Table II. Determined Dew and Bubble Points

	ρ, kg/m^3	T, K	P, MPa
20 wt % (17.7 mol %) HCFC 142b			
dew point	88.3 ± 0.1	336.4 ± 0.7	2.01 ± 0.05
dew point	139.9 ± 0.1	353.3 ± 0.9	2.91 ± 0.06
dew point	236.4 ± 0.1	369.8 ± 1.3	4.08 ± 0.07
dew point	297.4 ± 0.1	375.9 ± 1.4	4.57 ± 0.08
dew point	374.4 ± 0.1	378.5 ± 2.0	4.87 ± 0.10
dew point	471.3 ± 0.1	378.1 ± 2.5	4.89 ± 0.15
bubble point	619.3 ± 0.1	377.1 ± 1.2	4.86 ± 0.09
bubble point	779.9 ± 0.1	369.9 ± 0.7	4.31 ± 0.07
bubble point	983.1 ± 0.1	342.9 ± 0.6	2.55 ± 0.06
40 wt % (36.5 mol %) HCFC 142b			
dew point	85.1 ± 0.1	343.7 ± 0.5	1.89 ± 0.04
dew point	134.6 ± 0.1	361.7 ± 0.6	2.77 ± 0.05
dew point	314.6 ± 0.1	386.0 ± 1.6	4.53 ± 0.09
dew point	396.0 ± 0.1	385.9 ± 1.8	4.62 ± 0.10
bubble point	855.0 ± 0.1	366.8 ± 0.7	3.44 ± 0.06
bubble point	1078.5 ± 0.1	321.5 ± 0.4	1.38 ± 0.05
60 wt % (56.3 mol %) HCFC 142b			
dew point	94.9 ± 0.1	356.9 ± 0.6	2.08 ± 0.05
dew point	150.2 ± 0.1	375.3 ± 0.7	3.01 ± 0.05
dew point	189.0 ± 0.1	383.4 ± 0.9	3.52 ± 0.07
bubble point	524.4 ± 0.1	392.4 ± 2.1	4.43 ± 0.14
bubble point	660.1 ± 0.1	391.1 ± 1.0	4.35 ± 0.08
bubble point	829.1 ± 0.1	375.5 ± 0.7	3.42 ± 0.07
bubble point	1046.0 ± 0.1	329.2 ± 0.5	1.39 ± 0.06
80 wt % (77.5 mol %) HCFC 142b			
dew point	72.3 ± 0.1	352.9 ± 0.6	1.60 ± 0.05
dew point	114.5 ± 0.1	371.8 ± 0.8	2.36 ± 0.05
dew point	198.4 ± 0.1	391.8 ± 0.9	3.46 ± 0.06
dew point	314.3 ± 0.1	402.3 ± 1.2	4.21 ± 0.08
dew point	395.6 ± 0.1	402.4 ± 2.0	4.26 ± 0.09
bubble point	518.1 ± 0.1	401.7 ± 1.4	4.28 ± 0.10
bubble point	652.3 ± 0.1	398.6 ± 0.8	4.08 ± 0.07
bubble point	822.0 ± 0.1	379.5 ± 0.5	2.95 ± 0.06
bubble point	1037.3 ± 0.1	328.7 ± 0.4	1.06 ± 0.04

60 wt % HCFC 142b locate at the position near the vapor pressure curve of CFC 12, as shown in Figure 3.

For the HCFC 142b + HCFC 22 system, Valtz et al. (*12*) reported the saturated liquid densities and bubble-point pressures along four isotherms, and then they calculated the saturated vapor densities and dew-point pressures with the aid of the Peng-Robinson equation. We prepared Figure 4 to compare our dew- and bubble-point data with values reported by Valtz et al. along three isotherms, i.e., 322.8, 348.4, and 372.5 K. In Figure 4 solid symbols indicate values reported by Valtz et al., including their calculated values, while other symbols indicate those by the present study. It should be noted, however, that our dew and bubble points have been interpolated so as to compare them along the common isotherms reported by Valtz et al., in Figure 4. The broken curves and solid curves in Figure 4 indicate the bubble-point and dew-point curves calculated from the Raoult's law, respectively.

Although the bubble-point pressure data at 372.5 and 348.4 K by Valtz et al. (*12*) are in good agreement with our data, both data show lower pressure than the Raoult's law. On the other hand, both sets of the dew- and bubble-point data agree well with the Raoult's law at 322.8 K. Our dew-point pressure data show a good agreement with Raoult's law at 372.5 and 348.4 K.

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Binary Diffusion Coefficients of the Methanol/Water System in the Temperature Range 30–40 °C

Yeng E. Lee and Sam F. Y. Li*

Department of Chemistry, National University of Singapore, 10 Kent Ridge Crescent, Republic of Singapore 0511

Measurements of the mutual diffusion coefficient of the methanol/water system have been performed by using the Taylor dispersion technique. The results extend over the complete composition range for the mixtures and over the temperature range of 30–40 °C. The system exhibits a minimum in the diffusivity as a function of composition at constant temperature, which is characteristic of alcohol/water mixtures.

Introduction

A knowledge of the transport properties of fluids, i.e. the viscosity, diffusivity, and thermal conductivity, is frequently required for designing new technological processes and also in research work. In particular, diffusion is important in the design of chemical reactors, liquid/liquid extraction units, and absorbers, as well as distillation columns. In addition, the study of fluid-state theory, mass-transfer phenomena, and molecular

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interactions can be further aided by the accurate determination of diffusion coefficients.

For the determination of mutual diffusion coefficients of liquid/liquid systems, several well-established methods are known (*1*). The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures are performed by the interferrometric method (*2*). However, this technique has been proven to be tedious and difficult to be applied to conditions far from ambient (*1*). The method based on the phenomenon of Taylor dispersion, on the other hand, is direct and offers the advantages of speed and simplicity. In fact, it has now been established as the absolute method to be used. In essence, the technique makes use of the velocity profile characteristic of laminar flow to enhance the dispersion of the pulse brought about by molecular diffusion alone. The pulse ultimately assumes a Gaussian distribution whose temporal variance is dependent on both the average flow velocity and molecular diffusivity, D_{12}. At the end of the diffusion tube, the concentration vs time data is recorded as the peak elutes. The normalized first and second temporal moments are calculated, from which the diffusion coefficient is obtained.

Earlier studies seem to suggest that the diffusion coefficient is highly dependent on molecular structures. For alkanes, for example, it was observed that the diffusion coefficients of *n*-alkane mixtures exhibit a linear dependence on composition in contrast to those of branched alkane systems, where an unexpected maximum is obtained at a molar fraction of about 0.5 (*3*). Also, studies of the diffusion of hexane isomers in argon (*4*), of heptane and octane isomers in the gas phase (*5*, *6*), and of pentane and isopentane mixtures in the gas phase (*7*) seem to show that the diffusion coefficient increases with increased branching. For mixtures of alcohol and water, studies on mixtures of water and isomers of propanol (*8*) reveal an interesting feature: In addition to the minimum in diffusivity which has been found to be characteristic of alcohol/water mixture (*9*), a local maximum occurs along an isotherm. It was suggested that this behavior arose from significant structural changes in the liquid mixtures.

In order to confirm this behavior, binary diffusion coefficients of water/methanol mixtures at various temperatures were measured as a function of composition.

Experimental Techniques

The Taylor dispersion technique involves the injection of a pulse of soluble material into a solvent of slightly different composition in laminar flow through a circular section tube. The concentration gradient established by the introduction of this sample, together with the action of the parabolic velocity profile of laminar flow, results in dispersion of the pulse. The ideal model of an instrument for the measurement of the diffusion coefficient by this technique consists of an infinitely long straight tube of uniform circularr cross-section, radius a_0, through which a fluid mixture passes in laminar flow with a mean velocity $\bar{u}_0$ (*2*). A δ-function pulse of a mixture of slightly different composition is injected at a distance L from the detection point. The mutual diffusion coefficient of the binary fluid mixture, D_{12}, is given by (*2*)

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

Here $A_0 = \pi a_0^2$ is the cross-sectional area of the tube. $\bar{t}_{\mathrm{id}}$ 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

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

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.

A schematic diagram of the Taylor dispersion instrument is shown in Figure 1. The diffusion tube is made from approximately 12 m of stainless steel tube having a nominal internal diameter of 0.55 mm. The tubing is wound in a smooth helical coil on a metal mould. The mould was filled with molten solder to ensure good thermal contact. The whole block was then placed in a water bath and its temperature maintained by a thermostat (Thermomix U; ±0.1 °C). At its upstream end, the diffusion tube was directly connected to an injection valve (Rheodyne 7010 model) fitted with a sample loop of nominal volume of 20 μL. At its downstream end, the diffusion tube was coupled to one side of a differential refractometer (Waters Associates R401) by means of a short length of insulated connecting tubing. The dimensions of the reservior were large enough to ensure that the pressure head for the liquid flow through the diffusion tube changed by no more than 0.1% over the duration of the experimental run. To ensure a uniform composition of the fluid in the reservoir at the inlet to the diffusion tube, continual stirring was maintained by a magnetic

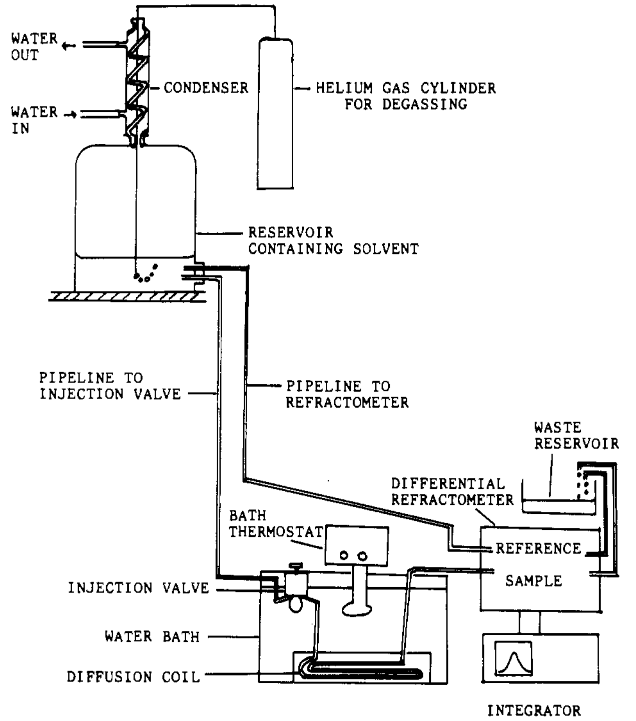

Figure 1. Schematic diagram of the Taylor dispersion instrument.

Table I. Characteristics of the Instrument

diffusion tube length, L, m	12.265
diffusion tube internal radius, a_0, mm	0.5527
coil radius, R_0, m	0.305
volume of injected sample, V_i, μL	20.0
volume of detector cell, V_{det}, μL	10.0
length of connecting tubing, L, m	0.35
radius of the connecting tubing, r, mm	0.1143

Table II. Diffusion Coefficients of the Methanol/Water System at Various Mole Fractions of Methanol

	$D_{12} \times 10$					
temp, K	1	0.90	0.75	0.50	0.25	0
303.13	2.22 ± 0.01	1.91 ± 0.01	1.55 ± 0.01	1.13 ± 0.02	1.07 ± 0.02	1.62 ± 0.02
308.13	2.45 ± 0.01	2.19 ± 0.02	1.71 ± 0.01	1.28 ± 0.02	1.20 ± 0.01	1.89 ± 0.01
313.13	2.67 ± 0.02	2.42 ± 0.05	1.90 ± 0.01	1.42 ± 0.04	1.33 ± 0.05	2.10 ± 0.01

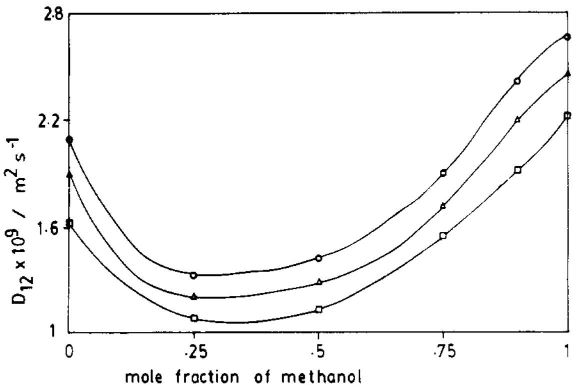

Figure 2. Composition dependence of the diffusion coefficient along the following isotherms (O) 303 K; (△) 308 K; (□) 313 K.

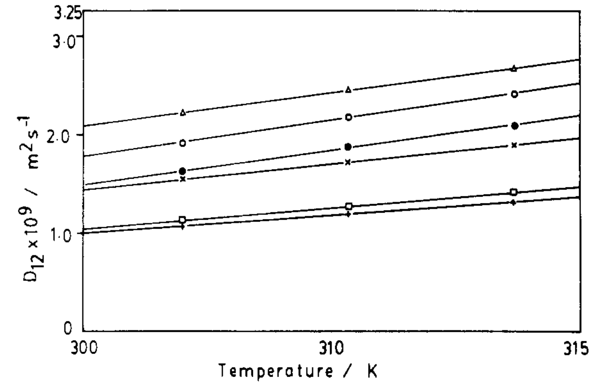

Figure 3. Temperature dependence of the diffusion coefficient at each methanol/water composition (% methanol): (△) 100%; (O) 90%; (●) 0%; (×) 75%; (□) 50%; (+) 25%.

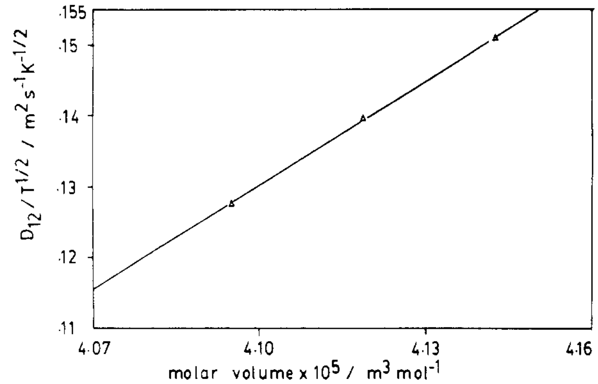

Figure 4. Graph of $D_{12}/T^{1/2}$ vs molar volume for methanol.

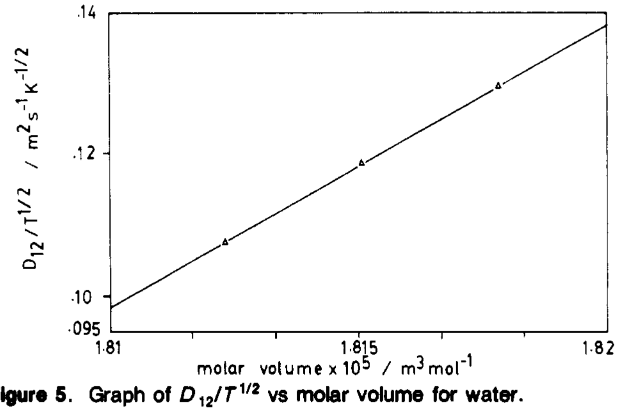

Figure 5. Graph of $D_{12}/T^{1/2}$ vs molar volume for water.

stirrer placed beneath the reservoir. A condenser was also fitted to the reservoir to prevent evaporation of the mixture, which might lead to a change in composition. The precise dimensions of the diffusion tube and its ancillary components are listed in Table I. The mixtures of methanol and water in mole fractions of 0, 0.25, 0.5, 0.75, and 1.0 of methanol were prepared gravimetrically from HPLC grade methanol (J. T. Baker Chemical, Phillipsburg) and doubly distilled deionized water. The pure liquids were first filtered through a membrane of pore size 0.45 μm and degassed by bubbling helium gas through before mixing. The design criteria and the small corrections given in ref 2 have been taken into account in the construction and operation of the present instrument. All the corrections are very small, contributing less than 0.1% to the measured diffusion coefficient. 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 (*2*).

Results and Discussion

The results obtained for the binary diffusion coefficient of mixtures of water/methanol are listed in Table II. Each reported value in this table is the average of three measurements. Figure 2 shows the composition dependence of the binary diffusion coefficient of the water/methanol mixtures along the isotherms of 303.13, 308.13, and 313.13 K. It can be seen that the system exhibits a minimum in binary diffusion coefficient at approximately 0.3 mole fractioon of methanol. Figure 3 shows the temperature dependence of the binary diffusion coefficient of each water/methanol composition. A linear relationship is obtained for each composition.

Dymond (*10*) 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. (*11*) developed an analogous expression for tracer diffusion in the form

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

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 the molar volume of the solvent. Figures 4 and 5 show the plot of $D_{12}/T^{1/2}$ for pure methanol and pure water, respectively. The densities required for the computation of the molar volume were obtained from literature (*12*). The hard-core volume, V_0, for the solvent is related to V_D by $V_D = bV_0$, where b = 1.3509 according to molecular dynamics calculations (*13*). The hard-sphere diameter, σ_D, was then computed on the basis of

$$V_0 = N\sigma_D{}^3/2^{1/2} \qquad (5)$$

where N is Avogadro's constant.

By a development analogous to that for self-diffusion, it can be shown that (*10*, *15*)

$$T^{1/2}/\eta = \beta'(V - V_\eta) = \beta'\,(V - 1.3509V_0) \qquad (6)$$

where η is the measured viscosity and V_η is the molar volume at which the fluidity approaches zero. V_η is analogous to V_D

Table III. Values of V_D, σ_D, V_η, and σ_η for Methanol and Water

	methanol	water		methanol	water
$V_D \times 10^6$, m^3	3.840	1.783	$V_\eta \times 10^6$, m^3	3.750	1.793
$\sigma_D \times 10^{10}$, m	1.883	1.458	$\sigma_\eta \times 10^{10}$, m	1.868	1.461

Table IV. Infinite Dilution Coefficient of Methanol in Water ($D_{12} \times 10^9$, m^2/s)

temp, °C	present work	previous work (*15*)
30	1.62 ± 0.02	1.76
35	1.89 ± 0.01	1.96
40	2.10 ± 0.01	2.19

and is used to serve as an independent check for the accuracy of the hard-core volume, V_0, calculated from the experimental data. The viscosity data required were obtained from literature (*14*). The hard-sphere diameter, σ_η, was then computed on the basis of

$$V_0' = N\sigma_\eta^3/2^{1/2} \qquad (7)$$

The values of V_D, σ_D, V_η, and σ_η for methanol and water are listed in Table III. Agreement between the hard-sphere diameters was within 1% for both methanol and water.

Attempts have been made in the search of literature to find values for the binary diffusion coefficient of methanol/water mixtures at various compositions. Unfortunately, only data for diffusion of methanol at infinite dilution in water are available (*15*). A comparison of the results are shown in Table IV for reference. The diffusion coefficients obtained in the present work are lower than those of Easteal and Woolf (*15*), with a deviation of 4–8%. Because the accuracy of the earlier measurements was not started, it is impossible to decide whether the discrepancy is significant. In general, the reproducibility of the measurements in the present work was generally high (within 1%).

Studies of 1-propanol/water and isopropyl alcohol/water systems reveal (*8*) that both systems exhibit a minimum as well as a maximum in the diffusivity as a function of composition at constant temperature. In contrast, the water/methanol system exhibits only a local minimum. In view of this unusual behavior displayed by the diffusion coefficient, it is worthwhile to examine other transport properties of the mixtures in search of analogous behavior.

The shear viscosity data measured as a function of composition at 30 °C are available (*14*). The data display a maximum in the viscosity at a composition (0.3 mole fraction of methanol) close to that at which the mutual diffusion coefficient shows a minimum. No minimum is observed in the plot of viscosity vs composition. Bearing in mind the analogous behavior of viscosity and diffusivity, the experimental results are in good agreement with the literature.

Experimental data on the heat of mixing for the water/methanol system at 25 °C under a pressure of 0.1 MPa was reported by Tomaszkiewicz (*16*). An exothermic minimum in the heat of mixing at low methanol concentration (approximately 0.3 mole fraction) is observed. Unfortunately, data in the temperature range of interest (303–313 K) are not available. Nevertheless, this is of sufficient evidence that some structural changes have taken place in the mixture. These changes are probably of a cooperative nature since water and methanol are known to associate through hydrogen bonding.

Summary

The binary diffusion coefficient of mixtures of methanol with water have been measured as a function of composition at various temperatures. The binary diffusion coefficient of each composition mixture varies linearly with temperature. However, a minimum in binary diffusion coefficient is observed at approximately 0.3 mole fraction of methanol along an isotherm. Due to the unavailability of reliable values of the parameters involved, theoretical values for the binary diffusion coefficient for the system could not be evaluated. It is thus not possible to determine the extent of agreement between the experimental and the theoretical values. Nevertheless, the minimum in binary diffusion coefficient at 0.3 mole fraction of methanol agrees with data on the viscosity as well as the heat of mixing of the system. The latter is suggestive of sudden structural changes occurring in the water/methanol mixture at approximately 0.3 mole fraction of methanol. It is highly probable that such changes involve interactions such as hydrogen bonding between the water and methanol molecules in the mixtures.

Registry No. Methanol, 67-56-1; water, 7732-18-5.

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