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Liquid Mutual Diffusivities of the H_2O/D_2O System[1]

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The liquid-phase mutual diffusivities of the water (H_2O) and deuterium oxide (D_2O) system at 298.2 K were measured using an instrument based on the Taylor dispersion technique. The instrument has been designed to match, as closely as possible, the mathematical model of ideal Taylor dispersion, minimizing all the departures from the ideal model. The diffusivities were measured over the entire concentration range and the results follow a linear dependence on molar fraction given by $10^9 \mathscr{D}_{12} = 2.24 - 0.36 x_{D_2O}$, where $\mathscr{D}_{12}$ is in $m^2 \cdot s^{-1}$. Comparison with highly accurate data obtained by a Rayleigh interferometer seems to indicate that the accuracy of the present instrument is 1%. The hard-sphere model was applied to the estimation of the mutual diffusivities of this system and good agreement was found with experiment, deviations being $\pm 3.5\%$.

KEY WORDS: deuterium oxide; diffusivity; mass transfer; Taylor dispersion technique; water.

1. INTRODUCTION

Diffusivity measurements are fundamental information in a number of engineering applications, in the study of mass transfer processes, and in the development of liquid state theories.

The method used in this work is the chromatographic broadening technique, for which the theory is described elsewhere [1]. In this method, a pulse is injected in a stream of different concentration that is flowing in a tube. In a short time, a significant dispersion of this pulse is achieved by the coupled effect of the laminar-flow velocity profile and the molecular dif-

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fusion. The flow of the fluid also allows a single fixed concentration detector to observe all of the dispersed solute as a function of elapsed time. The technique is therefore rapid and simple.

The theory of the method provides a set of working equations and conditions for an apparatus based on this principle that enables us to make diffusivity measurements reducing the systematic errors to a level below that of experimental precision, typically ±1%.

In our previous work [2], measurements of mutual diffusivities were obtained for mixtures of *n*-heptane/*n*-octane and *n*-heptane/*n*-dodecane. The former were compared with values of Alizadeh and Wakeham [3], obtained by the same method. The latter were compared with the results of Lo [4], obtained with the diaphragm-cell method. The same deviation of about −7% was found relative to both sets of results. The need for further investigation to determine the cause of this deviation was then recognized. In this sense the present work is, partly, a further test of the measuring equipment. The H_2O/D_2O system was chosen, as some accurate results for this mixture were published by Longsworth [5] using Rayleigh interferometry.

2. CHROMATOGRAPHIC METHOD—WORKING EQUATIONS

The ideal model of an apparatus to measure diffusivities using the Taylor dispersion method consists of an infinitely long straight tube of uniform, circular cross section, radius a_0, through which flows, in the laminar regime with the mean velocity $\bar{u}_0$, a binary mixture of a fluid with physical properties independent of composition. A mixture of the same components but of a slightly different composition is injected in the tube as a δ-function pulse that is dispersed by the combined action of molecular diffusion and parabolic velocity profile. Under suitable conditions it is possible to calculate the mutual diffusivity $\mathscr{D}_{12}$ of the binary mixture from the two first temporal moments of the concentation Gaussian distribution at distance L from the injection point [1],

$$\mathscr{D}_{12} = \frac{a_0^2}{24\bar{t}_{id}} \left[\frac{(1 + 4\Gamma_{id}^2/\bar{t}_{id}^2)^{1/2} + 3}{(1 + 4\Gamma_{id}^2/\bar{t}_{id}^2)^{1/2} + 2\Gamma_{id}^2/\bar{t}_{id}^2 - 1} \right] \left[\frac{1}{2} + \frac{1}{2}(1 - \delta_a)^{1/2} \right] \tag{1}$$

In Eq. (1), $\bar{t}_{id}$ denotes the first raw moment of the distribution, Γ_{id}^2 denotes its second central moment, and

$$\delta_a = 12.7997\xi_0 \tag{2}$$

with

$$\xi_0 = \bar{u}_0 a_0^2 / 48L\mathscr{D}_{12} \tag{3}$$

There are some restrictions for the applicability of Eq. (1) which affect the equipment design. First is to ensure laminar flow,

$$2\bar{u}_0 a_0 \rho/\eta < 2000 \tag{4}$$

where ρ is the fluid density and η is its viscosity. Second, there are mathematical approximations that amount to less than ±0.01%, provided that [1]

$$\bar{t} > 10a_0^2/\mathscr{D}_{12} \tag{5}$$

$$\bar{t} < La_0/700\mathscr{D}_{12} \tag{6}$$

The need for isothermal dispersion leads to helicoidal coiling of the tube with a radius R_c, which originates secondary flow. This effect can be minimized, to less than 0.05%, if the condition given by Eq. (7) is fulfilled [1]:

$$\bar{t} > \left(\frac{a_0^3 L^2 \rho}{5\eta\mathscr{D}_{12} R_c}\right)^{1/2} \tag{7}$$

Other effects cannot be rendered negligible by design. These are the finite volume of the detector at the end of the tube, the finite volume of injection, and the difference in the radius of the tube that connects the diffusion tube to the detector. The corresponding corrections can be applied in the form [1]

$$\bar{t}_{id} = \bar{t} + \sum_i \delta\bar{t}_i \tag{8}$$

$$\Gamma_{\mathrm{id}}^2 = \Gamma^2 + \sum_i \delta\Gamma_i^2 \tag{9}$$

where $\bar{t}$ and Γ^2 denote the experimentally determined moments and δt_i and $\delta\Gamma_i^2$ are, respectively, the corrections to the moment and the variance of the peak.

Finally, a correction is due to the fact that, in contrast with the ideal model, physical properties of the mixture, namely, the diffusivity, are dependent on the concentration. Therefore, the measured diffusivity must correspond to a reference mole fraction x_{ref} given by

$$x_{\mathrm{ref}} = x_{\mathrm{f}} + \delta x \tag{10}$$

where x_{f} is the molar fraction of component 1 in the flowing mixture and δx is the correction. However, the corrections expressed in Eqs. (8)–(10) are reduced to no more than ±1% by suitable instrument design so that the systematic error arising from their estimation is smaller than the precision of the measurements.

3. INSTRUMENT DESIGN AND OPERATION

The application of the theory of the Taylor dispersion technique, according to the principles outlined above, led to the design parameters of the instrument shown in Table I. In this table, l is the length of the connection tube to the detector cell, V_D is the volume of the detection cell, and V_I is the volume of the injected sample. The detector chosen was a differential refractometer (Model R-401, Waters Associates) and V_D and l are its characteristics. All the fittings and valves as well as the diffusion tube are made of 316 stainless steel. The diffusion tube ($\frac{1}{16}$-in. OD) is wound around the inner wall of a U-shaped stainless-steel circular ring, which was filled with molten lead to ensure good thermal contact and covered with a stainless-steel cap. All of this block was suspended from a marble table to avoid vibration of the tube and subsequent enhanced dispersion. The sample is injected using a six-port injection valve (Specac Analytical Acess., Model PN30.501). The temperature is measured with a digital thermometer to 0.1°C (Crison, Model 620/3). The flow of the mixture is obtained by a liquid head from a stainless-steel constant-level reservoir.

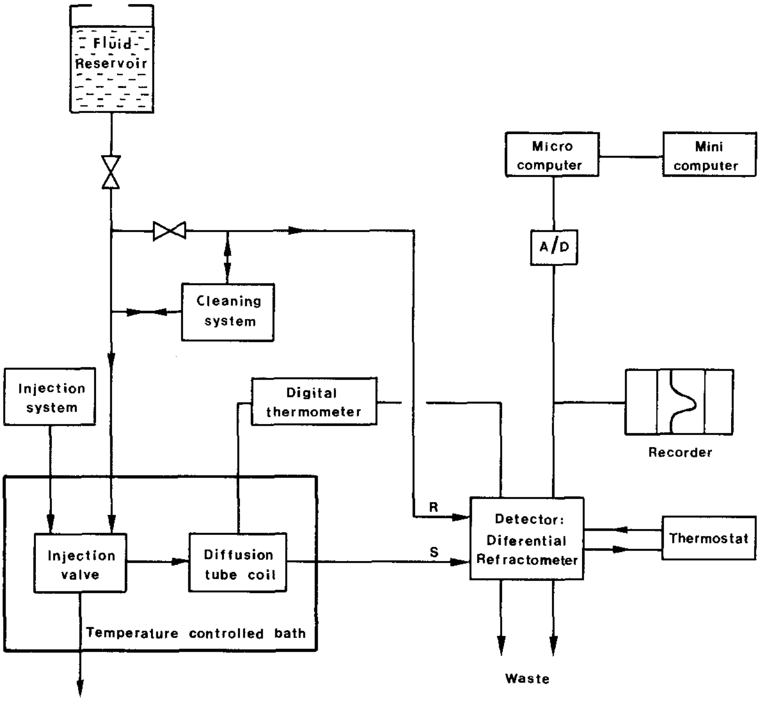

Fig. 1. Functional diagram of the diffusivity measuring instrument.

Table I. The Characteristics of the Diffusion Apparatus

Diffusion-tube length, L	13.1337 m
Diffusion-tube internal radius, a_0	3.904×10^{-4} m
Coil radius, R_c	0.1608 m
Injection volume, V_i	2×10^{-8} m^3
Detector volume, V_d	1×10^{-8} m^3
Length of connecting tube, l	0.3584 m
Internal radius of connecting tube, a_c	1.143×10^{-4} m

Figure 1 shows the functional diagram of the entire instrument, including the fluid lines, the tube and refractometer-cell cleaning system, the bath thermostat (Grant Instruments, SU6; ±0.1°C), the thermostat for the refractometer cell (Haake FE2, ±0.01°C), and the recorder (Omniscribe B-5000, Houston Instruments). The recorded peak is digitized with the aid of an eight-bit A/D converter, after being amplified (OMEGA, DC millivolt amplifier), and then recorded in a computer file. A minicomputer (Heathkit H8) is used as a data acquisition support of the instrument and also as a terminal to a Data General computer (Eclipse /140) used to process the peaks and evaluate the moments of the distribution (nonlinear least-squares adjustment of a Gaussian).

4. EXPERIMENTAL

Measurements of diffusivities were carried out for mixtures of H_2O (component 1)/D_2O (component 2) at 298.2 K. The D_2O was supplied by Sigma Chemical Co., with a minimum deuterium content of 99.8%. The H_2O was bidistilled and demineralized, with a final specific conductivity of $10^{-6}\ \Omega \cdot \text{cm}^{-1}$. The mixtures were prepared gravimetrically, with an error of less than 0.0001 in molar fraction.

In order to ensure that the instrument operates in accordance with the theory that describes it, the diffusion time for each experiment was chosen to be within the interval imposed by inequalities given by Eqs. (4)–(7). For the H_2O/D_2O system at 298.2 K, this interval is $2700 < \bar{t} < 4600$ s.

5. RESULTS

Table II displays the results obtained for the mutual diffusivities of mixtures of H_2O/D_2O for different molar fractions at 298.2 K.

Graphically determined values of $\bar{t}$ and Γ^2, corrected by Eqs. (8) and (9), were placed in Eq. (1). The precision of the results is ±1.5% and is due mainly to this graphical procedure.

Table II. Mutual Diffusivities for the H_2O/D_2O System at Temperature $T = 298.2$ K

D_2O molar fraction, x_2	$\mathscr{D}_{12} \times 10^9$ $(m^2 \cdot s^{-1})$
0.003	2.24
0.255	2.16
0.502	2.06
0.751	1.96
0.995	1.89

The following linear relation between diffusivity and molar fraction was obtained:

$$10^9 \mathscr{D}_{12} = 2.24 - 0.36 x_2 \tag{11}$$

where $\mathscr{D}_{12}$ is in $m^2 \cdot s^{-1}$.

6. DISCUSSION

The linear dependence of diffusivity on molar fraction follows the simple and entirely empirical equation

$$\mathscr{D}_{12} = x_1 \mathscr{D}_{21}^0 + x_2 \mathscr{D}_{12}^0 \tag{12}$$

where $\mathscr{D}_{21}^0$ and $\mathscr{D}_{12}^0$ are the limiting mutual diffusivities, that can be applied to a number of experimental results for ideal systems [6, 7] and indicates that the system H_2O/D_2O behaves like an ideal solution. This is a rather common fact for isotopic mixtures, and no evidence was found to the contrary for this system [8].

Figure 2 shows the comparison of our results with those of Longsworth [5] for the same H_2O/D_2O mixtures. The deviation is less than 1%. As this value is below the experimental errors of our measurements, good agreement is obtained between both sets of results. Considering that the measurements by Longsworth were determined by a Rayleigh interferometric method, which is one of the most accurate for the determination of mutual diffusivities, the observed agreement shows that the equipment used is working according to its theoretical model, producing accurate measurements. The precision of the present method can still be improved by ±0.5 to ±1% by the full use of the automatic processing programs being developed. This enables one to fit a Gaussian curve to the experimental concentration distribution, from which the corresponding moments can be derived.

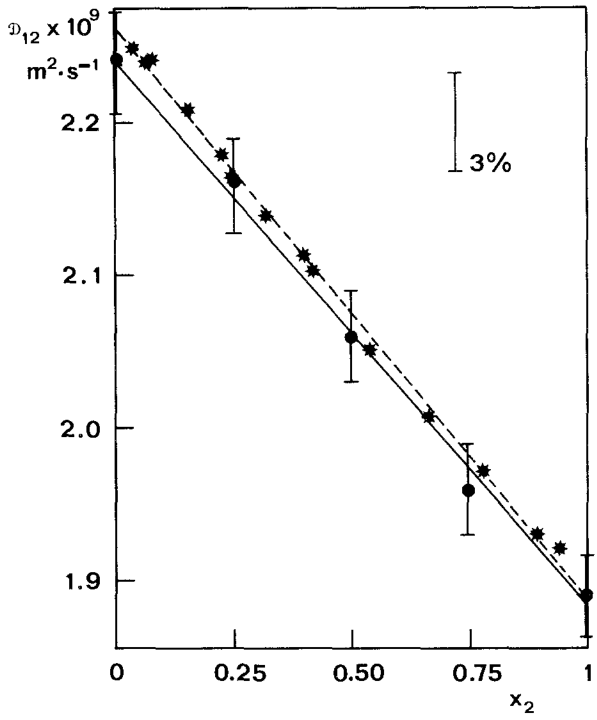

Fig. 2. Mutual diffusivities for H_2O/D_2O mixtures at different molar fractions. Temperature, $T = 298.2$ K. (●——●) Present work; (★----★) Longsworth [5].

Concerning the previous results obtained with the same instrument for *n*-alkane mixtures [2], for which deviations of −7% were found relative to the values determined by Alizadeh and Wakeham [3] and by Lo [4], we are now inclined to consider the possibility that the deviations probably lie in an undetected systematic error in the referred measurements.

The van der Waals model was applied to the system H_2O/D_2O and theoretical and experimental values of diffusivity were compared. This theory considers that the movements of the molecules in the liquid state are governed by a potential, composed of a hard spherical core, surrounded by a uniform attractive part, weak and very extense in space [9, 10]. It also considers that the real fluid is composed of rough hard spheres, with diameter σ, thus permitting translational–rotational coupling during a collision [11].

The application of this theory to pure fluids (viscosity and diffusion) enables the determination of the hard-core volume $V_0 = N_0\sigma^3/\sqrt{2}$, where

N_0 is the Avogadro number. Jonas et al. determined for H_2O and D_2O the values of $\sigma_{H_2O} = 0.275$ nm [12] and $\sigma_{D_2O} = 0.272$ nm [13].

The rough hard-spheres theory was extended to binary mixtures by Czworniak et al. [14] and Bertucci and Flygare [15], assuming that the kinetic diffusivity, D_{12}, of a real two-component fluid is equal to that of a two-component mixture of rough hard spheres of masses equal to those of the corresponding molecules with the same temperature, number density, and molar fraction of the real fluid. According to this,

$$D_{12} = D_{12}^{\mathrm{Ens}} A C \left(\frac{m_1}{m_2}, \frac{\sigma_1}{\sigma_2}, x_1, \xi \right) \tag{13}$$

where D_{12}^{Ens} is the mutual diffusivity for a mixture of soft hard spheres, as derived from the Enskog transport equation, C is a function of the packing fraction ξ, mass and size ratios, m_1/m_2, σ_1/σ_2, and a linear function of composition, introduced by Czworniak et al. [14] to compensate for the correlated motions in hard-spheres fluids after the molecular dynamics calculations of Alder et al. [16]. The translational–rotational coupling constant for the mixture, A, independent of density, composition, and temperature, was introduced by Chandler [17]. He implied that the roughness of real molecules is a result of nonspherical symmetry forming an irregular surface and treated A as an adjustable parameter bounded by the conservation of angular momentum so that $0 < A \leqslant 1$.

The experimental diffusivity, $\mathscr{D}_{12}$, is related to the kinetic diffusivity, D_{12}, by the expression

$$\mathscr{D}_{12} = D_{12} \left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln x_1} \right) \right] \tag{14}$$

where γ_1 is the activity coefficient of component 1.

As we have seen, the mixture H_2O/D_2O can be considered to behave like an ideal solution. Therefore, the densities needed for the calculation of D_{12}^{Ens} and C were estimated, using Amagat's law, from the densities of the pure components and the activity coefficient was taken as unity ($\mathscr{D}_{12} = D_{12}$).

The value of the coupling constant for the mixtures, $A = 0.16$, was obtained by least-squares fitting of the relation between D_{12}^{exp} and $D_{12}^{\mathrm{Ens}} \times C$, for experimental data both obtained in this work and obtained by Longsworth [5].

Figure 3 shows the deviation between the experimental results and the theoretical values of diffusivities of H_2O/D_2O system. The deviations are of the order of $\pm 3.5\,\%$, a departure bigger than the experimental uncertainty of the data points. The figure shows a systematic deviation, probably due

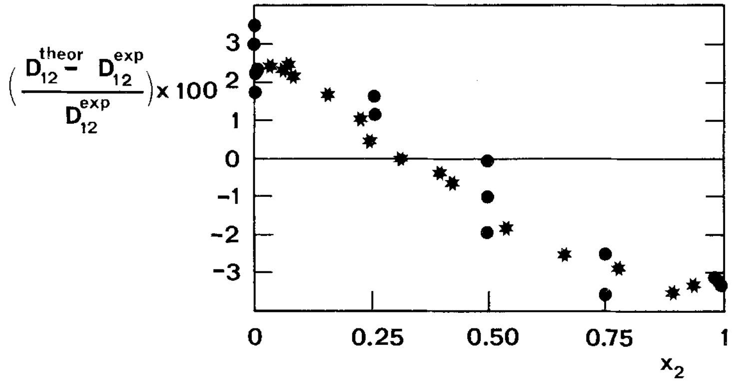

Fig. 3. Deviations between experimental and van der Waals theoretical diffusivities for H_2O/D_2O system. (●) Present work; (★) Longsworth [5].

to the values of the hard-core volumes for the pure components used in this calculation. This discrepancy would presumably disappear if the limiting diffusivities were used to obtain the hard-core volumes.

The low value of A (0.16) points to the importance of the hydrogen or deuterium bonding in increasing the roughness of H_2O and D_2O molecules, thus decreasing diffusion and the rough-spheres diffusivity relative to the soft hard-spheres diffusivity, $D_{RHS} = A \cdot D_{SHS}$.

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