diffusion in the form

$$D_{12}/T^{1/2} = \beta(V - V_D) \quad (4)$$

where β is a function of the solute and solvent interaction and V_D is a function only of the solvent and represents the molar volume at which diffusivity approaches zero. Therefore, the rough hard-sphere predicts that $D_{12}/T^{1/2}$ would form a straight line when plotted vs molar volume of the solvent. If this relationship holds, then it would be possible to predict D_{12} for a given solute/solvent pair by determining the two constants, β and V_D.

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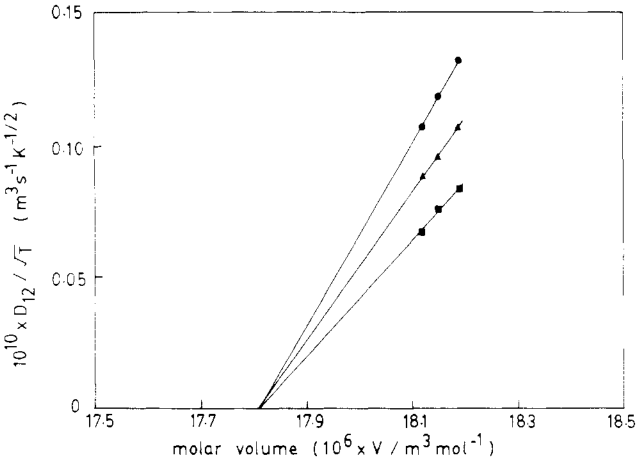

Figure 1. Free-volume relationship for mutual diffusion of several alcohols in water. Symbols: (●) methanol, (▲) ethanol, (■) 1-butanol.

Table II. Coefficients β and V_D for Methanol, Ethanol, and 1-Butanol

solute	$10^5\beta$, mol m^{-1} s^{-1} K$^{-1/2}$	$10^6 V_D$, m^3 mol^{-1}
methanol	0.3650	17.82
ethanol	0.2846	17.81
1-butanol	0.2235	17.82

Figure 1 illustrates the plots of $D_{12}/T^{1/2}$ for the alcohol/water systems. The linear relationship was demonstrated for all three systems studied. In Table II, the values of β and V_D obtained are listed. With the values of V_D obtained, the rigid-sphere diameter for the solvent can be calculated by means of the following equation:

$$V_D = bV_0 = BN\sigma_2^3 \qquad (5)$$

where N is the Avogadro constant, σ_2 is the hard-sphere diameter of the solvent molecules, and b is a constant used to account for the effects of correlated molecular motions in hard-sphere fluids (*16*, *17*). The constant b has been found to be 1.3509 from linear regression of the molecular dynamics simulation results of Easteal et al. (*18*). Subsequently, the molecular diameter of the solvent was calculated with eq 5 to be 0.314 nm.

By a development analogous to that for diffusion, Dymond (*19*) has shown that the viscosity of hard-sphere fluids can be represented by

$$T^{1/2}/\eta = \beta'(V - V_\eta) \qquad (6)$$

where η is the measured viscosity and V_η is the molar volume at which fluidity approaches zero. This quantity is analogous to V_D calculated from diffusion data and therefore can also be used to determine the molecular diameter of the solvent. Viscosity data from literature (*20*) were obtained. The values of V_η and σ_η were also determined by plotting $T^{1/2}/\eta$ versus V. The agreement between V_D and V_η was within 0.2%, and the diameters determined from both properties were in complete agreement.

Literature Cited

(1) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. *Int. J. Thermophys*. **1980**, *1*, 243.
(2) Alizadeh, A.; Wakeham, W. A. *Int. J. Thermophys*. **1982**, *3*, 307.
(3) Matos Lopes, M. L. S.; Nieto de Castro, C. A. *High Temp.—High Press*. **1985**, *17*, 599.
(4) Matos Lopes, M. L. S.; Nieto de Castro, C. A.; Padrel de Oliveira, C. M. *Fluid Phase Equilib*. **1987**, *36*, 195.
(5) Matthews, M. A.; Rodden, J. B.; Akgerman, A. *J. Chem. Eng. Data* **1987**, *32*, 319.
(6) Li, S. F. Y.; Wakeham, W. A. *Int. J. Thermophys*. **1989**, *10*, 995.
(7) Li, S. F. Y.; Lee, H. K.; Yue, L. S., 3rd Asian Chemical Conference, Aug 28-Sept 2, 1989, Brisbane, Australia.
(8) Chandler, D. *J. Chem. Phys*. **1975**, *62*, 1358.
(9) Bertucci, J.; Flygare, W. H. *J. Chem. Phys*. **1975**, *63*, 1.
(10) Czworniak, K. J.; Andersen, H. C.; Pecora, R. *Chem. Phys*. **1975**, *11*, 451.
(11) Matthews, M. A.; Akgerman, A. *J. Chem. Phys*. **1987**, *87*(4), 2285.
(12) Matthews, M. A.; Rodden, J. B.; Akgerman, A. *J. Chem. Eng. Data* **1987**, *32*, 317.
(13) Matthews, M. A.; Akgerman, A. *AIChE J*. **1987**, *33*, 881.
(14) Padrel de Olleira, C. M.; Fareleira, J. M. N. A.; Nieto de Castro, C. A. Presented at 10th Symposium on Thermophysical Properties, Gaithersburg, MD, USA, June 20-23, 1988.
(15) Easteal, A. J.; Woolf, L. A. *J. Phys. Chem*. **1985**, *89*, 1066.
(16) Dymond, J. H. *J. Chem. Phys*. **1974**, *60*, 969.
(17) Chen, S. H.; Davis, H. T.; Evans, D. F. *J. Chem. Phys*. **1982**, *77*(5), 2250.
(18) Easteal, A. J.; Woolf, L. A.; Jolly, D. L. *Physica* **1983**, *A121*, 286.
(19) Dymond, J. H. *Chem. Soc. Rev*. **1985**, *14*, 317.
(20) Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; Touloukian, Y. S., Ed.; Wiley: New York, 1975.

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Osmotic Coefficients of Some Cobalt-Amine-Type Salts from Cryoscopic Measurements

Jesus M. Arsuaga, Alejandro Martin, Mercedes Caceres,* and Javier Nuñez

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

Osmotic coefficients of aqueous solutions of tris(ethylenediamine)cobalt(III) chloride, tris(ethylenediamine)cobalt(III) bromide, tris(ethylenediamine)cobalt(III) iodide, tris(ethylenediamine)cobalt(III) nitrate, and tris(ethylenediamine)cobalt(III) perchlorate have been measured from 0.000 to 0.025 mol·kg^{-1}. The freezing-point method was used for the determination of the osmotic coefficients. These results were fitted to semiempirical least-squares equations, and these equations were used to calculate the mean molal activity coefficients.

Introduction

The osmotic and activity coefficients of single and mixed electrolytes have been available in the literature for many years. A considerable number of aqueous solutions containing salts were investigated by Scatchard and his collaborators who developed the freezing-point method for the determination of the osmotic coefficients to a high degree of precision. The same method was used by Lange to investigate other systems at low solute concentrations, and more recently by Prue et al. and Lilley and Scott. A bibliography of these previous investigations is reported in ref 1.

The object of this work is to continue our investigations on cobalt-amine salts (*1*) and present experimental results on

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