Correlation of the mutual diffusion coefficients of binary liquid mixtures

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Abstract

A correlative UNIDIF model for the mutual diffusion coefficients of binary liquid mixtures is developed using statistical thermodynamics and the absolute reaction rate theory. In this model, a mole fraction average of the logarithm of the pure-component limiting diffusion coefficients is taken as a reference term. The model expresses the excess part of the diffusion coefficient relative to this reference term in a form similar to that of a UNIQUAC equation which comprises two parts due to the combinatorial and residual contributions. The combinatorial part depends on the molecular sizes and shapes. The residual part includes two binary interaction parameters, which are obtained from data regression, for each binary mixture. Mutual diffusion coefficients of nonpolar + nonpolar, nonpolar + polar and polar + polar fluid mixtures are correlated in this study. Optimal binary interaction parameters are presented. Correlation results using the UNIDIF model for mutual diffusion coefficient are satisfactory and are superior to those from other methods. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Method of calculation; Diffusion coefficient; Mixture

1. Introduction

Transport properties, such as the viscosity, thermal conductivity and diffusion coefficient, are essential to the design of chemical processes and equipment involving fluid flow, heat and mass transfer, and chemical reactions. Although viscosity and thermal conductivity of liquid mixtures have been correlated using statistical thermodynamics and local composition concepts [1,2], a similar method for the treatment of liquid mutual diffusion coefficients has yet not been presented. Simple equations are not adequate to express the concentration dependence of liquid mutual diffusion coefficients. Correlation of the mutual diffusion coefficients can be presented using the hydrodynamic

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or absolute reaction rate theory. A review of liquid diffusion of non-electrolyte solutions has been presented by Ghai et al. [3]. A recent discussion for the estimation of diffusion coefficients of dense fluids on binary and multicomponent mixtures has been shown by Riazi and Whitson [4]. Most correlation equations express the mutual diffusion coefficient as the product of an ad hoc compositional average of the limiting diffusion coefficients and a thermodynamic factor, which contains the composition dependence of the activity. The thermodynamic factor is calculated from an activity coefficient model where the optimal binary interaction parameters are obtained from data regression. Siddiqi and Lucas [5] have compared various calculation methods using the NRTL model. They showed satisfactory results for nonpolar liquid mixtures, but larger deviations for polar systems. Cussler [6] proposed the cluster diffusion model and suggested a mutual diffusion correlation equation with two empirical parameters for a binary system. Further application of the cluster diffusion model has been presented by Cullinan [7] and Rollins and Knaebel [8]. Recently, Pertler et al. [9] reviewed various correlation equations for mutual diffusion coefficient and compared them for the binary mixtures which may have liquid phase separation.

Cao et al. [1] developed a statistical thermodynamics model for the viscosities of liquid mixtures. On the basis of the lattice theory, they started from the partition function and expressed the potential energy function by a local composition equation. They also applied the reaction rate theory [10] to express the frequency of molecular movement. The kinematic viscosity was finally written in a local composition form with two interaction parameters for each binary system. A method similar to that of Cao et al. [1] is employed for mutual diffusion coefficients of binary liquid mixtures in this study. The mutual diffusion coefficients are written also in a local composition form with combinatorial and residual contributions. Molecular size, shape and interaction effects are included in this correlation equation. This equation is then applied in calculating the mutual diffusion coefficients of nonpolar and polar binary mixtures. Correlation results and comparisons with other methods are presented in this study.

2. Development of the mutual diffusion coefficient model

Cao et al. [1] developed a statistical thermodynamics model for the viscosity of liquid mixtures. A similar approach is applied here to develop a mutual diffusion coefficient model. According to the lattice theory [11], the partition function of a liquid mixture is written as:

$$\Omega = \Omega^s \prod_{i=1}^n \left(\frac{2\pi m_i kT}{h^2} \right)^{3N_i/2} \frac{\omega_i}{\omega_i^s} \exp\left(-\frac{U_{0i}}{kT}\right) \quad (1)$$

where U_{0i} is the potential energy of lattice i in a mixture, n is the number of components in a mixture, N_i is the number of molecules in component i , ω is the number of configurations of a lattice, and the superscript s represents the boundary condition of a Starveman's model. U_{0i} is the potential energy of a lattice in a mixture, and is expressed by a local composition model:

$$-U_{0i} = \frac{zq_i N_i}{2} \sum_{j=1}^n U_{ji} \theta_{ji} \quad (2)$$

The local composition parameter θ_{ji} is approximated according to the equation of Abrams and Prausnitz [12]:

$$\theta_{ji} = \frac{\theta_j \tau_{ji}}{\sum_{l=1}^n \theta_l \tau_{li}} \quad (3)$$

where θ_j is the average fraction of the surface area q_j of component j :

$$\theta_j = \frac{x_j q_j}{\sum_{l=1}^n x_l q_l} \quad (4)$$

The interaction parameter τ_{ji} in Eq. (3) is written as a Boltzmann factor of the binary interaction energy a_{ji} and the coordination number z :

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \quad (5)$$

$$a_{ji} = \frac{z}{2k}(U_{ji} - U_{ii}) \quad (6)$$

The absolute reaction rate theory [10] has been used to describe the transport properties of fluid mixtures. According to this theory, a molecule traveling between two neighboring equilibrium states has to overcome an energy barrier. The frequency of movement in a fluid mixture is expressed as:

$$k_{am} = \prod_{i=1}^n \left(\frac{kT}{2\pi m_i}\right)^{x_i/2} \exp\left(\frac{z}{2kT} \sum_{i=1}^n x_i q_i \sum_{j=1}^n U_{ji} \theta_{ji}\right) \quad (7)$$

According to the absolute reaction rate theory [10], the diffusion coefficient is proportional to the product of the frequency of movement (k_a) and the square of the distance between two equilibrium

Table 1

Correlative equations for the mutual diffusion coefficients of binary mixtures

Equations	Equation names	References
$D_{12} = (x_1 D_2^0 + x_2 D_1^0)$	Geet–Adamson	[15]
$D_{12} = (x_1 D_2^0 + x_2 D_1^0) \times ((d \ln a_1)/(d \ln x_1))$	Modified Darken	[16]
$D_{12} = (D_2^0)^{x_1} (D_1^0)^{x_2} \times ((d \ln a_1)/(d \ln x_1))$	Vignes	[17]
$D_{12} = (1)/(\eta_m)(x_1 \eta_1 D_2^0 + x_2 \eta_2 D_1^0) \times ((d \ln a_1)/(d \ln x_1))$	Carman–Stein	[18]
$D_{12} = (1)/(\eta_m)(n_1 D_2^0)^{x_1} (\eta_2 D_1^0)^{x_2} \times ((d \ln a_1)/(d \ln x_1))$	Leffler–Cullinan	[19]
$D_{12} = D_0 \{1 + C \times [(1)/(x_1 x_2)((d \ln x_1)/(d \ln a_1) - 1)]^b\}^{-0.5}$; $b \cong 1.23$, $C \cong 0.17$, D_0 = reference diffusion coefficient	Guerman	[20]
$D_{12} = (kT)/(2\pi \eta_m V_m^{1/3}) [1 + (1)/(2\pi x_1 x_2)((d \ln x_1)/(d \ln a_1) - 1)]^{-0.5}$	Cullinan 1	[7,8]
$D_{12} = \sqrt{f_{12}^0} D_{12}^0 (\eta_2)/(\eta_m)(V_2^{1/3})/(V_m^{1/3}) [1 + (1)/(2\pi x_1 x_2)((d \ln x_1)/(d \ln a_1) - 1)]^{-0.5}$; D_{12}^0 = limiting diffusion coefficient, $f_{12}^0 = 1 - (1)/(2\pi) \lim_{x_1 \rightarrow 0} (d \alpha_{12})/(d x_1)$, and $\alpha_{12} = (d \ln a_1)/(d \ln x_1)$	Cullinan 2	[8]

Table 2
Calculation results of the mutual diffusion coefficients of binary liquid mixtures

System (component 1 + component 2)	No. of data points	Temp. range (K)	UNIDIF parameters (K)		AAD (%) ^a				References	
			a_{21}	a_{12}	Modified darken		Vignes			UNIDIF
					NRTL	UNIQUAC	NRTL	UNIQUAC		
<i>Normal alkanes</i>										
<i>n</i> -Hexane + <i>n</i> -dodecane	30	298.15–308.15	0	0	3.6	8.3	1.4	5.8	1	[21–23]
<i>n</i> -Octane + <i>n</i> -dodecane	21	298.15–333.15	0	0	1.9	4.2	0.9	3.1	0.6	[15]
<i>n</i> -Heptane + <i>n</i> -decane	21	298.15	0	0	1.5	1.3	2.3	1.4	2.8	[24]
<i>n</i> -Heptane + <i>n</i> -dodecane	20	298.15	0	0	6.5	10.6	3.9	7.8	2.6	[24]
<i>n</i> -Heptane + <i>n</i> -hexadecane	7	298.25	0	0	6	14.7	1.2	9	2	[21,22]
<i>n</i> -Hexane + <i>n</i> -heptane	25	300.00–328.00	0	0	0.6	0.6	0.6	0.6	0.6	[25]
<i>n</i> -Heptane + <i>n</i> -octane	25	293.00–343.00	0	0	0.2	0.3	0.2	0.2	0.2	[25]
<i>n</i> -Heptane + <i>n</i> -tetradecane	23	298.15	0	0	8.5	15.7	3.5	10.4	1.9	[24]
<i>n</i> -Dodecane + <i>n</i> -hexadecane	9	298.15	0	0	1.7	2.4	0.6	1.1	0.4	[23]
<i>n</i> -Hexane + <i>n</i> -hexadecane	8	298.25	0	0	7.8	21.3	2.4	14.1	3.1	[26,22]
<i>n</i> -Hexane + <i>n</i> -octane	25	295.00–23.00	0	0	0.3	0.9	0.4	0.5	0.6	[25]
<i>n</i> -Octane + <i>n</i> -tetradecane	24	298.15	0	0	5	9.4	2.6	6.3	2	[24]
<i>Nonpolar + nonpolar</i>										
Carbon tetrachloride + cyclohexane	16	298.15–308.15	−38.6275	45.2095	0.2	0.2	0.2	0.2	0.2	[27,22]
<i>n</i> -Hexane + carbon tetrachloride	12	298.15–303.15	−41.6152	43.1222	0.7	1.7	1	1	1	[28]
<i>n</i> -Heptane + carbon tetrachloride	6	303.15	−32.6056	30.9176	0.7	1.5	0.9	0.7	1	[28]

<i>n</i> -Octane + carbon tetrachloride	6	303.15	−39.302	36.8812	2.5	1.4	2.3	3.2	2.8	[29]
<i>n</i> -Decane + carbon tetrachloride	4	298.15	129.3732	−100.1124	0.4	1.9	0.3	1.3	0.9	[29,21]
Dodecane + carbon tetrachloride	4	298.15	132.3892	−100.5871	0.5	5.1	0.5	4.7	0.5	[29]
3-Methylpentane + carbon tetrachloride	6	303.15	−15.88	15.4745	0.7	2.7	1.2	1.3	1.2	[30]
2,3-Dimethylpentane + carbon tetrachloride	6	303.15	64.6053	−53.9069	0.3	3.1	0.3	1.3	0.3	[29]
2,2,4-Trimethylpentane + Benzene + <i>n</i> -hexane	6	303.15	−26.7465	25.6102	0.4	2.5	1.6	1	1.8	[29]
Benzene + <i>n</i> -hexane	11	298.15	145.7153	−83.6627	0.4	3.5	0.3	2.1	0.5	[31,32]
Benzene + <i>n</i> -heptane	34	293.15–358.15	−63.0805	80.5367	4.8	3.8	4.5	3.7	4.1	[32]
Cyclohexane + benzene	69	293.15–333.15	17.4422	−3.747	1.2	2.1	1.2	2.1	0.9	[33–36]
<i>Nonpolar + polar</i>										
<i>n</i> -Hexane + chloroform	6	303.15	91.8544	−62.6214	1.1	5	1.1	4	1.1	[30]
<i>n</i> -Heptane + chloroform	6	303.15	141.5674	−98.788	0.7	3.6	0.7	3.1	1.7	[30]
<i>n</i> -Octane + chloroform	6	303.15	127.8976	−90.0145	0.5	4.7	0.5	4.2	1.4	[30]
Chloroform + carbon tetrachloride	12	298.15	−59.4366	82.5829	1.1	2.1	1.1	1.9	1.1	[37]
3-Methylpentane + chloroform	6	303.15	−27.7578	51.8701	0.7	5.7	0.7	4.5	0.6	[30]
2,3-Dimethylpentane + chloroform	6	303.15	28.1744	−17.9382	1.1	4.1	1.1	3.3	0.8	[30]
2,2,4-Trimethylpentane + chloroform	6	303.15	29.0131	−19.1057	0.4	5.8	0.4	5.2	0.8	[30]

Table 2 (continued)

System (component 1 + component 2)	No. of data points	Temp. range (K)	UNIDIF parameters (K)		AAD (%) ^a				References	
			a_{21}	a_{12}	Modified darken		Vignes			UNIDIF
					NRTL	UNIQUAC	NRTL	UNIQUAC		
<i>Nonpolar + polar</i>										
Acetone + benzene	31	298.15	91.7255	−45.923	1.7	2.2	1.7	1.9	1.5	[8,36,38]
Acetone + carbon tetrachloride	12	298.15– 298.30	221.6764	−108.5594	4.4	6.5	4.2	6	4.8	[39,38]
Acetone + cumene	12	283.15– 303.15	138.6635	−62.2699	1.7	8.8	1.7	8.6	3.4	[40]
Acetone + cyclohexane	9	298.15	186.2569	−37.7967	6.7	15.5	6.2	14.4	2.9	[41]
Methyl ethyl ketone + carbon tetrachloride	7	298.15	168.5107	−95.9914	1.9	3.5	1.8	2.6	0.8	[42]
Acetic acid + carbon tetrachloride	9	298.15	−9.7821	85.3011	1.6	7.4	1.6	7.4	1.7	[8]
Isobutyric acid + cumene	12	283.15– 303.15	102.9102	−71.1125	1.5	2.4	1.5	2.3	1	[39]
Methanol + benzene	8	313.15	434.508	−22.1893	10.9	15.9	10.6	15.5	3	[40]
Ethanol + benzene	17	298.30– 313.13	280.2374	−76.9792	14.4	7.8	14.2	7.9	3	[39]
Methanol + carbon tetrachloride	11	293.15	545.7224	−22.3977	39.4	49	39.4	49	8.8	[43]
Ethanol + carbon tetrachloride	9	298.15	231.8918	−76.4117	1.8	13	1.8	12.7	3.4	[42]
<i>n</i> -Propanol + carbon tetrachloride	11	293.15	225.1052	−104.6465	12.2	11.6	12.1	11.4	6.6	[43]
<i>n</i> -Butanol + carbon tetrachloride	11	293.15	178.3019	−100.6528	7.9	6.6	7.9	6.6	4.5	[43]
<i>n</i> -Propanol + toluene	15	298.15	217.6398	−37.2243	25.4	26.2	23.2	22.3	9.3	[44]
<i>Polar + polar</i>										
Diethyl ether + chloroform	8	298.15	−10.7778	−23.1012	1	3.4	1.2	4.5	0.8	[45]
Acetone + chloroform	43	298.15– 328.15	67.6603	−78.6114	2.1	1.9	2.1	2.1	1.5	[46,39,36,47]

Acetone + 1,2-dichlorobenzene	13	283.15– 303.15	35.5799	10.0297	2	8.6	2.2	6.1	1.8	[40]
Chloroform + acetic acid	28	298.15	7.7763	–18.7927	0.9	1.4	0.9	1.5	0.9	[48]
Acetic acid + 5-methyl-2-hexanone	19	283.15– 303.15	56.6768	–61.9336	2.3	3.1	2.3	3.1	3.5	[40]
Acetic acid + methyl isobutyl ketone	20	283.15– 303.15	6.123	–22.667	1.8	1.8	2	1.4	1.3	[40]
Acetic acid + <i>n</i> -butyl acetate	18	283.15– 303.15	58.9295	–62.9653	1.2	3	1.5	2.4	2.2	[40]
Acetic acid + water	19	283.15– 303.15	148.1547	–14.3877	7.2	6.4	7.1	6.1	4.7	[40]
Isobutyric acid + water	14	283.15– 303.15	270.1402	36.7759	39.3	56.1	39.3	56	6	[40]
Acetone + water	45	298.15– 328.15	152.4723	81.2199	17.4	17.1	13.8	13.5	3.5	[39,36,47]
Methyl isopropyl ketone + water	8	293.15– 298.15	137.0036	130.5447	1.3	8.6	1.1	7.9	0.9	[9]
Methanol + water	25	278.15– 313.13	194.5302	–10.7575	9	3.8	8.5	3.4	2.5	[49,50]
Ethanol + water	24	313.15– 346.15	215.7552	–67.3855	14.1	9.6	14.1	9.6	5.2	[47]
<i>n</i> -Butanol + water	36	298.15	217.281	–68.992	11.1	11.9	10.8	11.2	2.8	[9]
Dimethylformamide + water	10	278.15	61.7660	–3.5889	2	26.9	1.7	10.4	1.4	[13]
<i>n</i> -Methylpyrrolidone + water	10	278.15	136.4422	–54.0832	8.2	34.8	8.1	26.6	3.1	[13]
Grand average	1042				5.6	7.6	5.1	6.7	2.3	

$$^a \text{AAD}(\%) = \sum_{i=1}^n |(D_{12,i}^{\text{cal}} - D_{12,i}^{\text{exp}}) / (D_{12,i}^{\text{exp}})| \times 100.$$

positions (λ^2). For a fluid mixture, a thermodynamic factor, which is the partial derivative of activity with respect to composition, can be combined with the averaged limiting diffusion coefficients to express the mutual diffusion coefficient. On the other hand, the diffusion coefficient can be written in as the product of λ_m^2 and k_{am} from the absolute reaction rate theory. Taking the k_{am} in Eq. (7) as an effective specific rate where the nonideality of the fluid mixture is included in the local composition parameters, the diffusion coefficient is then written as:

$$D = \lambda_m^2 k_{am} = \lambda_m^2 \prod_{i=1}^n \left(\frac{kT}{2\pi m_i} \right)^{x_i/2} \exp \left(\frac{z}{2kT} \sum_{i=1}^n x_i q_i \sum_{j=1}^n U_{ji} \theta_{ji} \right) \quad (8)$$

where the distance parameter is assumed to follow the simple mixing rule

$$\lambda_m = \sum x_i \lambda_i \quad (9)$$

To derive the mutual diffusion coefficient, we consider a lattice fluid mixture consisting of components 1 and 2. When these two components interchange their positions, there results changes in the frequency of movement and the distance of equilibrium position. Since k_{am} and λ_m are functions of composition, their derivatives with respect to the composition of component i ($i = 1$ or 2) are

Fig. 1. Calculation results for the mutual diffusion coefficients of the binary mixtures of n -alkenes.

Fig. 2. Calculation results for the mutual diffusion coefficients of the binary mixture cyclohexane(1)+benzene(2) at various temperatures.

required to express the effect due to the interchange of molecular positions in the mutual diffusion process. Also, the number of available sites for the movement of component i ($i = 1$ or 2) during the mutual diffusion process is proportional to the mole fraction of the other component. The product of the number of available sites for the molecular movement and the derivatives of the frequency or distance parameter with respect to composition gives the effective absolute reaction rate parameters for the mutual diffusion process:

$$\ln k_{a,12} = x_2 \left[\frac{\partial(n \ln k_{am})}{\partial n_1} \right]_{T,P,n_2} + x_1 \left[\frac{\partial(n \ln k_{am})}{\partial n_2} \right]_{T,P,n_1} \quad (10)$$

$$\ln \lambda_{12} = x_2 \left[\frac{\partial(n \ln \lambda_m)}{\partial n_1} \right]_{T,P,n_2} + x_1 \left[\frac{\partial(n \ln \lambda_m)}{\partial n_2} \right]_{T,P,n_1} \quad (11)$$

where k_{am} and λ_m are expressed by Eqs. (7) and (9) for a binary mixture, respectively. The mutual diffusion coefficient for a binary mixture is then written analogously to Eq. (8) as

$$\ln D_{12} = 2 \ln \lambda_{12} + \ln k_{a,12} \quad (12)$$

Fig. 3. Comparison of the calculated results for the mutual diffusion coefficients of the binary mixture acetone(1) + benzene(2) at 298 K from various correlation methods.

Substituting the expressions of $k_{a,12}$ and λ_{12} , the mutual diffusion coefficient is:

$$\begin{aligned}
 \ln D_{12} &= \ln D_{21} \\
 &= 2 \left\{ \ln(x_1 \lambda_1 + x_2 \lambda_2) + \frac{x_2 \lambda_1 + x_1 \lambda_2}{x_1 \lambda_1 + x_2 \lambda_2} - 1 \right\} \\
 &\quad + \frac{1}{2} \left\{ x_2 \ln \frac{kT}{2\pi m_1} + x_1 \ln \frac{kT}{2\pi m_2} \right\} + \frac{z}{2kT} \{ x_2 q_1 U_{11} + x_1 q_2 U_{22} \} \\
 &\quad - \{ x_2 q_1 (\theta_{21}^2 \ln \tau_{21} + \theta_{22}^2 \tau_{12} \ln \tau_{12}) + x_1 q_2 (\theta_{12}^2 \ln \tau_{12} + \theta_{11}^2 \ln \tau_{21}) \}
 \end{aligned} \tag{13}$$

The mutual diffusion coefficient in Eq. (13) is divided into two parts, representing the combinatorial and residual contributions, respectively:

$$\ln D_{12} = \ln D_{12}^{\text{combinatorial}} + \ln D_{12}^{\text{residual}} \tag{14}$$

Fig. 4. Calculation results for the mutual diffusion coefficients of the binary mixture ethanol(1)+benzene(2) at various temperatures.

where

$$\ln D_{12}^{\text{combinatorial}} = 2 \left\{ \ln(x_1 \lambda_1 + x_2 \lambda_2) + \frac{x_2 \lambda_1 + x_1 \lambda_2}{x_1 \lambda_1 + x_2 \lambda_2} - 1 \right\} + \frac{1}{2} \left\{ x_2 \ln \frac{kT}{2\pi m_1} + x_1 \ln \frac{kT}{2\pi m_2} \right\} + \frac{z}{2kT} \{x_2 q_1 U_{11} + x_1 q_2 U_{22}\} \quad (15)$$

and

$$-\ln D_{12}^{\text{residual}} = x_2 q_1 (\theta_{21}^2 \ln \tau_{21} + \theta_{22}^2 \tau_{12} \ln \tau_{12}) + x_1 q_2 (\theta_{12}^2 \ln \tau_{12} + \theta_{11}^2 \tau_{21} \ln \tau_{21}) \quad (16)$$

At the limiting condition of infinite dilution, the diffusion coefficients for both components in a binary liquid mixture are obtained from Eq. (13) at $x_1 = 0$ and $x_2 = 0$:

$$\ln D_1^0 = 2 \left\{ \ln \lambda_2 + \frac{\lambda_1}{\lambda_2} - 1 \right\} + \frac{1}{2} \ln \frac{kT}{2\pi m_1} + \frac{z q_1 U_{11}}{2kT} - q_1 (\ln \tau_{21} + \tau_{12} \ln \tau_{12}) \quad (17)$$

and

$$\ln D_2^0 = 2 \left\{ \ln \lambda_1 + \frac{\lambda_2}{\lambda_1} - 1 \right\} + \frac{1}{2} \ln \frac{kT}{2\pi m_2} + \frac{z q_2 U_{22}}{2kT} - q_2 (\ln \tau_{12} + \tau_{21} \ln \tau_{21}) \quad (18)$$

Based on these expressions, the mutual diffusion coefficient of a binary mixture can be expressed in terms of the limiting values and the following composition dependence:

$$\begin{aligned} \ln D_{12} = & x_2 \ln D_1^0 + x_1 \ln D_2^0 \\ & + 2 \left\{ x_1 \ln \frac{x_1}{\phi_1} + x_2 \ln \frac{x_2}{\phi_2} \right\} + 2 x_1 x_2 \left\{ \frac{\phi_1}{x_1} \left(1 - \frac{\lambda_1}{\lambda_2} \right) + \frac{\phi_2}{x_2} \left(1 - \frac{\lambda_2}{\lambda_1} \right) \right\} \\ & + \left\{ x_2 q_1 [(1 - \theta_{21}^2) \ln \tau_{21} + (1 - \theta_{22}^2) \tau_{12} \ln \tau_{12}] \right. \\ & \left. + x_1 q_2 [(1 - \theta_{12}^2) \ln \tau_{12} + (1 - \theta_{11}^2) \tau_{21} \ln \tau_{21}] \right\} \end{aligned} \quad (19)$$

where ϕ_i ($i = 1$ or 2) is defined as

$$\phi_i = \frac{x_i \lambda_i}{\sum_{i=1}^2 x_i \lambda_i} \quad (20)$$

Eq. (19) is employed in correlating the mutual diffusion coefficients of binary liquid mixtures. It is named the UNIDIF equation since it resembles the functional expression of the UNIQUAC model. To

Fig. 5. Comparison of the calculated results for the mutual diffusion coefficients of the binary mixture methanol(1)+water(2) from various correlation methods.

apply the UNIDIF equation, the limiting diffusion coefficients are taken from either experimental data or from empirical correlation equations. The equilibrium distance parameter λ_i is assumed to be proportional to the cubic root of either the molecular volume or volume parameter r_i in the UNIQUAC model. The interaction parameters a_{ij} (i or $j = 1$ or 2) are regressed from experimental data of binary mutual diffusion coefficients.

3. Results and discussion

Mutual diffusion coefficients of binary nonpolar and polar liquid mixtures are correlated in this study using the UNIDIF model with two binary parameters. Calculation results from other correlation equations, as listed in Table 1, are also compared in this work. The correlative equations listed in Table 1 contain the limiting diffusion coefficients, molar volumes and viscosities of pure fluids, and the thermodynamic factor which is the partial derivative of the activity with respect to composition. The limiting diffusion coefficients are taken from experimental data whenever they are available. The thermodynamic factor required to compare the correlative equations listed in Table 1 is evaluated by employing either the UNIQUAC or the NRTL activity coefficient model, with the binary parameters

Fig. 6. Comparison of the calculated results for the mutual diffusion coefficients of the binary mixture acetone(1)+water(2) at 298 K from various correlation methods.

in the activity coefficient models regressed using experimental mutual diffusion coefficient data. The calculation results of this study, and the comparison with those from the modified Darken and Vignes equations are listed in Table 2. For the binary mixtures of *n*-alkanes, no binary interaction parameter in either model is included, and only the combinatorial part of the UNIQUAC equation is included in evaluating the thermodynamic factor for the modified Darken or Vignes equation. The calculation results from the UNIDIF model are satisfactory and the absolute average deviation (AAD) in mutual diffusion coefficient is 1.6%, which is superior to those from the modified Darken or Vignes equations. Fig. 1 presents the comparison of the calculated results from the UNIDIF model for the *n*-alkane binary systems of *n*-hexane + *n*-dodecane and *n*-heptane + *n*-tetradecane with those from the modified Darken and the Vignes equations. It is demonstrated that the UNIDIF model gives good prediction results without any fitted parameter. The modified Darken and Vignes equations with thermodynamic factor evaluated from the combinatorial UNIQUAC model yield significant errors. For the nonpolar + nonpolar binary mixtures, the UNIDIF model yields comparable results to those from the other two correlative equations, all with their optimally fitted binary parameters, as shown in Table 2. Fig. 2 shows the calculated results of the mutual diffusion coefficients of cyclohexane + benzene at various temperatures. Three models give comparable results with their optimally fitted binary parameters. Fig. 3 shows a typical example for a polar + nonpolar binary mixture of acetone and benzene. Five models are compared for this binary mixture. The UNIDIF and the Vignes models

Fig. 7. Comparison of the calculated results for the mutual diffusion coefficients of the binary mixture triethylamine(1) + water(2) at 292 K.

used two best-fitted parameters for the diffusion coefficients, respectively. The results for the three Cullinan type equations are directly taken from the literature data [8] where the thermodynamic factors are evaluated based on the vapor–liquid equilibrium data. It is observed that the UNIDIF and the Vignes models give good calculation results while those predicted from Cullinan type equations show appreciable errors. Fig. 4 compares the calculated results for the polar + nonpolar mixture of ethanol and benzene. The UNIDIF model yields better agreement with experimental data than that from the modified Darken equation. Figs. 5 and 6 present the calculation results for the polar aqueous mixtures. In the methanol and water binary mixture shown in Fig. 5, satisfactory results are obtained from the UNIDIF model. The modified Darken and the Vignes equations, with thermodynamic factors fitted from the NRTL model, give larger errors. The calculated mutual diffusion coefficients for the acetone + water binary mixture from various models are shown in Fig. 6. Those predicted from the Cullinan type equations and the Guerkan equation are taken from literature [8] where the thermodynamic factors are evaluated based on the vapor–liquid equilibrium data. It is again demonstrated that the UNIDIF model gives good agreement with the experimental data. The other four models show appreciable deviations in the entire composition range. Fig. 7 shows the calculated mutual diffusion coefficient results for a partially miscible mixture of trimethylamine and water at 292.15 K, where two-phase region exists between the mole fraction of trimethylamine of 0.0245 and 0.21. With two temperature-independent binary parameters in the UNIDIF model, satisfactory agreement with the

Fig. 8. Comparison of the calculated results for the mutual diffusion coefficients of the binary mixture *n*-methylpyrrolidone(1)+water(2) at 278 K.

Table 3

Correlations of the limiting diffusion coefficients of binary mixtures

Equations	Equation names	References
$D_{AB}^0 = 9.89 \times 10^{-8} T \eta_B^{-0.907} V_A^{-0.45} V_B^{-0.265}$	Siddiqi–Lucas	[5]
$D_{AB}^0 = (7.4 \times 10^{-8} (\phi M_B)^{1/2} T) / (\eta_B V_A^{0.6})$; ϕ = association factor of solvent B	Wilke–Chang	[51]
$D_{AB}^0 = 8.93 \times 10^{-8} ((V_A)/(V_B^2))^{1/6} ((P_B)/(P_A))^{0.6} (T)/(\eta_B)$	Tyn–Calus	[52]
$D_{AB}^0 = [(9.97 \times 10^{-8}) / ((I_A V_A)^{1/3}) + (2.40 \times 10^{-8} A_B S_B V_B) / (I_A S_A V_A)] (T) / (\eta_B)$; I, S, A = adjustable parameters	Nakanishi	[53]

experimental data is obtained for both coexisting liquid phases. The modified Darken and the Vignes equations, with thermodynamic factors fitted from either the UNIQUAC or the NRTL model, show large errors and even negative diffusion coefficients in some concentration ranges. Fig. 8 presents the calculated mutual diffusion coefficients for the binary mixture of *n*-methylpyrrolidone + water. The UNIDIF model yields satisfactory results with an AAD about 3%. The other two models of Carman–Stein and Leffler–Cullinan contain viscosity and thermodynamic factor in their equations. The experimental data of viscosity are taken from literature [13,14] and the thermodynamic factors are evaluated by fitting the mutual diffusion coefficient data from the NRTL equation. It is observed that

Fig. 9. Effect of the limiting diffusion coefficients on the correlation results for the binary mixture methanol(1)+carbon tetrachloride(2) at 293 K.

application of the viscosity effect does not bring useful contribution to the correlation of the mutual diffusion coefficients. Table 2 lists the comparison for the calculations of the mutual diffusion coefficients of polar + polar binary mixtures from various models. It is clearly observed that the UNIDIF model gives the best correlation results for the polar mixtures with an ADD about 3%. The other models show relatively larger peak and average deviations for the polar systems, especially for the aqueous mixtures. This work used the experimental limiting diffusion coefficients as the reference points. Correlation equations for the limiting diffusion coefficients can be applied when no experimental data are available. Four empirical equations for the limiting diffusion coefficients are listed in Table 3. Fig. 9 shows a comparison of the calculation results for the binary mixture of methanol and carbon tetrachloride with various choices of the correlative equations of the limiting diffusion coefficients. It is demonstrated that the limiting diffusion coefficients have appreciable effect in correlating the mutual diffusion coefficients in the complete concentration range, and improved correlation equations for the limiting values are required in further studies. Fig. 10 shows a distribution of calculation errors for various binary mixtures using the UNIDIF model. The symbols in Fig. 10 represent various nonpolar and polar mixtures investigated in this study. We have correlated the mutual diffusion coefficients over 1000 data points at various temperatures. The UNIDIF model derived in this study with two temperature-independent binary parameters yields an overall AAD of 2.3%, which is better than the results calculated from other models, as shown in Table 2. Fig. 10 shows that the difference between the experimental and the calculated mutual diffusion coefficients

Fig. 10. Distributions of calculated errors from this study.

from the UNIDIF model is within $\pm 0.5 \times 10^{-9} \text{ m}^2/\text{s}$. Further generalization to a group contribution model is currently undergoing.

4. Conclusion

A new correlative UNIDIF model for the mutual diffusion coefficients of binary liquid mixtures is developed in this study. This equation resembles the functional form of a UNIQUAC equation and two temperature-independent binary interaction parameters are included in the UNIDIF model. The best-fitted binary parameters of the UNIDIF model for extensive nonpolar and polar mixtures are investigated. Satisfactory correlation results are presented for the UNIDIF model of both the miscible and partially miscible systems. The UNIDIF model shows superior results to those from other correlative models with their optimal binary parameters.

5. Notations

a	Interaction energy
D	Diffusion coefficient
h	Planck constant
k	Boltzmann constant
k_a	The frequency of movement
m	Weight of a molecule
n	The number of components in a mixture
N	The number of molecules
q	Surface area fraction
P	Pressure
T	Temperature
U	Potential energy
x	Mole fraction
z	Coordination number

Greek letters

λ	Diffusion length
τ	Interaction parameter
θ	Local composition parameter
ϕ	The fraction of diffusion length, λ
ω	The number of configurations of a lattice
Ω	The partition function of a liquid mixture

Superscripts

0	Infinite dilution
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Subscripts

i, j	The property of component i, j
m	Mixture property

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