Mutual Diffusion Coefficients of Some Aqueous Alkanolamines Solutions

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The diffusion coefficients of alkanolamines in water at infinite dilution and the mutual diffusion coefficients of aqueous diglycolamine, triethanolamine, 2-amino-2-methyl-l-propanol, and 2-piperidineethanol solutions have been studied by using the Taylor dispersion method. Experimental results for temperatures from (30 to 70) °C and at atmospheric pressure as functions of the concentration of alkanolamines from {0.5 to 3 (or 4)} $\text{kmol}\cdot\text{m}^{-3}$ are reported. The uncertainty of the measurement is estimated to be ±2.0%. The diffusion coefficients of alkanolamines in water at infinite dilution were found to vary systematically with the molar mass of the alkanolamines. The obtained mutual diffusion coefficients were correlated by using both a simple relation and the UNIDIF equation. The measured mutual diffusivity data are also well represented by a free-volume expression. The results of this study can be used to develop the kinetic model for gas absorption using aqueous alkanolamine solutions as absorbents.

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1. Introduction

For the removal of CO_2 and H_2S from gas streams, aqueous alkanolamine solutions are the industrially important solvents used in the natural gas, petroleum chemical plants, and ammonia industries. A wide variety of alkanolamines such as monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), di-2-propanolamine (DIPA), *N*-methyldiethanolamine (MDEA), triethanolamine (TEA), 2-amino-2-methyl-l-propanol (AMP), and 2-piperidineethanol (2-PE) can be used.[1]

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 useful for investigating the structure of liquids and developing theories of the liquid state.[2] By using a diaphragm cell technique, the mutual diffusivities of MEA, MIPA (mono2-propanolamine), DEA, DIPA, DGA, EDA (ethylenediamine), and TEA in aqueous solutions have been reported at 25 °C and atmosphere pressure as a function of concentration.[3,4] Snijder et al.[5] have studied the diffusion coefficients of MEA, DEA, MDEA, and DIPA in aqueous solutions from (25 to 75) °C and concentrations up to 5.0 $\text{kmol}\cdot\text{m}^{-3}$ using the Taylor dispersion technique. Using the Taylor dispersion method, the mutual diffusivities of MDEA in aqueous solutions for temperatures of (298.2 to 373.2) K have been reported as a function of composition and temperatures.[6] The binary diffusion coefficients of aqueous TEA solutions at 25 °C have been reported by Leaist et al.[7] using the Taylor dispersion method. The mutual diffusion coefficients of aqueous AMP and 2-PE have not yet been reported in the literature, and the mutual diffusivity coefficients of aqueous DGA and TEA solutions were reported only at 25 °C in the literature. For measuring the mutual diffusion coefficients of solutions, many different techniques such as the diaphragm cell method,[8] optical method,[9−12] and Taylor dispersion method[13−15] are available. Among the various techniques, the Taylor dispersion method has been shown to be relatively fast, and reasonable results can be obtained.[5,16−18] A rigorous evaluation of design criteria for the Taylor dispersion technique was given by Alizadeh et al.[16] The purpose of this study is to determine experimentally the mutual diffusivity of DGA, TEA, AMP, and 2-PE in aqueous solutions for temperatures of (30 to 70) °C using the Taylor dispersion method. The experimental results will be correlated by a simple equation of Snijder et al.,[5] a local composition-based UNIDIF model,[19] and the equation of rough hard-sphere theory.[2,20,21]

2. Experimental Section

Chemicals. DGA is Tokyo Kasei Kogyo reagent grade with a purity of 98%; 2-PE is Arcos reagent grade with a purity of 99%; TEA is Riedel-de Haën reagent grade with a purity 98.5%; AMP is Fluka reagent grade with a purity of 95%. A water purification system (the Barnstead EASYpure line-fed) is used to provide type I reagent-grade water with extremely low organic content. It uses a three-stage deionization process combined with a 0.2-μm filter to polish distilled water to produce water with a resistivity of up to 18.3 $\text{M}\Omega\cdot\text{cm}$ 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 mutual diffusion coefficients for the binary mixtures were measured in a Taylor dispersion apparatus. The apparatus employed in this study is similar to those shown by previously investigators.[17,18,22] The experimental setup is shown in Figure 1. Specific details regarding this apparatus are described below.

A metering pump (ECOM spol. s r.o., LCP 4020.3) was used to provide constant laminar flow at a rate of (0.08 to 0.12) $\text{mL}\cdot\text{min}^{-1}$. The pump was calibrated with water by using a measuring buret at 25 °C. A pulse damper (Lo-Pulse Damper, P/N no. 992181) was installed downstream from the pump to reduce any pressure fluctuation from the

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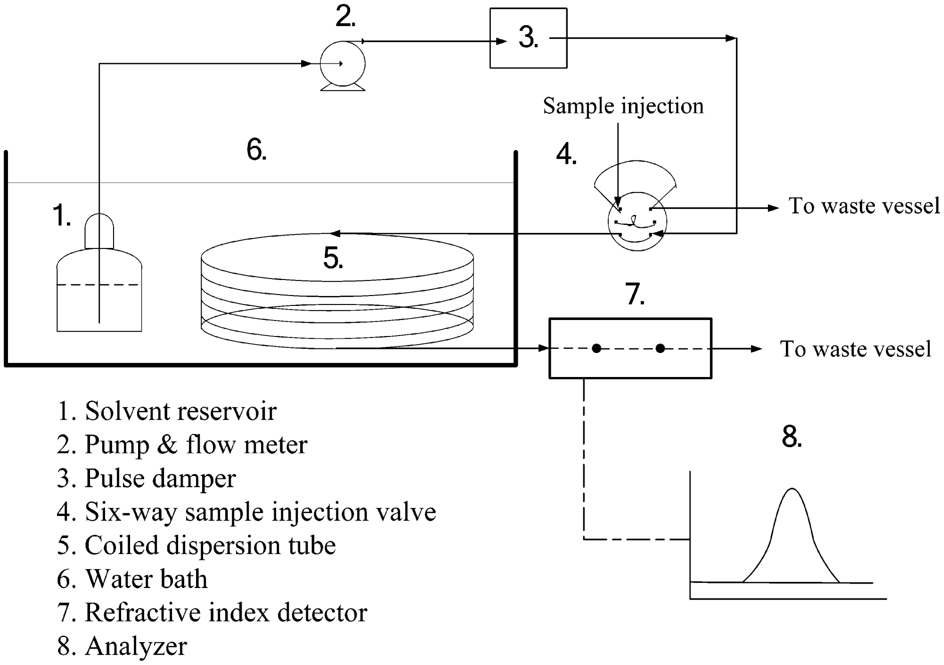

Figure 1. Experimental setup for the Taylor dispersion method.

pump. When aqueous solution was used, the purge procedure performed by the pump was necessary to eliminate any air bubbles that may trapped inside the pumping block. The carrier fluid flows through a six-port injection value (Rheodyne, model 7725i) upstream from the diffusion coil and then flows into a 316-stainless steel diffusion tube that was maintained at the constant temperature of a 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 (L) is 50.218 m with an internal radius (a_0) of 0.268 mm and is horizontally tempered in a 20-cm coil radius (R_c). The value of L/a_0 is 1.874×10^5, which is close to the value of Baldauf and Knapp[18] (i.e., 2×10^5). By switching a six-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 only a small concentration (0.05 to 0.1 kmol·m^{-3}) greater than that of the carrier fluid and normally is not of the pure compound. On the basis of the correction equation for the carrier solution composition due to the injected sample (Alizadeh et al.[16]), the contribution of the correction term is usually found to be less than 0.1% of the solution composition. Thus, the correction term for the solution concentration due to the injected sample is negligible in this study. For a diffusion coefficient at infinite dilution, the solution is pure water; the injected sample contains only a very small amount of solute in solution. The dispersion of the pulse was established through the parabolic velocity profile of the laminar flow. To prevent the secondary flows in a helical coil, the flow rate was controlled at (0.08 to 0.12) mL·min^{-1} to ensure the validity of the condition $\text{De}^2\text{Sc} \leq 20$, as suggested by Alizadeh et al.,[16] where the Dean number is $\text{De} = \text{Re}\ w^{-1/2}$, the Schmidt number is $\text{Sc} = \eta/\rho D_{12}$, $w = R_c/a_0$, the Reynolds number is $\text{Re} = 2a_0\bar{u}_0\rho/\eta$, η is viscosity, ρ is the density of solution, and $\bar{u}_0$ is the average velocity. The solvent reservoir and the capillary are temperature controlled by a thermostat. Between the six-way valve and the refractive index detector, the tube outside 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. Normally, the circuit of the reference cell is closed, and the flow passes directly into the sample cell. When a reference cell key is activated, an electrovalve is then opened. The flow pass through the two cells, and the reference cell is filled with the flowing fluid. The instrument detects the difference in concentration between the sample and reference cell. The instrument has a sensitivity ranging from $1/16 \times 10^{-5}$dRIU (refractive index unit) to 64×10^{-5}dRIU and with a linearity of 5×10^{-3}dRIU, drift of less than 5×10^{-7}dRIU/h, and noise of 1×10^{-8} dRIU. The analogue output was transferred to a computer system by an integrating converter INT5 (DataApex, Chromatography Station, CSW 1.7). In the data analysis system, the retention time, the Kirkland asymmetry factor, and the variance of an eluted peak were generated. The Kirkland asymmetry factor denotes the value of b_i/a_i, where a_i is the left-hand half-width at $^1/_{10}$ height of the peak and b_i is the right-hand half-width at $^1/_{10}$ height of the peak. Bueno et al.[23] pointed out that the value of the Kirkland asymmetry factor is smaller than 1.05 for an eluted peak, representing the good symmetry of the concentration curve. The characteristics of the instrument and the experimental conditions in this study are presented in Table 1.

Corrections due to the finite volumes of the injection loop and the detector cell were made to the first two temporal moments based on the equations of Alizadeh et al.[16] Some equations applied from Alizadeh et al.[16] are presented in Appendix I. To utilize the diffusivity equation of Alizadeh et al.[16] for a straight tube, the following two conditions have to be satisfied:

$$\frac{D_{12}t}{{a_0}^2} > 10 \qquad \text{or} \qquad \text{Pe} = \frac{\bar{u}_0 a_0}{D_{12}} < 0.1\frac{L}{a_0} \tag{1}$$

and

$$\frac{\bar{u}_0 a_0}{D_{12}} > 700 \qquad \text{or} \qquad \text{Pe} > 700 \tag{2}$$

Table 1. Characteristics of the Instrument and the Experimental Conditions

instrument conditions	
diffusion tube length, L/m	50.218
diffusion tube internal radius, a_0/mm	0.268
L/a_0	1.874×10^5
0.1 (L/a_0)	18740
coil radius, R_c/m	0.20
R_c/a_0	746.3
volume of injected sample, V_i/μL	20
volume of detector sample, V_D/μL	8
length of connecting tubing/m	0.2
experimental conditions	
flow rate/ml·min^{-1}	0.08 to 0.12
average velocity, $\bar{u}_0$/m·min^{-1}	0.42 to 0.45
retention time/min	100 to 120
Reynolds number	<100
Peclet number	$700 < 1000$ to $10\,000 < 18\,740$
De^{2}Sc	<20
Kirkland asymmetry factor	<1.05

where t is the retention time. In our case, to satisfy both eqs 1 and 2, the values of the Peclet number have to be in the region of $700 < \text{Pe} < 18\,740$.

The dispersion coefficient in coiled tubes can be characterized by the group De^{2}Sc. For a value of De^{2}Sc < 100, there will be no significant difference with the straight tube.[24] Alizadeh et al.[16] has further pointed that a choice of conditions such as

$$\text{De}^2\text{Sc} \leq 20 \tag{3}$$

will ensure that the effect of the coiling of the diffusion tube on the second central moment of the distribution is no greater than ±0.05%.

In this study, the temperature uncertainty was estimated to be ±0.05 K. The gravimetrically prepared aqueous solutions (using an A&D model FX-40C analytical balance) had a precision of ±0.1 mg. The uncertainty in the composition was estimated to be ±0.005 kmol·m^{-3}. A valid experimental run will be the one in which the Kirkland asymmetry factor of the eluted peak is less than 1.05 and the obtained mutual diffusion coefficient satisfies the conditions of eqs 1 to 3. The uncertainty of the measurement due to the coiling of the diffusion tube is estimated to be less than ±0.05%. For each state condition, three to five replicate experimental runs were normally carried out. The repeatability of the measured diffusivities was within ±1%. The standard deviation of the measured diffusivity is mostly ±1% and no worse than ±1.8%. The uncertainty of the diffusivity measurement is estimated to be ±2%.

3. Results and Discussion

To test the accuracy of the apparatus, we measured the mutual diffusion coefficients of methanol (1) + water (2) at 25 °C and atmospheric pressure. The results are presented in Table 2. To verify the validity of the experimental runs, the Kirkland asymmetry factor, the Reynolds number, the Peclet number, and the value of De^{2}Sc are also presented in Table 2. The densities and viscosities of methanol + water were provided by Nikam and Nikumbh.[25] As shown in Table 2, all of the experimental runs meet the required conditions (i.e., the Kirkland asymmetry factor < 1.05, $700 < \text{Pe} < 18\,740$, and De^{2}Sc ≤ 20). A comparison between the measured mutual diffusion coefficients and the literature values[26,27] for this system is shown in Figure 2. As shown in Figure 2, the measured mutual diffusion coefficients agree well with the values of Derlacki et al.[26] and Hao and Leaist.[27] The smoothed line is determined from all available data. The average absolute percentage deviation (AAD%) for the calculation of the mutual diffusivity coefficients measured in this study is 1.8%.

Table 2. Mutual Diffusion Coefficient D_{12} of Methanol (1) + Water (2) at 25 °C and Atmospheric Pressure

x_1	Kirkland asymmetry factor[a]	Re	Pe	De^{2}Sc	10^9D_{12}/m^2·s^{-1}
0	1.034−1.049	4.8	1381−1420	17.7−18.2	1.556 ± 0.015[b]
0.05	1.026−1.041	4.3	1813−1881	14.0−14.6	1.347 ± 0.025
0.1	1.024−1.049	3.6	1978−2037	12.9−13.3	1.237 ± 0.014
0.2	1.010−1.039	2.5	1832−1896	12.5−13.0	1.096 ± 0.017
0.4	1.039−1.051	2.5	2071−2100	14.1−14.2	0.981 ± 0.006
0.6	1.017−1.044	2.9	1603−1641	12.7−13.0	1.195 ± 0.015
0.8	1.038−1.046	5.2	1616−1639	15.1−15.3	1.613 ± 0.006

[a] Denotes the value of b_i/a_i, where a_i is the left-hand half-width at 1/10 height of a peak and b_i is the right-hand half-width at 1/10 height of the peak. [b] Standard deviations determined from three to five replicate experiments.

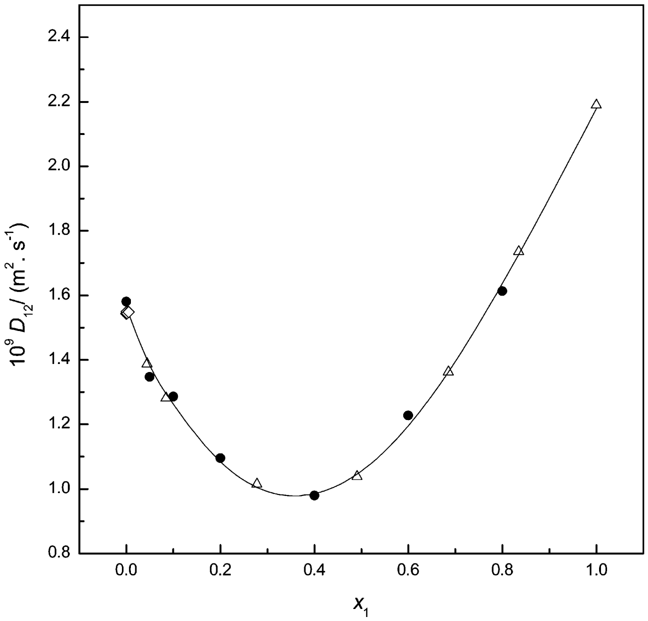

Figure 2. Mutual diffusivity coefficients of methanol (1) + water (2) at 25 °C and atmospheric pressure: ●, this work; △, data of Derlacki et al.;[26] ◇, data of Hao and Leaist;[27] line, smoothed values.

Table 3. Diffusion Coefficients D°_{12} of Alkanolamines in Water at Infinite Dilution and Atmospheric Pressure

	$10^9D^\circ_{12}$/m^2·s^{-1}			
t/°C	DGA + H$_2$O	TEA + H$_2$O	AMP + H$_2$O	2-PE + H$_2$O
30	0.958 ± 0.010[a]	0.796 ± 0.003	0.976 ± 0.007	0.826 ± 0.006
40	1.172 ± 0.028	1.000 ± 0.013	1.214 ± 0.027	1.047 ± 0.003
50	1.426 ± 0.013	1.234 ± 0.005	1.502 ± 0.013	1.289 ± 0.006
60	1.718 ± 0.010	1.484 ± 0.009	1.751 ± 0.025	1.568 ± 0.003
70	2.034 ± 0.009	1.745 ± 0.014	2.130 ± 0.008	1.843 ± 0.023

[a] Standard deviations determined from three to five replicate experiments.

The infinite dilution diffusivity coefficients of alkanolamines in water for temperatures of (30 to 70) °C and at atmospheric pressure are presented in Table 3. A comparison of the diffusivity coefficients of alkanolamines in water at infinite dilution is shown in Figure 3. The values of the infinite dilution diffusivity coefficients of alkanolamines in water depend on the characteristics of the solutions such as the sizes of solute and solvent and also the intermolecular interactions between the solute and solvent. At a constant temperature, the magnitudes of the infinite

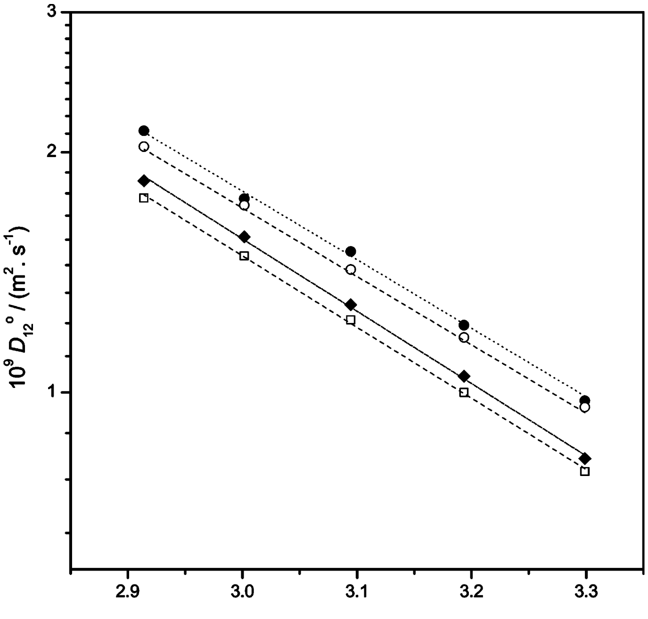

Figure 3. Infinite dilution diffusion coefficients of alkanolamines in water at atmospheric pressure: ●, AMP; ○, DGA; ♦, 2-PE; □, TEA; lines, calculated using eq 4.

Table 4. Mutual Diffusion Coefficient D_{12} of Aqueous Alkanolamine Solutions at Atmospheric Pressure

t/ °C	C/ (kmol·m^{-3})	10^9D_{12}/m^2·s^{-1}			
		DGA + H_2O	TEA + H_2O	AMP + H_2O	2-PE + H_2O
30	0.5	0.879 ± 0.004[a]	0.691 ± 0.004	0.816 ± 0.003	0.582 ± 0.005
40	0.5	1.130 ± 0.006	0.873 ± 0.006	1.039 ± 0.008	0.753 ± 0.010
50	0.5	1.339 ± 0.025	1.079 ± 0.004	1.291 ± 0.018	0.939 ± 0.005
60	0.5	1.637 ± 0.011	1.299 ± 0.014	1.567 ± 0.012	1.148 ± 0.021
70	0.5	1.911 ± 0.015	1.542 ± 0.004	1.864 ± 0.013	1.381 ± 0.007
30	1.0	0.806 ± 0.015	0.601 ± 0.003	0.717 ± 0.002	0.444 ± 0.004
40	1.0	1.011 ± 0.002	0.763 ± 0.007	0.920 ± 0.003	0.553 ± 0.009
50	1.0	1.265 ± 0.021	0.944 ± 0.005	1.149 ± 0.002	0.751 ± 0.011
60	1.0	1.527 ± 0.011	1.139 ± 0.008	1.398 ± 0.003	0.952 ± 0.007
70	1.0	1.825 ± 0.014	1.360 ± 0.004	1.680 ± 0.007	1.113 ± 0.010
30	2.0	0.720 ± 0.005	0.447 ± 0.004	0.567 ± 0.001	0.243 ± 0.001
40	2.0	0.918 ± 0.003	0.580 ± 0.003	0.740 ± 0.003	0.324 ± 0.006
50	2.0	1.140 ± 0.003	0.716 ± 0.008	0.930 ± 0.002	0.414 ± 0.003
60	2.0	1.376 ± 0.004	0.884 ± 0.010	1.145 ± 0.010	0.559 ± 0.010
70	2.0	1.652 ± 0.018	1.073 ± 0.015	1.364 ± 0.006	0.702 ± 0.012
30	3.0	0.641 ± 0.006	0.333 ± 0.003	0.446 ± 0.002	0.161 ± 0.003
40	3.0	0.823 ± 0.013	0.474 ± 0.005	0.589 ± 0.007	0.217 ± 0.004
50	3.0	1.028 ± 0.007	0.579 ± 0.006	0.753 ± 0.006	0.299 ± 0.007
60	3.0	1.231 ± 0.019	0.723 ± 0.010	0.931 ± 0.010	0.365 ± 0.007
70	3.0	1.501 ± 0.003	0.859 ± 0.012	1.127 ± 0005	0.448 ± 0.008
30	4.0	0.558 ± 0.006		0.342 ± 0.002	
40	4.0	0.733 ± 0.003		0.467 ± 0.005	
50	4.0	0.939 ± 0.006		0.611 ± 0.009	
60	4.0	1.152 ± 0.007		0.758 ± 0.003	
70	4.0	1.389 ± 0.015		0.948 ± 0.012	

[a] Standard deviations determined from three to five replicate experiments; the uncertainty of the measurement is estimated to be ±2.0 %.

Table 5. Parameters Determined for the Mutual Diffusivity Coefficient Equation, (Eq 4)

system	parameters			no. of data points	AAD%[a]
	A_1	A_2	A_3		
DGA + H_2O	−13.7667	−2134.47	-1.10×10^{-4}	30	2.0
TEA + H_2O	−13.7381	−2194.05	-2.60×10^{-04}	25	2.1
AMP + H_2O	−13.2922	−2285.77	-2.17×10^{-04}	30	2.4
2-PE + H_2O	−12.8805	−2475.63	-4.91×10^{-04}	25	4.5
			overall	110	2.7

[a] $\text{AAD\%} = \dfrac{\sum_{i=1}^{n}\left(\dfrac{|D_{\text{exp}} - D_{\text{calcd}}|}{D_{\text{exp}}}\right) \times 100\%}{n}$, where n is the number of data points.

dilution diffusivity coefficient of alkanolamines in water are found to be in the order of AMP (molar mass 89.14) > DGA (105.14) > 2-PE (129.2) > TEA (149.19), which indicates that a lighter solute (alkanolamine) moves faster in water. Lines in Figure 3 are calculated from eq 4, which will be described shortly.

The measured mutual diffusion coefficients of aqueous alkanolamines solutions are presented in Table 4 for temperatures from (30 to 70) °C and concentrations from (0.5 to 3) kmol·m^{-3} for aqueous TEA and 2-PE and (0.5 to 4) kmol·m^{-3} for aqueous DGA and AMP solutions. The available densities and viscosities of solutions in the literature were applied directly: DGA + H_2O,[28] TEA + H_2O,[29] AMP + H_2O,[30,31] and 2-PE + H_2O.[30,31] A simple equation of Snijder et al.,[5] representing the diffusion coefficient as a function of temperature and concentration of solution, is applied to represent the measured mutual diffusion coefficients. The equation has the following form,

$$\ln(D_{12}/\text{m}^2\text{·s}^{-1}) = A_1 + A_2/(T/\text{K}) + A_3C/(\text{kmol·m}^{-3}) \quad (4)$$

where A_i are parameters that are determined from both the infinite dilution diffusion coefficient data (values in Table 3) and the mutual diffusion coefficient data (values in Table 4). The fitted results are presented in Table 5. The overall AAD% (average absolute percentage deviation) of the diffusion coefficient calculations is 2.7%. For the purpose of comparison, the AAD% values of the diffusion coefficient calculations using the same equation (i.e., eq 4) for aqueous MEA, DEA, MDEA, and DIPA solutions are 5%, 7%, 9%, and 6%, respectively.[5] Although eq 4 is just a simple equation, it can represent satisfactorily the mutual diffusion coefficients of aqueous alkanolamines solutions measured in this study. The results of the diffusivity coefficient calculation for the aqueous AMP solution are shown in Figure 4. As shown in Figure 4, the value of the logarithm of the mutual diffusion is a linear equation with respect to the reciprocal temperature of the system, and it decreases as the concentration of solute increases at a constant temperature.

The concentration dependence of the diffusion coefficients in eq 4 is assumed to follow a simple linear-concentration relation, which may not be adequate to represent the composition dependence of mutual diffusion coefficients in liquids. Correlations for the composition dependence of the mutual diffusivity coefficients are available in the literature.[32−34] On the basis of the absolute reaction rate theory and the local composition model, a so-called UNIDIF equation for the calculation of the mutual diffusion coefficients of a binary solution has been proposed.[35] The UNIDIF model has been extensively tested for mutual diffusion coefficients of various nonpolar and polar mixtures, and satisfactory results have been observed.[35] Thus, this model will also be applied in this study to represent the measured mutual diffusion coefficients for aqueous alkanolamine systems. A brief description of the UNIDIF model is presented in Appendix II.

In the application of the UNIDIF model, the molar volume and the surface area of alkanolamines and water were estimated from Reid et al.,[36] D_{21}° is calculated form the correlation of Wilke and Chang,[37] and the measured values of D_{12}° in Table 3 are directly applied. The results of

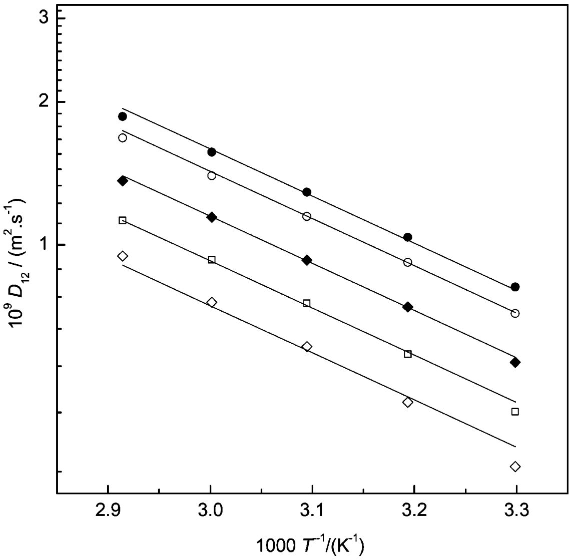

Figure 4. Mutual diffusivity coefficients of aqueous AMP solutions as a function of temperature: ●, 0.5 kmol·m^{-3} AMP + H_2O; ○, 1.0 kmol·m^{-3} AMP + H_2O; ♦, 2.0 kmol·m^{-3} AMP + H_2O; □, 3.0 kmol·m^{-3} AMP + H_2O; ◇, 4.0 kmol·m^{-3} AMP + H_2O; solid lines, calculated using eq 4.

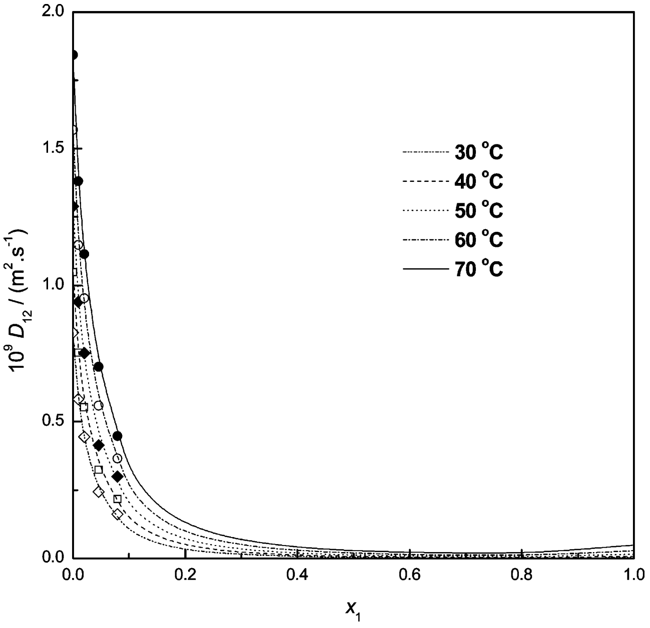

Figure 5. Mutual diffusivity coefficients of aqueous 2-PE solutions as a function of mole fraction of 2-PE; ●, 70 °C; ○, 60 °C; ♦, 50 °C; □, 40 °C; ◇, 30 °C; solid lines, calculated from the UNIDIF model.

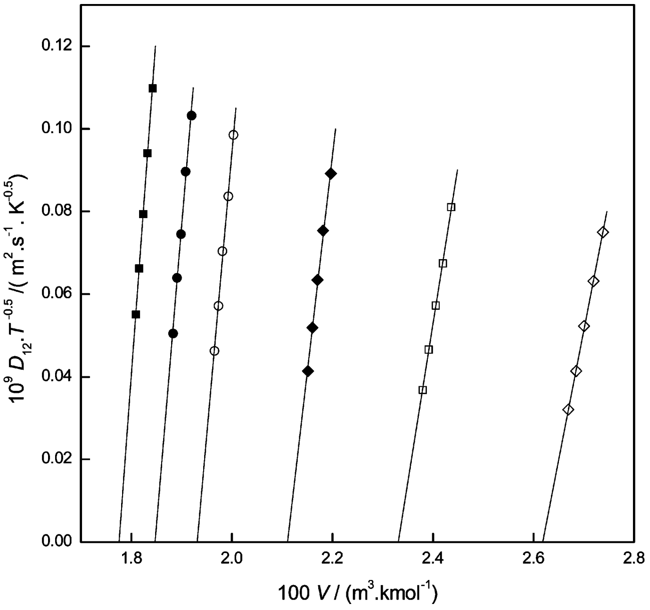

Figure 6. Free-volume relation for mutual diffusivity coefficients of aqueous DGA solutions: ■, H_2O; ●, 0.5 kmol·m^{-3} DGA + H_2O; ○, 1.0 kmol·m^{-3} DGA + H_2O; ♦, 2.0 kmol·m^{-3} DGA + H_2O; □, 3.0 kmol·m^{-3} DGA + H_2O; ◇, 4.0 kmol·m^{-3} DGA + H_2O; solid lines, calculated using eq 5.

Table 6. Parameters Determined for the UNIDIF Model

systems	a_{21}/K	a_{12}/K	no. of data points	AAD%[a]
DGA + H_2O	7.5885	44.1929	25	1.8
TEA + H_2O	−51.8468	92.7319	20	1.4
AMP + H_2O	−65.2518	142.284	25	1.5
2-PE + H_2O	−60.3932	196.042	20	2.8
		overall[b]	90	1.9

[a] $\mathrm{AAD\%} = \dfrac{\sum_{i=1}^{n}\left(\dfrac{|D_{\mathrm{exp}} - D_{\mathrm{calcd}}|}{D_{\mathrm{exp}}}\right) \times 100\%}{n}$, where n is the number of data points. [b] Data points do not include the diffusion coefficients at infinite dilution.

calculations of mutual diffusion coefficients and the two parameters determined are presented in Table 6. The overall AAD% of the mutual diffusion coefficient calculations is 1.9%, not including the diffusion coefficients at infinite dilution. Compared to the result of using eq 4 (2.7 %), the UNIDIF model yields a fairly good result (1.9%) using only two parameters. Thus, the UNIDIF model may provide better composition dependence than eq 4. In Figure 5, a comparison between the calculated and the experimental mutual diffusion coefficient of aqueous 2-PE solutions as function of mole fraction is shown. As shown in Figure 5, the obtained mutual diffusion coefficients of aqueous 2-PE solution can be well represented by the UNIDIF model.

Because of the equation of Dymond,[38] which gives an accurate representation of self-diffusion coefficients of hard-sphere molecules, an equivalent equation for the diffusion coefficient in terms of the solution molar volume has been introduced[21,22,39] as

$$\frac{D}{T^{1/2}} = \gamma[V - V_{\mathrm{D}}] \tag{5}$$

where V is the volume of solution, V_{D} is the molar volume of solution at which the diffusion coefficient goes to zero, and $V - V_{\mathrm{D}}$ is the free volume of the solution. In eq 5, γ is a solution constant that depends on the average collision diameter, σ_{AB}, and molecular masses of solute and solvent.[22] In this study, eq 5 is also applied to represent the measured mutual diffusivity data. The available densities of aqueous alkanolamines solutions in the literature were applied, as mentioned earlier. In Figures 6 and 7, the plots of $D_{12}T^{-0.5}$ versus V are shown for aqueous DGA and TEA solutions, respectively. As shown in Figures 6 and 7, the measured mutual diffusivity data are well represented by the free-volume expression of the form of eq 5. Constants γ and V_{D} for each solution can be readily determined. Determined constants γ and V_{D} are presented in Table 7.

In Figure 8, the free-volume relations for diffusivity coefficients at infinite dilution of aqueous alkanolamines

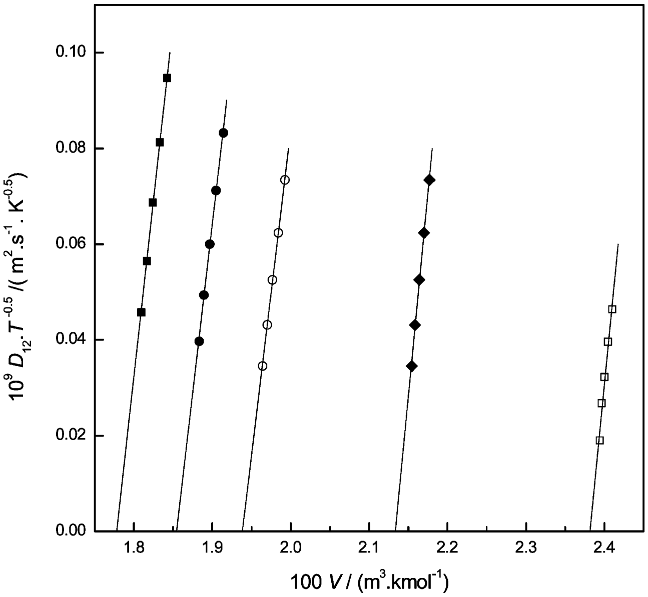

Figure 7. Free-volume relation for mutual diffusivity coefficients of aqueous TEA solutions: ■, H_2O; ●, 0.5 kmol·m^{-3} TEA + H_2O; ○, 1.0 kmol·m^{-3} TEA + H_2O; ♦, 2.0 kmol·m^{-3} TEA + H_2O; □, 3.0 kmol·m^{-3} TEA + H_2O; solid lines, calculated using eq 5.

Table 7. Solution Constant, γ, Molar Volume of Frozen Diffusion, V_D, and Average Collision Diameter σ_{AB} (or σ_B) for Aqueous Alkanolamine Solutions

system	x_1	γ	$100V_D$/m^3·kmol^{-1}	$10^{10}\sigma_{AB}$(or σ_B)/m
DGA + H_2O	0	1.6608	1.7763	3.13
	0.0094	1.4452	1.8476	3.17
	0.0197	1.3623	1.9311	3.22
	0.0436	1.0518	2.1111	3.32
	0.0732	0.7668	2.3311	3.43
	0.1106	0.6260	2.6179	3.56
TEA + H_2O	0	1.4800	1.7781	3.13
	0.0094	1.4083	1.8545	3.18
	0.0196	1.3578	1.9385	3.22
	0.0431	1.7044	2.1336	3.33
	0.0718	1.6768	2.3816	3.45
AMP + H_2O	0	1.6653	1.7756	3.13
	0.0094	1.4645	1.8439	3.17
	0.0194	1.2062	1.9136	3.21
	0.0421	0.8296	2.0712	3.30
	0.0690	0.5887	2.2615	3.39
	0.1013	0.3942	2.4912	3.51
2-PE + H_2O	0	1.4477	1.7739	3.13
	0.0095	1.0843	1.8781	3.19
	0.0202	0.8317	1.9913	3.25
	0.0457	0.4325	2.2610	3.39
	0.0792	0.2103	2.6041	3.56

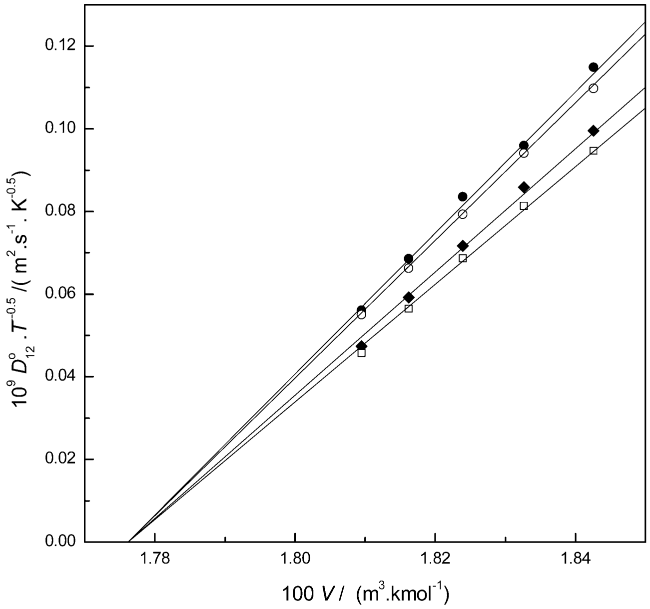

Figure 8. Free-volume relation for diffusivity coefficients at infinite dilution of aqueous alkanolamines solutions: ●, AMP; ○, DGA; ♦, 2-PE; □, TEA; lines, calculated using eq 5.

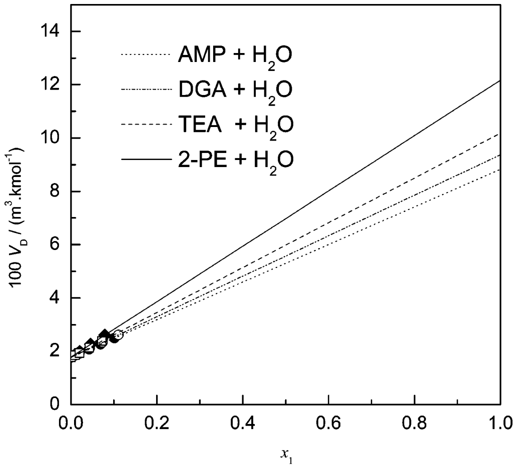

Figure 9. Molar volume of frozen diffusion as a function of mole fraction: ●, AMP + H_2O; ○, DGA + H_2O; ♦, 2-PE + H_2O; □, TEA + H_2O; lines, smoothed curves.

solutions are shown. As shown in Figure 8, the free volume expression fits the data well and the values of V_D are approaching to a constant value of 1.776 × 10^{-2} m^3·kmol^{-1}, the theoretical molar volume of frozen diffusion. At the infinite dilution and the same temperature, the free-volume of solutions are in the order of AMP > DGA > 2-PE > TEA which also corresponds to the order of D°_{12} of alkanolamines in water at the infinite dilution, as shown in Figure 8. At the same temperature, the order of D°_{12} observed in Figure 8 is consistent with the order of D°_{12} in Figure 3.

In Figure 9, plots of V_D verses mole fraction of alkanolamines are shown. As shown in Figure 9, the values of V_D increase as the mole fraction of alkanolamines increases. The lines in Figure 9 are just smoothed curves from the points and extrapolate to mole fraction up to 1. Except for 2-PE + H_2O, the values of V_D of aqueous alkanolamine solutions are in the order of TEA + H_2O > DGA + H_2O > AMP + H_2O, which corresponds to the same order as for the molecular size of alkanolamine (i.e., TEA (molar mass 149.19) > DGA (105.14) > AMP (89.14)). The interaction of the cyclic structure of 2-PE with water may cause this abnormal behavior of 2-PE + H_2O.

For diffusion coefficients at infinite solution, V_D can be considered to be the hypothetical solvent molar volume at which the diffusivity approaches zero, and the value of V_D depends only on the solvent.[21,22] The value of V_D can further be related to the hard-sphere diameter[21] as

$$V_D = bV_0 = bN\sigma_B{}^3/2^{1/2} \tag{6}$$

where N is Avogadro's number, V_0 is the close-packed hard-sphere volume, b is 1.358 as given by Tyrrell and Harris,[2] and σ_B is the molecular diameter of solvent.

For the diffusion coefficient away from the neighbor at infinite dilution, V_D can be considered to be the hypothetical solution molar volume at which the diffusion is frozen, and

Table 8. Comparison of the Estimated Hard-Sphere Diameter σ_A from Linear Extrapolated Diameters of σ_{AB} with the van der Waals Diameter σ_{vdW} According to Bondi[40]

system	$10^{10}\sigma_A$/m	$10^{10}\sigma_{vdW}$/m	σ_A/σ_{vdW}
DGA + H_2O	7.03	5.85	1.20
TEA + H_2O	7.57	6.58	1.15
AMP + H_2O	6.77	5.63	1.20
2-PE + H_2O	8.48	6.44	1.32

V_D depends on the characteristics of the solution. In this case, eq 6 becomes[21]

$$V_D = bN\sigma_{AB}{}^3/2^{1/2} \tag{7}$$

where σ_{AB} is the average collision diameter of the solute and solvent molecules at a particular concentration of solution. In Table 7, the calculated σ_{AB} (or σ_B) from V_D using eqs 6 and 7 are also presented.

When x_1 (mole fraction of alkanolamines) → 0, σ_{AB} should reduce to σ_B (i.e., the hard-sphere diameter of water), whereas when $x_1 \to 1$, σ_{AB} will tend toward σ_A (i.e., the hard-sphere diameter of alkanolamine). Because the diffusivity measurement for x_1 approaching 1 is not performed, the σ_A, the hard-sphere diameter of alkanolamine, cannot be calculated. Alternatively, the van der Waals diameter, σ_{vdW}, of alkanolamines can be estimated from the van der Waals volume, which is calculated from the group contribution method of Bondi.[21,40] In the work of Wong and Hayduk,[21] the ratio of σ_B, the hard-sphere diameter of solvent, to σ_{vdW}, the van der Waals diameter of solvent, was found to be an average value of 0.969, and there is a good agreement between the two diameter values (i.e., the hard-sphere and van der Waals diameters). Thus, the calculated σ_{vdW} based on the Bondi method can roughly represent a close value of the hard-sphere diameter of fluids interested. On the assumption of the linear dependence of σ_{AB} on the mole fraction of alkanolamine, the estimated σ_A (i.e., σ_{AB} at $x_1 \to 1$) can be calculated. A comparison of the linear extrapolated diameters σ_A and σ_{vdW} according to Bondi is presented in Table 8. The values of the estimated σ_A are larger than those of σ_{vdW}. The ratios of σ_A to σ_{vdW} varies from 1.15 to 1.32, as presented in Table 8. Thus, the linear extrapolated diameters, σ_A, reasonably relate to the estimated van der Waals diameters, σ_{vdW}.

4. Conclusions

The diffusion coefficients of alkanolamines in water at infinite dilution and the mutual diffusion coefficients of aqueous DGA, TEA, AMP, and 2-PE solutions at atmospheric pressure have been measured by using the Taylor dispersion technique. Results for the binary system of methanol and water showed that the experimental setup provides accurate mutual diffusion coefficient measurements. The diffusion coefficients of alkanolamines in water at infinite dilution are found to vary systematically with the molecular weight of the alkanolamines. The obtained mutual diffusion coefficient data are well correlated by a simple relation, the UNIDIF equation, or the free-volume expression. In the free-volume formula, the derived molar volume of frozen diffusivities are found to vary with the mole fraction of alkanolamines. The results of this study can be used as a database for developing the kinetic model for gas absorption using aqueous alkanolamine solutions as absorbents.

Appendix I. Mutual Diffusion Coefficient Due to Alizadeh et al.[16]

Corrections due to the finite volumes of the injection loop and the detector cell were made to the first two temporal moments based on the equations of Alizadeh et al.[16] The mutual diffusion coefficient, D_{12}, of a binary fluid mixture is determined[16,17] by

$$D_{12} = \frac{a_0^2}{24\bar{t}_{id}}\left[\frac{\left(1 + 4\frac{\sigma_{id}^2}{\bar{t}_{id}^2}\right)^{1/2} + 3}{\left(1 + 4\frac{\sigma_{id}^2}{\bar{t}_{id}^2}\right)^{1/2} + 2\frac{\sigma_{id}^2}{\bar{t}_{id}^2} - 1}\right]\left[\frac{1}{2} + \frac{1}{2}(1 - \delta_a)^{1/2}\right] \tag{8}$$

where a_0 is the internal radius of the diffusion tube, $\bar{t}_{id}$ is the first moment, and σ_{id}^2 is the variance in an ideal experiment. Also,

$$\delta_a = 12.7997\zeta_0 \tag{9}$$

and

$$\zeta_0 = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + \{\bar{t}_{id}^4 + 4\bar{t}_{id}^2\sigma_{id}^2\}^{1/2}}{\{8\bar{t}_{id}^2 - 4\sigma_{id}^2\}} \tag{10}$$

The values of $\bar{t}_{id}$ and σ_{id}^2 are obtained from the measurement moments in a real experiment, and $\bar{t}_{exp}$ and σ_{exp}^2 are obtrained from corrections due to V_{DR}, the small sampling volume in the differential refractometer, and V_i, the volume of the sample injected as follows:

$$\bar{t}_{id} = \bar{t}_{exp} - \frac{L}{\bar{u}_0}\left(\frac{V_{DR}}{2\pi a_0^2 L}\right) - \frac{L}{\bar{u}_0}\left(\frac{V_i}{2\pi a_0^2 L}\right) \tag{11}$$

$$\sigma_{id}^2 = \sigma_{exp}^2 - \left(\frac{L}{\bar{u}_0}\right)^2\left\{\zeta_0\left(\frac{V_{DR}}{\pi a_0^2 L}\right) + \frac{1}{12}\left(\frac{V_{DR}}{\pi a_0^2 L}\right)^2\right\} - \frac{1}{12}\left(\frac{L}{\bar{u}_0}\right)^2\left(\frac{V_i}{\pi a_0^2 L}\right)^2 \tag{12}$$

L is the length of the capillary tube.

Appendix II. UNIDIF Equation

The UNIDIF equation[19] for the mutual diffusivity coefficients of binary liquid mixtures has the following form

$$\begin{aligned} \ln D_{12} = {} & x_2 \ln D_{12}^\circ + x_1 \ln D_{21}^\circ + 2\left[x_1 \ln\frac{x_1}{\phi_1} + x_2 \ln\frac{x_2}{\phi_2}\right] \\ & + 2x_1x_2\left[\frac{\phi_1}{x_1}\left(1 - \frac{\lambda_1}{\lambda_2}\right) + \frac{\phi_2}{x_2}\left(1 - \frac{\lambda_2}{\lambda_1}\right)\right] \\ & + \{x_2q_1[(1 - \theta_{21}^2)\ln\tau_{21} + (1 - \theta_{22}^2)\tau_{12}\ln\tau_{12}] \\ & + x_1q_2[(1 - \theta_{12}^2)\ln\tau_{12} + (1 - \theta_{11}^2)\tau_{21}\ln\tau_{21}]\} \end{aligned} \tag{13}$$

where λ_i is the equilibrium distance parameter (i.e., the diffusion length) and is assumed to be proportional to the cubic root of the molecular volume. ϕ_i is the fraction of the diffusion length,

$$\phi_i = \frac{x_i\lambda_i}{\sum_{i=1}^{2} x_i\lambda_i} \tag{14}$$

q_j is the surface area of component j, and θ_{ji} is the surface area fraction

$$\theta_{ji} = \frac{x_j q_j \tau_{ji}}{\sum_{j=1}^{2} x_j q_j \tau_{ji}} \tag{15}$$

The interaction parameter τ_{ji} is expressed as a Boltzmann factor of the binary interaction energy a_{ji},

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{16}$$

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