Mutual Diffusion Coefficients of Water + Ethylene Glycol and Water + Glycerol Mixtures

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The experimental technique and mathematical treatment for holographic interferometry, applied for the measurement for mass diffusivity, are described in detail. Experimental results at 25 °C are presented for three mixtures, water + NaCl, water + ethylene glycol, and water + glycerol. The water + NaCl mixture was used as a reference system to check the accuracy of this method. Measurements were conducted at three concentrations within the range 0.00874−0.0699 mass fraction NaCl. The results were compared to literature data and found to be within the variance of this measuring method. Measurements were conducted for the water + ethylene glycol system within the concentration range 0.0250−0.950 mass fraction ethylene glycol and within 0.0200−0.800 mass fraction glycerol for the water + glycerol system. Experimental results are compared to literature data where these data are available. The agreement for both systems are not as good as for the reference system. The mass diffusivity of the water + ethylene glycol system was found to vary from 11.70 to 3.75 × 10^{-10} m^2 s^{-1} at a concentration of 0.0250 and 0.950 mass fraction ethylene glycol, respectively. The corresponding values for the water + glycerol system varied from 9.28 to 1.63 × 10^{-10} m^2 s^{-1} at a concentration of 0.0200 and 0.800 mass fraction glycerol, respectively.

Introduction

A knowledge of the transport properties of fluids such as viscosity, thermal conductivity, and mass diffusivity is frequently required for the design of different processes. In particular, diffusion is important in the design of chemical reactors, separation processes such as extraction, absorption, and distillation, and absorption heat pump systems. Tyrrell and Harris (1984) described several well-established methods for the experimental determination of mass diffusivities of liquid−liquid systems. The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures are performed by the interferometric method.

In this paper, the mass diffusivity is presented for two potential absorption heat pump working media: water + ethylene glycol and water + glycerol. A large mass diffusivity is crucial in the absorber and generator components of an absorption heat pump. It affects the mass transfer process and is equally important for the heat transfer process as well, since both processes are coupled through the temperature and concentration gradients. The mass diffusivity was determined for both systems at 25 °C using the holographic interferometry method.

Experimental Technique

Optical methods for measurement of mass diffusivity offer accurate results without any chemical analysis. The application of the holographic technique to interferometric purposes was described by Heflinger et al. (1966). Mass diffusivity can be measured due to changes in refractive index of the diffusing solutions, giving rise to changes in the optical path length. The laser light is split into two beams, an object beam and a reference beam. A transparent diffusion cell containing two solutions of slightly different concentrations is exposed to the object beam. It is crucial to fill the solutions into the cell with great care. One way to do this is to start with the light solution and then slowly introduce the heavy solution from below, as recommended by Gabelmann-Gray and Fenichel (1979).

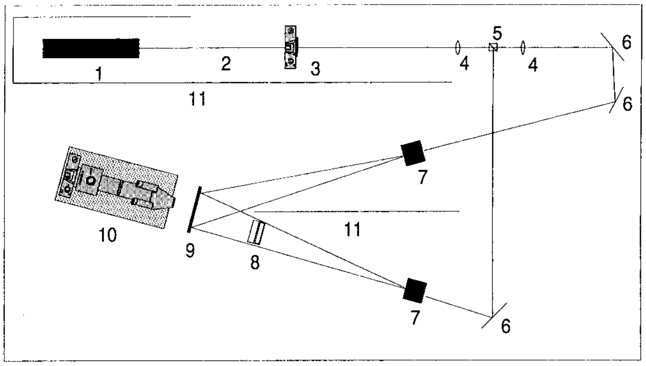

Figure 1. Experimental setup for holographic interferometry. (1) is the laser—a 5 mW helium−neon laser. The laser beam (2) is divided in a beam splitter (5) and filtered in the spatial filters (7). The object beam passes through the diffusion cell (8) before reaching the holographic plate (9). The interferograms are photographed through a microscope (10). (3) is the shutter for the laser beam, and (4) are half-wave plates, used to polarize the two beams in the same way. To avoid reflections, two shields (11) are used. (6) are mirrors.

When the holographic plate is exposed to the light, the interference between the two beams creates a holographic image of the cell. After development, the plate is placed back in exactly the same position. The holographic image of the cell is then superimposed on the real cell. Since the refractive index of the solutions is changing, a secondary interference between the image and the real cell can be observed. The diffusion cell can be recorded at different times by photographing the interference pattern, through a microscope, with an ordinary camera. This interferometric method is usually called real time holography. A more detailed description of this method is given by Gierow and Jernqvist (1994).

The experimental setup is shown in Figure 1. To avoid disturbances in the experiments, a very stable table must be used as a supporting carrier to the equipment. In our setup, a shock absorbing granite top is used.

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The mathematical background is based on Fick's second law of diffusion:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial y^2} \tag{1}$$

where c is the concentration (kg m^{-3}), t is time (s), D is the diffusion coefficient (m^2 s^{-1}), and y is a coordinate (m). Equation 1 can be solved for the following boundary conditions:

- When $t = 0$, the two solutions are separated by a sharp boundary at $y = 0$. The concentrations at each side of the boundary are homogeneous at c_1 and c_2.
- When $t > 0$, the concentrations at $y = 0$ are the same for both solutions, and the concentrations at $y = \pm\infty$ are c_1 and c_2.

The solution was given by Crank (1956) as follows

$$c(y,t) = \frac{c_1 + c_2}{2} + \frac{c_1 - c_2}{\sqrt{\pi}}\int_0^{\eta}\exp(-\eta^2)\,\mathrm{d}\eta \tag{2}$$

where

$$\eta = \frac{y}{2\sqrt{Dt}} \tag{3}$$

Due to the diffusion process the concentration gradient will change, and the concentration difference between 2 times t_1 and t_2 can be written as

$$c(y,t_1) - c(y,t_2) = \frac{c_1 - c_2}{\sqrt{\pi}}\int_{\eta_2}^{\eta_1}\exp(-\eta^2)\,\mathrm{d}\eta \tag{4}$$

where η_1 and η_2 are the corresponding values of η at t_1 and , respectively. If we assume a linear relation between refractive index and concentration between c_1 and c_2, this concentration difference can be rewritten as

$$n(y,t_1) - n(y,t_2) = B\int_{\eta_2}^{\eta_1}\exp(-\eta^2)\,\mathrm{d}\eta \tag{5}$$

where B is a constant. The interference fringes, numbered from the boundary between the liquids, arise where the difference in optical path length equals an odd number of half-wavelengths:

$$n(y,t_1) - n(y,t_2) = \frac{\lambda(2j + 1)}{2d} \tag{6}$$

where d (m) is the thickness of the diffusion cell and λ is wavelength (m). Several evaluation methods have been presented (Ruiz-Bevia, 1985a,b). Bochner and Pipman (1976) suggested a simple but mathematically exact evaluation method based on the extremes in the concentration difference gradient, y_0 and $-y_0$. At these extremes

$$\frac{\partial}{\partial\eta_1}\{c(y,t_1)\}\,\frac{\partial\eta_1}{\partial y} = \frac{\partial}{\partial\eta_2}\{c(y,t_2)\}\,\frac{\partial\eta_2}{\partial y} \tag{7}$$

Combined with

$$\frac{\partial}{\partial\eta}\{c(y,t)\} = \frac{c_1 - c_2}{\sqrt{\pi}}\exp(-\eta^2) \tag{8}$$

we get

$$\frac{1}{2\sqrt{Dt_1}}\exp\left(\frac{-{y_0}^2}{4Dt_1}\right) = \frac{1}{2\sqrt{Dt_2}}\exp\left(\frac{-{y_0}^2}{4Dt_2}\right) \tag{9}$$

and

$$D = \frac{z^2}{8}\,\frac{\left(\frac{1}{t_1} - \frac{1}{t_2}\right)}{\ln\left(\frac{t_2}{t_1}\right)} \tag{10}$$

where z (m) is the distance between the extremes in the concentration difference profile.

Finding the points y_0 and $-y_0$ might be a problem with an ordinary interferogram consisting of a set of horizontal interference fringes. By introducing a set of vertical interference fringes into the interferogram, one can obtain an interferogram with two distinct turns of the fringes where the points of these turns represent y_0 and $-y_0$ (Szydlowska and Janowska, 1982). The vertical fringes can, for example, be introduced by tilting a glass plate vertically in the path of the object beam.

Each evaluation of the mass diffusivity is based on two simple readings: a distance, z, and the time period t. The accuracy in measuring the distance z is, however, crucial, since a small error in z can cause larger errors in mass diffusivity. On the other hand, the fact that the mass diffusivity is calculated by measuring only one distance in the interferogram and recording one time makes this holographic interferometry method very simple and quite fast.

Experimental Procedure

The diffusion cell was made of makrolon and measured 5 cm in height, 1 cm in width, and 0.5 cm in depth. It was carefully designed on the basis of computer simulations of the diffusion process in order to obtain an appropriate number of interference fringes. It consisted of an inner chamber for the diffusing solutions, surrounded by an outer chamber for temperature-controlling purposes. It was thermostated to (25 ± 0.5) °C using a water bath where the temperature was controlled by a thermocouple. This temperature uncertainty is equivalent to an experimental uncertainty of approximately 1%. The cell was covered by a lid when it was full to minimize evaporation or absorption of moisture into the upper solution layer.

Each experiment was started by filling half of the cell with the light solution, and the heavy solution was then carefully pumped in from below through two narrow channels having a diameter of 2 mm each. A slow moving piston was used, giving a flow rate of 10 cm^3 h^{-1}. This process ensures that a minimum of disturbing mixing occurs.

The interferograms were photographed through a microscope. The film used was Kodak T-max 400 ASA, and the holographic plate was AGFA 10E-75. Further magnification was accomplished during the analysis of the photographs, resulting in a 10 times magnification. A sliding calliper was used to measure the distance between the extremes in the concentration difference profile. This measurement of distance represents the major source of error, since an error in this distance would be squared on computing the value of the mass diffusivity.

Three or four measurements were made at each concentration, with a concentration difference corresponding to a density difference of 1−2% between the solutions. This difference in density was found to be enough to fill the cell with both solutions without mixing. After the experiment was started, the diffusion process was allowed to proceed for about 10 min before the hologram was exposed, and the interferograms were photographed at least four times during each experiment between 30 and 200 min after

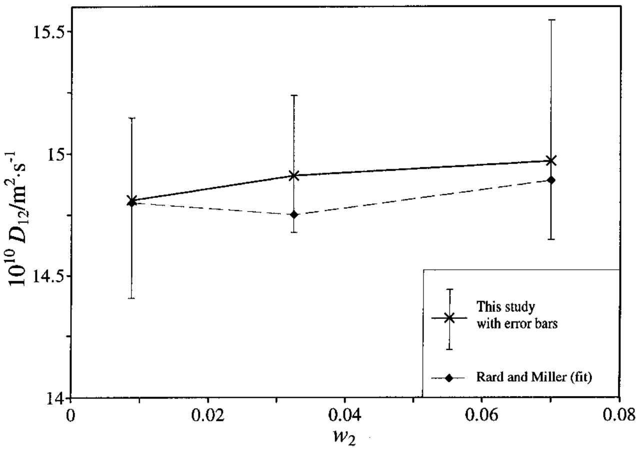

Figure 2. Mutual diffusion coefficients for the system water (1) + NaCl (2) at 25 °C.

Table 1. Mutual Diffusion Coefficients for the System Water (1) + NaCl (2) at 25 °C

mass fraction of NaCl		$10^{10}D_{12}$/m^2 s^{-1}			$10^{10}\sigma$/	no. of data
w_2	Δw_2	min	max	mean	m^2 s^{-1}	points
0.00874	0.0175	14.41	15.15	14.81	0.38	3
0.0324	0.0198	14.68	15.24	14.91	0.24	4
0.0699	0.0200	14.65	15.55	14.97	0.29	3

starting the experiment. The calculations are based on the assumption that there is a linear dependence between the refractive index and the concentration within the concentration interval used. This assumption was checked and found to be correct.

In order to check the accuracy of the method, experimental measurements were made for the water + NaCl system at three different concentrations in the range between 0.008 74 and 0.0699 mass fraction. The solutions were prepared by weight from pro analysi NaCl and distilled water.

Experimental measurements were made for the water ethylene glycol system at six different concentrations ranging between 0.0250 and 0.950 mass fraction ethylene glycol, while five different concentrations ranging between 0.0200 and 0.800 mass fraction glycerol were used for the water + glycerol system. The solutions were prepared by weight from pro analysi chemicals and distilled water.

The accuracy of the concentration is directly related to the scale accuracy and the purity of the chemicals. The scale unit used has an absolute error of 0.005 g, and pro analysi chemicals have a minimum concentration of 0.995 mass fraction. Samples of 100 g were prepared for the measurements. Combining these two sources of error results in an experimental uncertainty of 0.5%.

Results

The results for the water + NaCl system are displayed in Table 1 and Figure 2. Each value reported in Table 1 is the average of three or four measurements. The standard deviations at each concentration varied from 0.24 to 0.38 × 10^{-10} m^2 s^{-1}. In Figure 2 data from this study are compared to the smoothed graph presented by Rard and Miller (1979), which comprises diffusivity data from several authors obtained using different measurement techniques. The measured data differ between 0.1 and 1.1% from the smoothed graph. The difference was found to be within the variance of this measuring method.

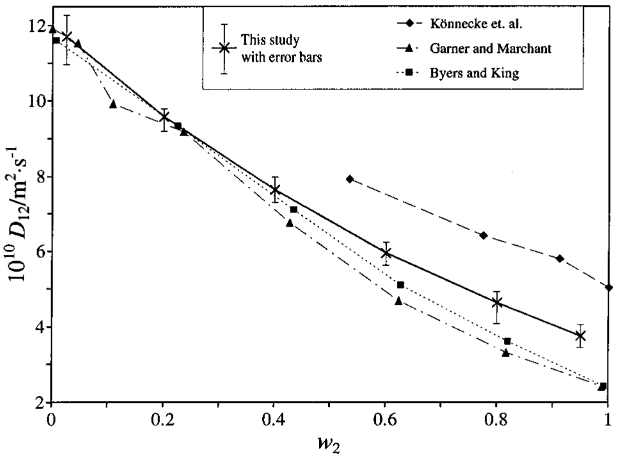

Figure 3. Mutual diffusion coefficients for the system water (1) + ethylene glycol (2) at 25 °C.

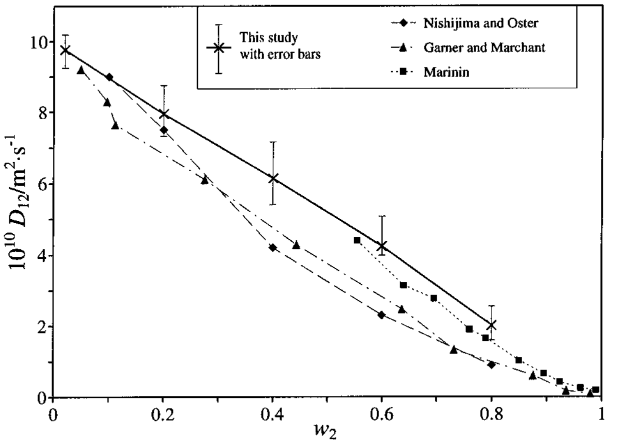

Figure 4. Mutual diffusion coefficients for the system water (1) + glycerol (2) at 25 °C.

Table 2. Mutual Diffusion Coefficients for the System Water (1) + Ethylene Glycol (2) at 25 °C

mass fraction of ethylene glycol		$10^{10}D_{12}$/m^2 s^{-1}			$10^{10}\sigma$/	no. of data
w_2	Δw_2	min	max	mean	m^2 s^{-1}	points
0.0250	0.0500	11.02	12.30	11.70	0.32	3
0.200	0.0800	9.22	9.82	9.58	0.16	3
0.400	0.0800	7.33	8.00	7.64	0.19	2
0.600	0.0800	5.65	6.26	5.95	0.14	3
0.800	0.0800	4.11	4.94	4.63	0.19	3
0.950	0.100	3.47	4.08	3.75	0.15	3

Table 3. Mutual Diffusion Coefficients for the System Water (1) + Glycerol (2) at 25 °C

mass fraction of glycerol		$10^{10}D_{12}$/m^2 s^{-1}			$10^{10}\sigma$/	no. of data
w_2	Δw_2	min	max	mean	m^2 s^{-1}	points
0.0200	0.0400	9.28	10.23	9.77	0.30	4
0.200	0.0400	7.36	8.80	7.95	0.44	3
0.400	0.0400	5.43	7.19	6.15	0.41	4
0.600	0.0400	4.01	5.10	4.24	0.29	3
0.800	0.0400	1.63	2.59	2.02	0.23	4

The results for the water + ethylene glycol system are given in Table 2 and Figure 3. The corresponding results for the water + glycerol system are depicted in Table 3 and Figure 4. Each value reported for the water + ethylene glycol system in Table 2 is the average of two or three measurements. The standard deviation σ at each concentration varied from 0.14 to 0.32 × 10^{-10} m^2 s^{-1}. Similarly, each value reported for the water + glycerol system in Table 3 is the average of three or four measurements. The standard deviation at each concentration varied from 0.23 to 0.44 × 10^{-10} m^2 s^{-1}. The deviations in the experimental values for the water + glycerol system are higher than the deviations for the water + ethylene glycol system, due to the fact that the concentration difference between the two solutions in the diffusion cell is higher for the water + ethylene glycol experiments, which gives a more stable measurement.

Figures 3 and 4 also compare the experimental values measured in this study with some values found in the literature (Nishijima and Oster, 1960; Garner and Marchant, 1961; Marinin, 1955; Könnecke et al., 1958; Byers and King, 1966). Nishijima and Oster (1960) used an interferometric microdiffusion method and reported nine data points for the water + glycerol system within the concentration range 0.10−0.90 mass fraction at 25 °C. Garner and Marchant (1961) used a Jamin-type interferometer and reported nine data points for the water + glycerol system and eight data points for the water + ethylene glycol system covering the entire concentration interval at 20 °C. Marinin (1955) used a polarization-interferometric method and reported ten data points for the water + glycerol system within the concentration range 0.55−0.99 mass fraction at 21 °C. Könnecke et al. (1958) used a Lamm diffusion-pipe, an interferometric method, and reported four data points for the water + ethylene glycol system within the concentration range 0.53−1.00 mass fraction at (20, 30, and 40) °C. Byers and King (1966) used a diaphragm cell and presented six data points for the water ethylene glycol system covering the entire concentration range at (25, 40, 55, and 70) °C. It should be mentioned that very few measurements covering a wide concentration range have ever been made for both systems. Furthermore, none of the reported literature data were obtained using the same measurement method.

It should be pointed out that literature data reported within the temperature interval 20−25 °C were selected for comparison with our experimental data to minimize the error introduced when viscosity data have to be used at other temperatures. Thus, the experimental data obtained at 20 °C by Garner and Marchant (1961) and Könnecke et al. (1958) and those measured at 21 °C by Marinin (1955) were recalculated, taking the effect of the viscosity, μ, (Sheeley, 1932), and absolute temperature, T, into account according to the Stokes−Einstein equation

$$\frac{D_1\mu_1}{T_1} = \frac{D_2\mu_2}{T_2} \tag{11}$$

The results for the system water + ethylene glycol are shown in Figure 3. There is a good agreement between our experimental values and those found in the literature within the concentration interval 0−0.40 mass fraction. Above 0.40 mass fraction our experimental data are significantly higher than those obtained by both Garner and Marchant (1961) and Byers and King (1966) but not as high as those reported by Könnecke (1958).

Figure 4 displays the results obtained for the system water + glycerol. There is good agreement between our experimental values and those reported by both Nishijima and Oster (1960) and Marinin (1955) throughout the concentration interval covered in this study. On the other hand, our experimental data are significantly higher than those reported by Garner and Marchant (1961).

The results given in Tables 1−3 reveal that the standard deviation of all experimental data for the three systems investigated has the same order of magnitude. It can be concluded that the accuracy of this holographic interferometric technique can be increased if more attention is given to improve the method with which the distance between the extremes in the concentration difference profile is measured.

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