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Measurements of Ternary Diffusion Coefficients of Aqueous Blended Alkanolamine systems: Diethanolamine + *N*-methyldiethanolamine + Water

Po-Hsun Lin,[a] Chih-Chiang Ko,[a] Meng-Hui Li[a,b]

[a] *R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan 32023, Republic of China*
[b]*Corresponding author.*

Abstract

Ternary diffusion coefficients of aqueous blended alkanolamine systems diethanolamine (DEA) + *N*-methyldiethanolamine (MDEA) + water using the Taylor dispersion technique have been measured for temperatures 30, 40 and 50 ^{o}C. The systems studied were aqueous solutions containing the total amine concentrations of 2, 3, and 4 kmol·m^{-3} with three (or four) molar amine ratios. The corresponding mutual diffusion coefficients of aqueous DEA and aqueous MDEA solutions were also measured. Working equations for the ternary diffusion coefficients presented by Leaist et al. (1998) was adopted to obtain the ternary diffusion coefficients. The main diffusion coefficients (D_{11} and D_{22}) and the cross coefficients (D_{12} and D_{21}) are reported as function of temperature and concentration of alkanolamines. The dependence of D_{ij} on temperature, concentration, and viscosity of solutions were discussed. The predicted values from the Onsager phenomenological coefficients, the activity, and partial molar volume of component are also performed and compared with the measured values.

Keywords: ternary diffusion coefficient, aqueous blended amines solutions, carbon dioxide capture, Taylor dispersion technique

1. Introduction

A wide variety of alkanolamines, such as monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), di-isopropanolamine (DIPA), *N*-methyldiethanolamine (MDEA), triethanolamine (TEA), 2-amino-2-methyl-l-propanol (AMP), and 2-piperidineethanol (2-PE), can be used as absorbents for the removal of CO_2 and H_2S from gas streams in the natural gas, petroleum chemical plants, and ammonia industries (Kohl and Nielsen, 1997).

Diffusion coefficients, viscosity, and density are thermophysical properties and are needed in the evaluation of mass transport properties. The rate of molecular diffusion in liquid is normally the rate-determining factor in unit operations, such as the absorption of acid gases in alkanolamine solutions and heterogeneous gas-liquid chemical reactions. Diffusion coefficients are also useful for investigating the structure of liquids and for developing theories of liquid states (Tyrrell and Harris, 1984). The mutual diffusion coefficients in aqueous alkanolamine solutions have been reported in the literature such as MEA, MIPA (monoisopropanolamine), DEA, DIPA, DGA, EDA (ethylenediamine) and TEA (Hikita et al., 1980; Hikita et al., 1981); MEA, DEA, MDEA, and DIPA (Snijder et al., 1993); MDEA (Rowley et al., 1997); TEA (Leaist et al., 1998); DGA, TEA, AMP, and 2-PE (Chang et al., 2005); DMEA (*N*,*N*-dimethylethanolamine), DEEA (*N*,*N*-diethylethanolamine), MIPA (monoisopropanolamine), PZ (piperazine) and sulfolane (Kao and Li, 2006).

The Taylor dispersion technique had been used frequently for measuring binary diffusion coefficients of various solutions (Taylor, 1953; Alizadeh et al., 1980; Baldauf and Knapp, 1983; Leaist et al., 1998). In the Taylor experiment a narrow band of solution is injected into a laminar carrier stream of different composition which flows in a long capillary tube. The injected solutes spread out as they flow along the tube. A differential refractometer monitors the broadened distribution of dispersed solutes as they flow out of the tube. The Taylor dispersion technique for measuring binary diffusion was extended to three- and four-component systems (Deng and Leaist, 1991). Ternary diffusion coefficients in liquids reported in the literature were catalogued into four classes of systems, electrolytes (e.g., LiCl-NaCl-water), electrolyte-non-electrolyte mixtures (e.g., KCl-glycine-water), non-electrolytes in water (glycine – sucrose - water), and organic liquids (e.g., acetone-benzene-cyclohexane) (Cussler, 1976).

Employing the advantages of each amine, the aqueous blended amines have been proposed to be used for acid gases removal in the absorption processes (Chakravarty et al., 1985). Blended amines such as MEA + MDEA + H_2O, MEA + AMP+ H_2O have been suggested for acid gases removal (Kohl and Nielsen, 1997). Some thermophysical properties such as density, viscosity, Henry's constant, diffusivity of a gas in liquid, and reaction kinetics data for the CO_2 absorption into aqueous blended alkanolamine have been reported in the literature. The ternary mutual diffusivity coefficients of MEA + MDEA + H_2O were reported using the Taylor dispersion technique (Ko et al., 2006). However, the ternary mutual diffusivity coefficient of DEA + MDEA + H_2O has not yet been reported in the literature. Thus, it is the objective of this research to measure the ternary mutual diffusivity coefficients in DEA + MDEA + H_2O systems.

2. Experimental

Chemicals. DEA is Riedel-de Haën reagent grade with purity of ≥ 99 mol % and MDEA is Riedel-de Haën reagent grade with purity ≥ 98.5 mol %. A water purification system (the Barnstead EASYpure LF) is used to provide Type I reagent-grade water with a resistivity of up to 18.3 MΩ-cm and with a total organic carbon content of less than 15 ppb. The prepared aqueous alkanolamines solutions have been degassed by using ultrasonic cleaner (Branson, Model 3510).

The ternary mutual diffusion coefficients of DEA + MDEA + H_2O were measured in a Taylor dispersion apparatus. The experimental setup is the same as described in (Chang et al., 2005). For ternary mutual diffusion measurements, the concentration of the injected solution is different from those of the binary system and will be described briefly.

A metering pump was used to provide constant laminar flow at a rate of 0.08 – 0.12 ml/min. A pulse damper was installed downstream of the pump to reduce any pressure fluctuation from the pump. The carrier fluid flows through a six-port injection value (Rheodyne, Model 7725i) at the upstream of the diffusion coil and then flows into a 316-stainless steel diffusion tube which was maintained at a constant temperature water bath with a thermometer (Hart Scientific model 1502) with an accuracy of ± 0.01 K monitoring the temperature of the bath. The length of the tube is 50.218 m with an internal radius of 0.268 mm and is horizontally tempered in a 20 cm coil radius. By switching a 6-way injection valve, a δ function pulse of 20 μL of concentration profile is introduced into the carrier fluid. The injected pulse of the solute usually consists of a solution with small concentration ($\Delta c_1 + \Delta c_2$) greater than that of the carrier fluid. Dispersion of the pulse was established through the parabolic velocity profile of the laminar flow. The initial concentration differences (Δc_1, Δc_2) were typically 0.05 mol dm^{-3}. A few runs were made with concentration differences one-half as large, as suggested by Deng and Leaist (Deng and Leaist, 1991). Since the results did not differ significantly, the measured diffusion coefficients can be interpreted as differential values at the composition of the carrier stream (c_1, c_2). To prevent the secondary flows in a helical coil, the flow rate was controlled at 0.08-0.12 ml/min to assure the validity of the condition $De^2Sc \leq 20$, as suggested by Alizadeh et al. (1980). The solvent reservoir and the capillary are temperature controlled by a thermostat. Between the six-way valve and the refractive index detector, the tube outsides the water bath was kept as short as possible and wrapped up well with heat-insulated materials. At the end of capillary, the concentration gradient was determined by a differential refractometer (Precision Instruments, IOTA 2) with a cell volume of 8 μL. The instrument contains two cells: the sample cell and the reference cell. The instrument detects the difference in concentration between the sample and reference cell. The analog output was transferred to a computer system by an integrating converter INT5 (DataApex, Chromatography Station, CSW 1.7). In the data analysis system, the detector signal is collected and plotted as function of time. A least squared procedure (Deng and Leaist, 1991) is applied to determine the ternary mutual diffusion coefficients. The working equation and the calculation procedure are described in the next section. The standard deviation of the D_{ik} values, $\pm 0.02 \times 10^{-9}$ $m^2 s^{-1}$, was estimated by repeating 3-5 sets of replicate runs.

3. Working equations for determination of ternary mutual diffusion coefficients

Deng and Leaist (1991) developed a simple least-squares procedure to calculate the ternary diffusion coefficients from the refractive index profiles. The working equations, representing the detector signal, to calculate ternary diffusion coefficients are as follows,

$$v(t) = v_{\max}\left(\frac{t_R}{t}\right)^{1/2}\left[W_1 \exp\left(-\frac{12D_1(t-t_R)^2}{r^2 t}\right) + (1-W_1)\exp\left(-\frac{12D_2(t-t_R)^2}{r^2 t}\right)\right] + B_0 + B_1 t \tag{1}$$

where $v_{\max}$ is the height of the eluted solute peak relative to the baseline, t_R the mean retention time, r the inner radius, B_0 the baseline detector voltage, $B_1 t$ is representing a small linear drifts in the baseline signal. D_1 and D_2 denote two overlapping Gaussians, centered on time t_R with variances $r^2L/24D_1U$ and $r^2L/24D_2U$ where L is the length of the tube, U the mean speed of stream.

In eq 1, W_1 and (1 - W_1) give the normalized weights of the exponential terms and are expressed in terms of a, b, D_1, and D_2 as follows,

$$W_1 = \frac{(a+b\alpha_1)D_1^{1/2}}{\left[(a+b\alpha_1)D_1^{1/2} + (1-a-b\alpha_1)D_2^{1/2}\right]} \tag{2}$$

The parameters a and b are constants for a given system and carrier stream composition (Deng and Leaist, 1991). In eq 2, α_1 is the fraction of the initial refractive index contributed by solute 1:

$$\alpha_1 = R_1\Delta c_1 / (R_1\Delta c_1 + R_2\Delta c_2) \tag{3}$$

where Δc_1 and Δc_2 are injected solution concentration ($\bar{c}_1$+Δc_1, $\bar{c}_2$+Δc_2) difference to the concentration ($\bar{c}_1$, $\bar{c}_2$) of the carrier stream. In eq 3, R_1 and R_2 are the molar refractivities of the solutes,

$$R_i = \frac{dn}{dc_i} \tag{4}$$

where n is the refractive index profile. The value of R_i is evaluated at the carrier stream composition, $\bar{c}_i$.

For each solution stream with solutes concentration ($\bar{c}_1$, $\bar{c}_2$), 6 to 10 injected solutions with various values of α_1 were performed. As mentioned by Deng and Leaist (1991), the values of α_1 are widely separated, such as 0.0 and 1.0 rather than 0.4 and 0.6. The values of $v_{\max}$, B_0, B_1, a, b, D_1, and D_2 are determined by a least-square method.

After the values of a, b, D_1, and D_2 determined from the refractive index profile for solution stream with solutes concentration ($\bar{c}_1$, $\bar{c}_2$), the ternary mutual diffusion coefficients can be calculated from the following equations (Deng and Leaist, 1991):

$$D_{11} = D_1 + \frac{a(1-a-b)}{b}(D_1 - D_2) \tag{5}$$

$$D_{12} = \frac{R_2}{R_1}\frac{a}{b}(1-a)(D_1 - D_2) \tag{6}$$

$$D_{21} = \frac{R_1}{R_2}\frac{(a+b)(1-a-b)}{b}(D_2 - D_1) \tag{7}$$

$$D_{22} = D_2 + \frac{a(1-a-b)}{b}(D_2 - D_1) \tag{8}$$

where D_{ii} is the main diffusion coefficient and D_{ij} the cross diffusion coefficient.

4. Results and Discussion

To test the accuracy of the apparatus, the mutual diffusion coefficients of DEA (1) + water were measured at 2.0 $\text{kmol}\cdot\text{m}^{-3}$ and atmospheric pressure. The measured mutual diffusion coefficients of DEA (1) + water were 0.600 ± 0.002, 0.762 ± 0.005, 0.969 ± 0.005, 1.191 ± 0.005, and 1.476 ± 0.006 × 10^{-9} $\text{m}^2\cdot\text{s}^{-1}$ for 30, 40, 50, 60, and 70 °C, respectively. The standard deviation was obtained from 4 to 6 replicated runs. A comparison between the measured mutual diffusion coefficients and the literature values (Hikita et al., 1980; Snijder et al., 1993) for this system is shown in Figure 1. In Figure 1, the concentration of the data of Hikita et al. was at 2.2 $\text{kmol}\cdot\text{m}^{-3}$ while the data of Snijder et al. was at 2.0 $\text{kmol}\cdot\text{m}^{-3}$. The solid line in Figure 1 was calculated using the correlation presented by Snijder et al. (1993). As shown in Figure 1, the obtained mutual diffusion coefficients of DEA (1) + water are in good agreement with literature values.

The ternary mutual diffusion coefficients of $MgCl_2$ (1) + $MgSO_4$ (2) + H_2O for a total salt concentration of 0.4 $\text{kmol}\cdot\text{m}^{-3}$ at 25 °C were also measured. The results are presented in Table 1. A comparison of the results is shown in Figure 2. The four mutual diffusion coefficients, D_{11}, D_{22}, D_{12}, D_{21} are generally in good agreement with the data of Deng and Leaist (1991).

The *x*-axis coordinate in Figure 2 is relative molar ratio of amines and is defined as

$$f_1 = \frac{\bar{c}_1}{(\bar{c}_1 + \bar{c}_2)} \tag{9}$$

where $\bar{c}_1$ and $\bar{c}_2$ are concentrations of the carrier stream.

The ternary mutual diffusion coefficients of DEA (1) + MDEA (2) + H_2O for a total amine concentration of 2.5 $\text{kmol}\cdot\text{m}^{-3}$ for temperatures 30, 35, 40 °C are presented in Table 2. The corresponding mutual diffusion coefficients in binary systems were also performed and are also presented in Table 2. The plot of ternary mutual diffusion coefficients vs. the relative concentration of solutes at 40 °C is shown in Figure 3. In Figure 3, the binary mutual diffusion coefficients calculated from the equation of Snijder et al. (1993) are also shown for the purpose of comparison.

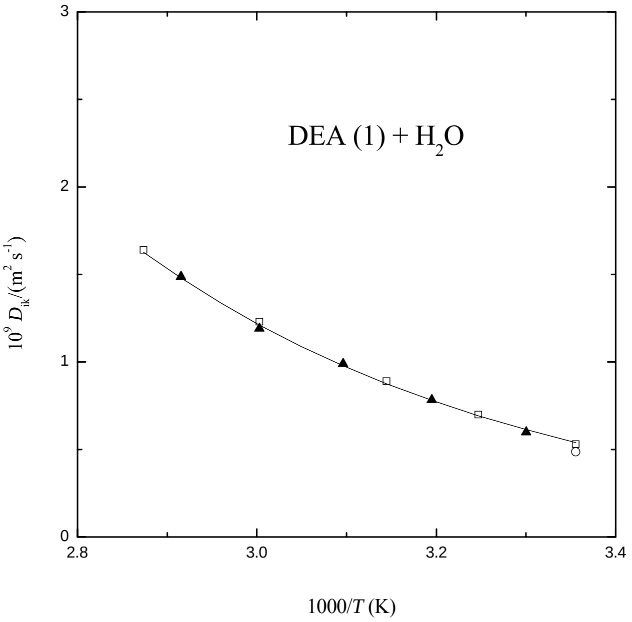

Figure 1: Mutual diffusion coefficients of aqueous DEA (2.0 kmol·m^{-3}) solution. □, data of Snijder et al. (1993); data of Hikita et al. (1980) at 2.2 kmol·m^{-3}; ▲, this study; solid line, calculated using equation of Snijder et al. (1993)

Table 1: Ternary diffusion coefficients of $MgCl_2$ (1) + $MgSO_4$ (2) + H_2O for a total salt concentration of 0.4 kmol·m^{-3} at 25 °C

Conc./(kmol·m^{-3})		$10^9 D_{ij}/(m^2 \cdot s^{-1})$				
c_1	c_2	D_{11}	D_{12}	D_{21}	D_{22}	R_2/R_1
0	0.4				0.468	
					0.473*	
0.1	0.3	1.207	-0.063	-0.390	0.522	0.990
		1.390*	-0.000*	-0.460*	0.540*	0.980*
0.2	0.2	1.084	-0.031	-0.221	0.539	0.960
		1.250*	-0.030*	-0.240*	0.600*	0.980*
0.3	0.1	1.028	0.051	-0.101	0.593	1.150
		1.140*	-0.080*	-0.070*	0.650*	0.980*
0.4	0	0.807				
		0.831*				

* Data of Deng and Leaist (1991)

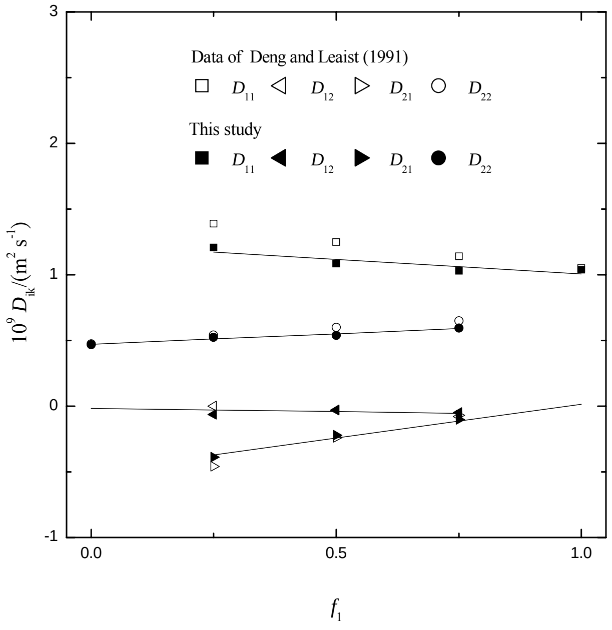

Figure 2: Ternary mutual diffusion coefficients of $MgCl_2$ (1) + MgSO4 (2) + H_2O at a total salt concentration of 0.4 kmol·m^{-3} and 25 ^oC

Table 2: Ternary diffusion coefficient of DEA (1) + MDEA (2) + H_2O for a total amine concentration of 2.5 kmol·m^{-3}

$t/^oC$	Conc./(kmol·m^{-3})		$10^9 D_{ij}/(m^2·s^{-1})$			
	c_1	c_2	D_{11}	D_{12}	D_{21}	D_{22}
30	0	2.5				0.469
	0.5	2.0	0.459	-0.068	0.004	0.498
	1.0	1.5	0.466	-0.073	0.004	0.502
	1.5	1.0	0.467	-0.091	0.008	0.523
	2.0	0.5	0.475	-0.104	0.012	0.548
	2.5	0	0.548			
40	0	2.5				0.586
	0.5	2.0	0.554	-0.101	0.008	0.612
	1.0	1.5	0.606	-0.131	0.021	0.712
	1.5	1.0	0.606	-0.129	0.022	0.714
	2.0	0.5	0.642	-0.137	0.011	0.722
	2.5	0	1.227			
50	0	2.5				0.739
	0.5	2.0	0.768	-0.101	0.002	0.798
	1.0	1.5	0.796	-0.119	0.007	0.854
	1.5	1.0	0.758	-0.125	-0.017	0.854
	2.0	0.5	0.779	-0.136	0.017	0.877
	2.5	0	0.878			

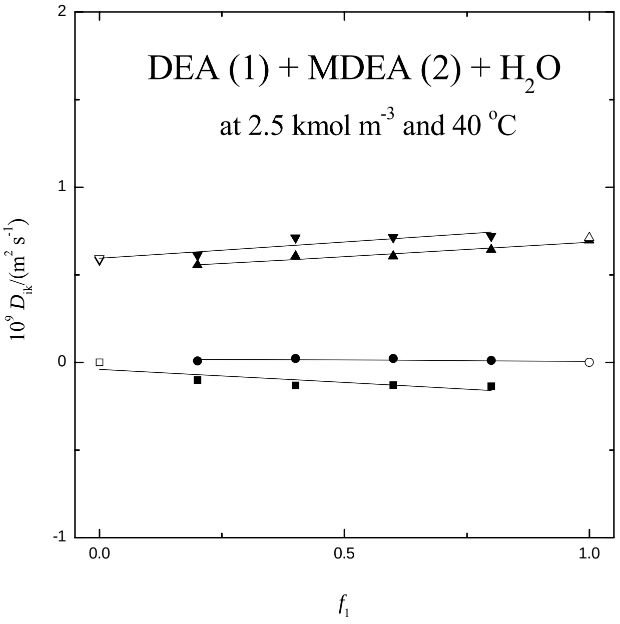

Figure 3: Ternary diffusion coefficients of DEA (1) + MDEA (2) + H_2O solutions at a total concentration of 2.5 kmol·m^{-3} and 40 °C. ▲, D_{11}; ■, D_{12}; ●, D_{21}; ▼, D_{22}; Solid lines: smoothed values. Binary values of D_{11} and D_{22}: △, ▽, calculated from eq of Snijder et al. (1993)

At the limiting condition of $f_1 \to 1$ (i.e., $c_2 \to 0$), the main mutual diffusion coefficient D_{11} approaches the binary value for DEA + H_2O, as shown in Figure 3. In this limit, D_{21}, the diffusion of MDEA due to the concentration gradient of DEA, vanishes because the gradient in DEA cannot produce a coupled flow of MDEA if the solution is free of MDEA, as shown in Figure 3. Similarly, as $f_1 \to 0$ (i.e., $c_1 \to 0$), the D_{22} is approaching the binary diffusion value in MDEA + H_2O; D_{12} vanishes due to free of DEA in solution, as shown in Figure 3.

The ratio of D_{12} to D_{11} varies from -0.132 to -0.219 while the ratio of D_{21} to D_{22} about 0.003 to 0.022. Thus, for DEA the cross diffusion effect due to the concentration gradient of MDEA is larger than that for MDEA due to the concentration gradient of DEA.

In Figure 4, the main diffusion coefficients D_{11} of DEA (1) + MDEA (2) + H_2O solutions as function of temperatures at a total of 2.5 kmol·m^{-3} are shown. As shown in Figure 4, D_{11} increases as the temperature increase at the same molar ratio; D_{11} increases as the molar ratio increases at the same temperature. The main diffusion coefficients D_{22} of DEA (1) + MDEA (2) + H_2O solutions as function of temperatures at a total of 2.5 kmol·m^{-3} are shown in Figure 5. Similarly, D_{22} increases as the temperature increase at the same molar ratio; D_{22} increases as the molar ratio increases at the same temperature.

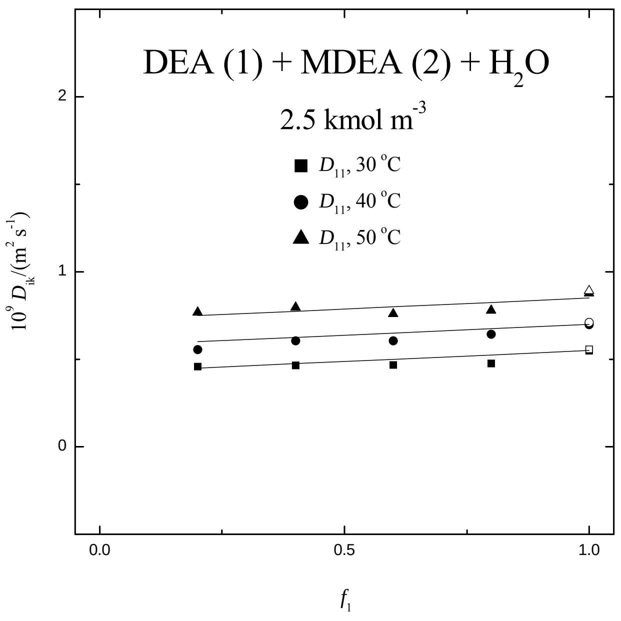

Figure 4: Comparison of main diffusion coefficients (D_{11}) of aqueous DEA + MDEA solutions at different temperatures. △, ○, □: calculated using eq of Snijder et al. (1993)

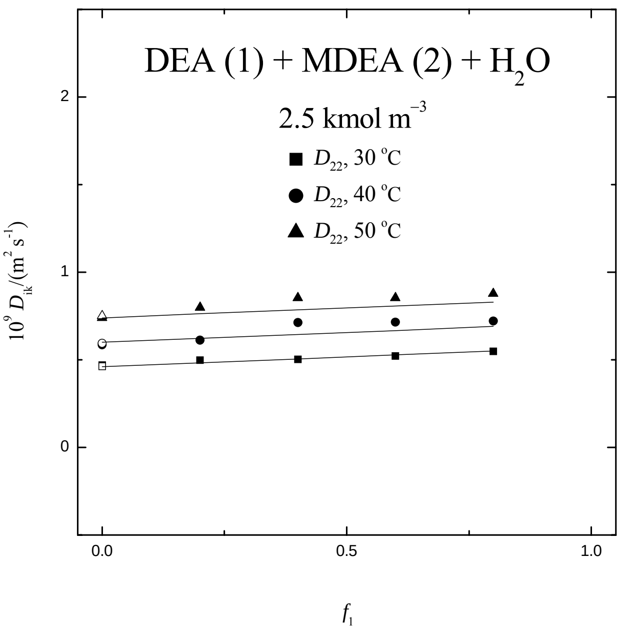

Figure 5: Comparison of main diffusion coefficients (D_{22}) of aqueous DEA + MDEA solutions at different temperatures. △, ○, □: calculated using eq of Snijder et al. (1993)

The ternary mutual diffusion coefficients of DEA (1) + MDEA (2) + H_2O for temperatures 30, 35, 40 °C are presented in Tables 3, 4, and 5, for a total amine concentrations of 3.0, 3.5, and 4.0 kmol·m^{-3}, respectively. The dependence of the ternary mutual coefficients on the temperature and molar ratio of amine is similar as in total amine concentration of 2.5 kmol·m^{-3} solution.

Table 3: Ternary diffusion coefficient of DEA (1) + MDEA (2) + H_2O for a total amine concentration of 3.0 kmol·m^{-3}

t/°C	Conc./(kmol·m^{-3})		10^9 D_{ij}/(m^2·s^{-1})			
	c_1	c_2	D_{11}	D_{12}	D_{21}	D_{22}
30	0	3.0				0.401
	0.5	2.5	0.313	-0.024	0.084	0.403
	1.0	2.0	0.378	-0.138	0.029	0.505
	2.0	1.0	0.404	-0.171	0.029	0.545
	2.5	0.5	0.406	-0.179	0.027	0.545
	3.0	0	0.496			
40	0	3.0				0.586
	0.5	2.5	0.506	-0.109	0.042	0.641
	1.0	2.0	0.507	-0.140	0.031	0.639
	2.0	1.0	0.532	-0.155	0.023	0.651
	2.5	0.5	0.551	-0.170	0.022	0.673
	3.0	0	0.647			
50	0	3.0				0.651
	0.5	2.5	0.680	-0.078	0.000	0.683
	1.0	2.0	0.670	-0.146	0.012	0.753
	2.0	1.0	0.677	-0.181	-0.028	0.820
	2.5	0.5	0.696	-0.172	0.016	0.802
	3.0	0	0.795			

Table 4: Ternary diffusion coefficient of DEA (1) + MDEA (2) + H_2O for a total amine concentration of 3.5 kmol·m^{-3}

t/°C	Conc./(kmol·m^{-3})		10^9 D_{ij}/(m^2·s^{-1})			
	c_1	c_2	D_{11}	D_{12}	D_{21}	D_{22}
30	0	3.5				0.369
	1.0	2.5	0.335	-0.097	0.026	0.436
	1.5	2.0	0.354	-0.110	0.024	0.457
	2.0	1.5	0.356	-0.114	0.019	0.450
	2.5	1.0	0.408	-0.123	0.005	0.460
	3.0	0	0.465			
40	0	3.5				0.471
	1.0	2.5	0.456	-0.066	0.006	0.496
	1.5	2.0	0.461	-0.058	0.007	0.504
	2.0	1.5	0.465	-0.162	0.033	0.610
	2.5	1.0	0.479	-0.171	0.029	0.620
	3.0	0	0.591			
50	0	3.5				0.651
	1.0	2.5	0.621	-0.077	0.004	0.658
	1.5	2.0	0.628	-0.099	0.009	0.689
	2.0	1.5	0.643	-0.151	-0.020	0.755
	2.5	1.0	0.666	-0.136	0.015	0.757
	3.0	0	0.738			

Table 5: Ternary diffusion coefficient of DEA (1) + MDEA (2) + H_2O for a total amine concentration of 4.0 kmol·m^{-3}

t/°C	Conc./(kmol·m^{-3})		$10^9\ D_{ij}$/(m^2·s^{-1})			
	c_1	c_2	D_{11}	D_{12}	D_{21}	D_{22}
30	0	4.0				0.324
	1.0	3.0	0.213	-0.095	0.032	0.214
	1.5	2.5	0.211	-0.137	0.046	0.371
	2.5	1.5	0.233	-0.142	0.043	0.389
	3.0	1.0	0.266	-0.140	0.032	0.400
	4.0	0	0.421			
40	0	4.0				0.417
	1.0	3.0	0.272	-0.041	0.129	0.417
	1.5	2.5	0.289	-0.050	0.116	0.441
	2.5	1.5	0.342	-0.153	0.023	0.462
	3.0	1.0	0.361	-0.198	0.036	0.531
	4.0	0	0.591			
50	0	4.0				0.520
	1.0	3.0	0.424	-0.030	0.128	0.549
	1.5	2.5	0.478	-0.145	0.015	0.571
	2.5	1.5	0.495	-0.149	-0.019	0.600
	3.0	1.0	0.531	-0.158	0.016	0.632
	4.0	0	0.669			

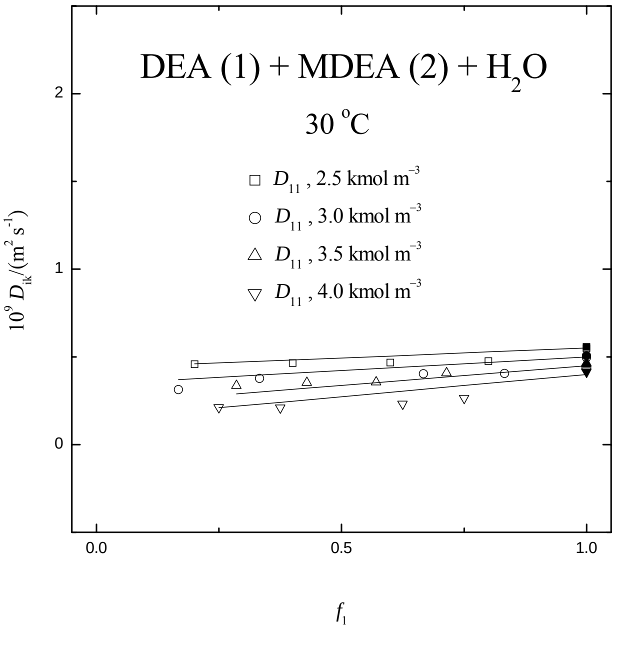

Figure 6: Comparison of main diffusion coefficients (D_{11}) of DEA (1) + MDEA (2) + H_2O solutions at different concentrations. Lines: smoothed; ■, ●, ▲, ▼: calculated using eq of Snijder et al. (1993)

At 30 °C, the plot of D_{11} as function of various total amine concentration is shown in Figure 6. As shown in Figure 6, at the same amine molar ratio D_{11} decreases as the total amine concentration increases which are the same behavior as for the binary mutual diffusion coefficient. The plot of D_{22} as function of various total amine concentration at 30 ^{o}C is shown in Figure 7. As shown in Figure 7, at the same amine molar ratio D_{22} decreases as the total amine concentration increases which are the same behavior as D_{11}.

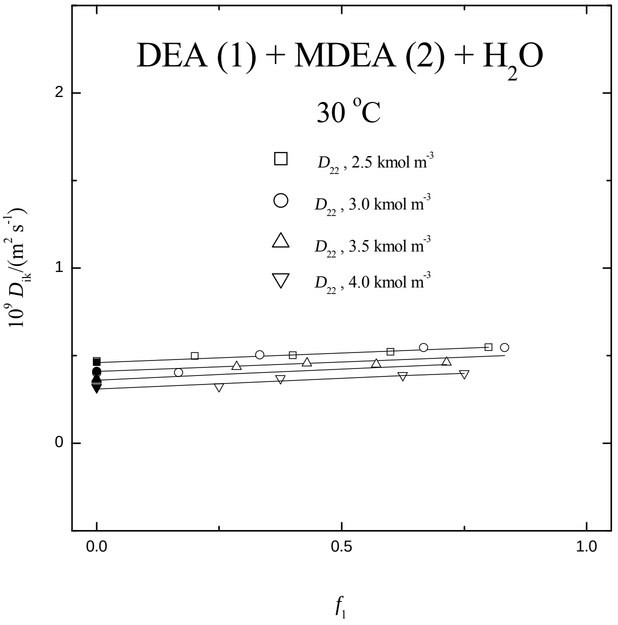

Figure 7: Comparison of main diffusion coefficients (D_{11}) of DEA (1) + MDEA (2) + H_2O solutions at different concentrations. Lines: smoothed; ■, ●, ▲, ▼: calculated using eq of Snijder et al. (1993)

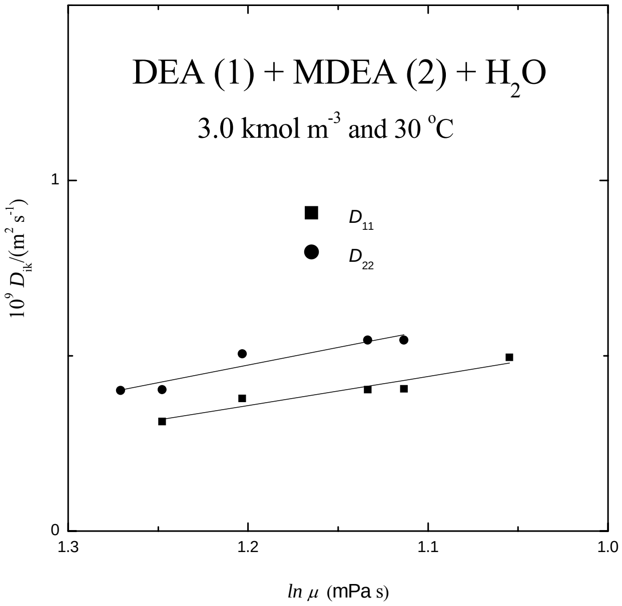

Figure 8: Main diffusion coefficients of aqueous DEA + MDEA solutions as functions of viscosity of solutions

In the stokes-Einstein equation, large spherical molecules diffusing into a dilute solution, the diffusion coefficients may proportional to the reciprocal of the viscosity of solvent. In Figure 8, the main diffusion coefficients, D_{11} and D_{22}, are plotted as function of viscosities of solutions. As shown in Figure 8, both of D_{11} and D_{22} decrease as the viscosity of solution increases.

When ternary diffusion coefficients in liquids are not available, one can make estimates by assuming that the Onsager phenomenological coefficients are a diagonal matrix and the main-term coefficients are related to the binary values (Cussler, 1984). The ternary diffusion coefficients in liquids can be calculated from the binary diffusion coefficients and the activity coefficients as follows,

$$D_{ij} = \sum_{l=1}^{n-1} \left(\frac{D_i c_i}{RT} \right) \left(\delta_{il} + \frac{c_l \bar{V}_i}{c_n \bar{V}_n} \right) \left(\frac{\partial \mu_l}{\partial c_j} \right)_{c_{k \neq j,n}} \tag{10}$$

where D_i is the mutual diffusion coefficient of binary system, $\bar{V}_i$ is the partial molar volume, δ_{il} is Kronecker delta, for $i = l$, $\delta_{il} = 1$, $i \neq l$, $\delta_{il} = 0$. The partial molar volume can be calculated as follows (Leaist and Kanakos, 2000),

$$\bar{V}_i = \frac{M_i - \dfrac{\partial \rho}{\partial c_i}}{\rho - c_1 \dfrac{\partial \rho}{\partial c_1} - c_2 \dfrac{\partial \rho}{\partial c_2}} \tag{11}$$

The densities of DEA (1) + MDEA (2) + H_2O were calculated from the correlation of Hsu and Li (1997). The partial molar volume of water is calculated from the following equation (Leaist and Kanakos, 2000),

$$1000 \text{ cm}^3\text{dm}^{-3} = c_1 \bar{V}_1 + c_2 \bar{V}_2 + c_3 \bar{V}_3 \tag{12}$$

In equation 10, the activity can be calculated from the activity coefficient and the mole fraction of component. The activity coefficients of amines are calculated from the UNIFAC model using the computer program of Sandler (2006). The calculated partial molar volumes and the activities are listed in Table 6.

The predicted results from eqs 10 – 12 for ternary diffusion coefficients for DEA (1) + MDEA (2) + H_2O at a total of 2.5 $\text{kmol} \cdot \text{m}^{-3}$ and at 25 $^{\circ}$C as function of molar ratios of amine are shown in Figure 9. In Figure 9, the dotted lines denote the predicted values. Except for D_{11}, the predicted values for D_{22}, D_{21}, D_{12} are generally follows the trend of the experimental values. The abnormal behavior of predicated D_{11} may due to the activity coefficient prediction from the UNIFAC model. Nevertheless, as pointed out by Cussler (1984) that the predicted values from equation 10 can usually provide initial estimates values. Thus, we would not expect that accurate ternary diffusion coefficients can be obtained from eq 10.

Table 6: Calculations of partial molar volumes and activities at 30°C used in eqs 10 to 12

c_i (kmol·m^{-3})		$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_3$	$\left(\frac{d\ln a_1}{dc_2}\right)_{c_1}$	$\left(\frac{d\ln a_2}{dc_2}\right)_{c_1}$	$\left(\frac{d\ln a_1}{dc_1}\right)_{c_2}$	$\left(\frac{d\ln a_2}{dc_1}\right)_{c_2}$
c_1	c_2	(cm^3·mol^{-1})	(cm^3·mol^{-1})	(cm^3·mol^{-1})				
0.5	2.0	93.927	109.110	18.362	-0.126	0.284	1.926	-0.179
1.0	1.5	93.757	109.045	18.329	-0.137	0.438	0.897	-0.160
1.5	1.0	93.491	109.086	18.301	-0.146	0.761	0.588	-0.127
2.0	0.5	93.240	109.145	18.279	-0.133	1.820	0.378	-0.187
0.5	2.5	93.904	109.184	18.454	-0.095	0.217	1.984	-0.118
1.0	2.0	93.741	109.127	18.419	-0.093	0.316	0.944	-0.117
2.0	1.0	93.313	109.214	18.359	-0.102	0.804	0.430	-0.132
2.5	0.5	93.007	109.126	18.348	-0.113	1.830	0.338	-0.122
1.0	2.5	93.812	109.192	18.521	-0.048	0.266	0.972	-0.089
1.5	2.0	93.634	109.220	18.482	-0.065	0.339	0.634	-0.094
2.0	1.5	93.381	109.276	18.452	-0.056	0.517	0.465	-0.097
2.5	1.0	93.073	109.286	18.437	-0.059	0.851	0.354	-0.114
1.0	3.0	93.785	109.262	18.645	-0.006	0.251	1.006	-0.053
1.5	2.5	93.698	109.277	18.597	-0.013	0.307	0.661	-0.065
2.5	1.5	93.128	109.433	18.540	-0.030	0.546	0.386	-0.097
3.0	1.0	92.839	109.466	18.532	-0.045	0.858	0.324	-0.070

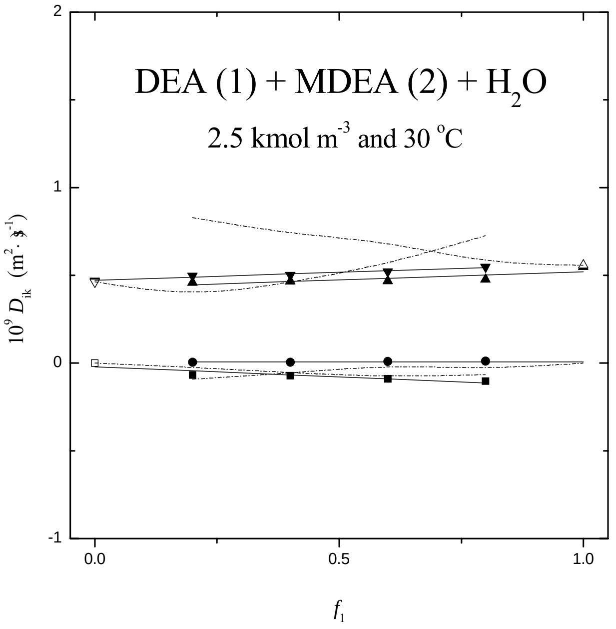

Figure 9: Ternary mutual diffusion coefficients of aqueous DEA (1) + MDEA (2) + H_2O solutions as functions of the relative DEA concentration at a total solute concentration 2.5 kmol·m^{-3} and 30 °C. ▲, D_{11}; ■, D_{12}; ●, D_{21};▼, D_{22}; lines: smoothed; △, ▽: calculated using eq of Snijder et al. (1993). Dashed lines: calculated D_{ik} using eq 10

5. Conclusion

Ternary diffusion coefficients of aqueous blended alkanolamine systems diethanolamine (DEA) + *N*-methyldiethanolamine (MDEA) + water using the Taylor dispersion technique have been measured for temperatures 30, 40 and 50 °C. The systems studied were aqueous solutions containing the total amine concentrations of 2, 3, and 4 kmol·m^{-3} with three (or four) molar amine ratios. For a DEA + MDEA + water system, D_{11} was found to be increase as the temperature and the molar ratio increase. Both of D_{11} and D_{22} decrease as the viscosity of solution increases. The ratio of D_{12} to D_{11} varies from -0.132 to -0.219 while the ratio of D_{21} to D_{22} about 0.003 to 0.022. Thus, for DEA the cross diffusion effect due to the concentration gradient of MDEA is larger than that for MDEA due to the concentration gradient of DEA. The predicted values from the Onsager phenomenological coefficients, the activity, and partial molar volume of component are generally follows the trend of the experimental values. The predicted values can usually provide good initial estimates values.

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