A local composition model for the prediction of mutual diffusion coefficients in binary liquid mixtures from tracer diffusion coefficients

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Abstract

In a recent publication (Moggride, 2012a), a simple equation was shown to accurately predict the mutual diffusion coefficients for a wide range of non-ideal binary mixtures from the tracer diffusion coefficients and thermodynamic correction factor, on the physical basis that the dynamic concentration fluctuations in the liquid mixture result in a reduction of the mean thermodynamic correction factor relative to the hypothetical case in which such fluctuations do not occur. The analysis was extended to cases where strong molecular association was hypothesised to occur in the form of dimerization of a polar species in mixtures with a non-polar one. This required modification of the average molecular mobility in the form of doubling the tracer diffusivity of the dimerized species (Moggridge, 2012b). Predictions were found to show good accuracy for the mixtures investigated. One of the difficulties with this approach is that it is an *a posteriori* correction: there is no *a priori* way of knowing whether strong cluster formation influences the observed molecular mobility, or what the appropriate size of the cluster is.

In this work, a modification is made to the average molecular mobility in the original equation by replacing the bulk mole fraction with local mole fraction calculated using the NRTL (non-random two liquid) model, to take account of strong molecular association that results in highly correlated movement during diffusion. The new equation enables an accurate description of mutual diffusion coefficients in mixtures of one strongly self-associating species and one non-polar species, as well as in non-ideal, non-associating mixtures. This result is significant because in this way there is no need of any prior knowledge on the degree of molecular association in the mixture for the prediction of mutual diffusion coefficients from tracer diffusivities.

Key words: tracer diffusion, mutual diffusion, local composition, thermodynamics, fluid mixture

1. Introduction

Diffusion in ideal liquid mixtures is well described by Fick's law, in which the driving force for the movement of a species is taken to be its concentration gradient. In a binary liquid mixture of species 1 and 2, the diffusive flux (J_1) can be expressed as:

$$J_1 = -D_{12} c_t \frac{dx_1}{dz} \tag{1}$$

where x_1 is the mole fraction, c_t is the total concentration, z is direction of diffusion in one dimension and D_{12} is the Fickian mutual diffusion coefficient.

However, in general, it is more correct to state that the diffusion flux originates from the deviation from equilibrium between molecular friction and thermodynamic interactions (Taylor and Krishna, 1993). Thus, from a thermodynamic perspective, the driving force is the chemical potential gradient (Gibbs 1906), giving the equation for a binary mixture:

$$J_1 = -D_{12}^* \frac{c_t x_1}{RT} \frac{d\mu_1}{dz} \tag{2}$$

where R is the gas constant, T is the absolute temperature, μ_1 is the chemical potential of component 1. D_{12}^* is an 'ideal' diffusion coefficient defining the average molecular mobility. Combination of Equations 1 and 2 gives the mutual diffusion coefficient as:

$$D_{12} = D_{12}^* \left[1 + \frac{dln\gamma_1}{dlnx_1} \right] \tag{3}$$

providing
$$c_1 = c_t x_1 \tag{4}$$

$$\mu_1 = \mu_0 + RT ln x_1 \gamma_1 \tag{5}$$

In Equations 3 and 5, γ is the activity coefficient. The term in the square bracket in Equation 3 is the thermodynamic correction factor.

Darken (1948) derived the 'ideal' diffusion coefficient D_{12}^* from the composition-dependent tracer diffusion coefficients (D_1^* and D_2^*) by employing the concept that the diffusion of each component in a binary mixture is related it to its mobility:

$$D_{12}^* = x_2 D_1^* + x_1 D_2^* \tag{6}$$

This is in agreement with molecular dynamics studies (Krishna and Van Baten, 2005) of mixtures of linear alkanes, which showed that an arithmetic average worked well in combining tracer diffusivities to give the Maxwell–Stefan diffusivity. Since Darken's formulation, there have been many attempts to validate or improve on the 'ideal' diffusion coefficient, in combination with Equation 3 to predict mutual diffusion coefficients (Carman and Stein, 1955; Oishi *et al.*, 1974; Powell *et al*, 1941; Wilke, 1949; Hartley and Crank, 1949; Caldwell and Babb, 1956; Leffler and Cullinan, 1970; Gainer, 1970; McKeigue and Gulari, 1984; Rathbun and Babb, 1966; Van Geet and Adamson, 1964; Vignes, 1966; Bosse and Bart, 2005; Cussler, 2009). More often, infinite dilution diffusion coefficients have been used as the starting point because they are more conveniently measured using conventional techniques (e.g. Van Geet and Adamson, 1964). However, none of these efforts is able to give a full description of the temperature and composition dependence of mutual diffusion coefficients for a range of non-ideal liquid mixture. In particular, such methods tend to underestimate the mutual diffusion coefficient for mixtures showing a positive deviation from Raoult's law, and overestimate it for those showing a negative deviation.

Recently, Li *et al.* (2001) incorporated the concept of local composition into the Darken equation to take account of association in a binary liquid mixture:

$$D_{12}^* = x_{22}D_1^* + x_{11}D_2^* \tag{7}$$

where x_{22} and x_{11} are the local mole fractions which are determined from the vapour-liquid equilibria using the Wilson model. Thus, the mutual diffusion coefficient becomes:

$$D_{12} = (x_{22}D_1^* + x_{11}D_2^*)\left[1 + \frac{dln\gamma_1}{dlnx_1}\right] \tag{8}$$

The same idea was later adopted by Zhou *et al.* (2013) incorporating local mole fractions with Vignes geometric average of tracer diffusion coefficients at infinite dilution. The accuracy of their predictions was somewhat improved compared to the prediction from the original Darken relation.

There have also been numerous attempts to improve on the thermodynamic correction factor (Rathbun and Babb, 1966; Cussler, 1980; Güerkan, 1987; Cullinan, 1985; Rollins and Knaebel, 1991; Clark and Rowley, 1986; Wu *et al.,* 1988; Matos Lopes *et al.,* 1988). It is generally agreed that Equation 3 exaggerates the effect of the thermodynamic correction factor on mutual diffusivity (Kosanovich and Cullinan, 1967; Ruthbun and Babb, 1966;

Cussler, 1980; Clark and Rowley, 1986). Equation 3 has also been shown to be unable to correctly explain the temperature dependence of mutual diffusivity in the vicinity of the solution critical point (Cussler, 1980). Subsequently, this behaviour as a function of temperature near the consolute point has been explained by critical point scaling laws (Clark and Rowley, 1986), as:

$$D_{12} = D_0 \left[\frac{T - T_C}{T_C} \right]^\alpha \tag{9}$$

where T_c is the consolute temperature, D_0 is a temperature independent constant and α is a parameter from dynamic scaling theory (De *et al.*, 2001), usually taken to be to be around two-thirds (Cussler, 2009; Clark and Rowley 1986; Wu el al., 1988). D'Agostino *et al.* (2011) used the temperature dependence in Equation 9 to modify the form of the thermodynamic correction factor (this assumes that the excess Gibbs energy is independent of temperature, which is usually the case over a small temperature range), giving the mutual diffusivity as:

$$D_{12} = D_{12}^* \left[1 + \frac{dln\gamma_1}{dlnx_1} \right]^\alpha \tag{10}$$

Substituting D_{12}^* with Equation 6 yields the expression for calculating the mutual diffusion coefficient from tracer diffusion coefficients:

$$D_{12} = (x_1 D_2^* + x_2 D_1^*) \left[1 + \frac{dln\gamma_1}{dlnx_1} \right]^\alpha \tag{11}$$

The parameter α holds the same physical meaning as in the critical point scaling law. The α value of 0.64 adopted by D'Agostino *et al.* (2011) successfully describes the mutual diffusion coefficients for hexane-nitrobenzene near the consolute temperature. It was argued that if the dynamic concentration fluctuations are truly driven by chemical potential then it should be possible to extend the equation (with α=0.64) over a wider range of temperatures and compositions, even far from the consolute point. This was validated for a range of other non-ideal binary liquid mixtures where there is not a strong correlation between the motions of different molecules (Moggridge, 2012a, D'Agostino *et al.*, 2013).

The use of weighted average of tracer diffusion coefficients assumes that the tracer diffusivity of each species is identified with its molecular mobility; this is correct if the molecules move independently. If one or more species in a liquid mixture show strong self-association, the motion of different molecules becomes strongly correlated, and this

assumption breaks down. This has been formalised by the use of velocity cross-correlations (McCall and Douglass, 1967; Weingärtner, 1990). The expression for predicting mutual diffusion coefficients in such cases (i.e., mixtures in which one species is hypothesized to dimerize) was obtained by Moggridge (2012b) as:

$$D_{12} = (x_1 D_2^* + 2x_2 D_1^*) \left[1 + \frac{d ln \gamma_1}{d ln x_1} \right]^\alpha \tag{12}$$

In which the value of 0.64 for α was retained. This equation was validated for the case of triethylamine-water mixtures over the whole composition range at temperatures between 5°C and 18°C (D'Agostino *et al*., 2012). A further study of four mixtures, methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride and ethanol-carbon tetrachloride, showed that predictions of mutual diffusion coefficients using Equation 12 match very well the experimental values for alcohol mole fractions above 0.2. At low alcohol concentrations, the assumption of dimerization fails; in the limit of infinite dilution the molecules must exist as monomers. Thus Equation 12 is not able to describe accurately the mutual diffusion coefficient of the full composition range.

In general, modifications of Equation 3 for mutual diffusivity prediction based on the Darken equation rely on either taking into account the effect of molecular association on diffusion or scaling down the effect of the thermodynamic correction factor. In this work, based on the concept of local composition effects on the molecular mobility term introduced by Li *et al.* (2001), and based on scaling law considerations for the thermodynamic factor described in D'Agostino *et al*. (2011), the following equation is proposed for the prediction of mutual diffusion coefficients of binary liquid mixtures from tracer diffusivity values:

$$D_{12} = (x_{11} D_2^* + x_{22} D_1^*) \left[1 + \frac{d ln \gamma_1}{d ln x_1} \right]^\alpha \tag{13}$$

in which molecular association is accounted for by using the local mole fraction of each species, while the scaling power α to the thermodynamic correction factor is retained. This equation will be evaluated for four liquid mixtures (methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride and ethanol-carbon tetrachloride) in which the movement of molecules are hypothesised to be highly correlated as a result of strong species self-association. (i.e., described well by Equation 12), as well as for mixtures where such correlation is not expected (i.e., where Equation 11 is adequate to describe their mutual diffusion coefficients). The significant advantage of Equation 13 is that it enables predictions

of mutual diffusion coefficient for binary liquid mixtures without making any assumption about whether highly correlated movement occurs or not.

A reliable method for predicting mutual diffusion coefficients from tracer diffusion data would be very useful, because obtaining accurate tracer diffusivities is now routine using PFG-NMR (See for example Stejskal and Tanner, 1965; Kukla *et al.*, 1996) and molecular dynamics simulation also allow their calculation (See for example Ferrario *et al.*, 1990; Krishna and Van Baten, 2005). It would be therefore become possible to determine with good accuracy liquid mutual diffusion coefficients in situations where their measurements is challenging, such as within porous materials.

2. Method

2.1. Diffusion and VLE data

The mixtures studied in this work are methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride, ethanol-carbon tetrachloride, acetonitrile-water, acetone-water, acetone-carbon tetrachloride, heptane-benzene, hexane-benzene, methanol-water, acetone-benzene, octamethylcyclotetrasiloxane-benzene, octamethylcyclotetrasiloxane-carbon tetrachloride, acetone-chloroform and diethyl ether-chloroform at 25°C, and water-N-methylpyrrolidone at 20°C. The mutual diffusion and tracer diffusion coefficients and VLE data of the mixtures are from the same sources as those in Moggridge (2012a) and Moggridge (2012b), except that tracer diffusion coefficients for acetone-chloroform are from D'Agostino *et al*. (2013). Mutual diffusion coefficients, tracer diffusion coefficients and VLE data for both octamethylcyclotetrasiloxane-benzene and octamethylcyclotetrasiloxane-carbon tetrachloride at 25°C are taken from Marsh (1968a), Mills and Hertz (1980) and Marsh (1968b).

In two cases (methanol-carbon tetrachloride and ethanol-benzene) VLE data are not available at 25°C, the temperature at which both mutual and tracer diffusion data are available. In these cases, the thermodynamic correction factors and interaction parameters used for calculating the local mole fractions for methanol-carbon tetrachloride are interpolated from those calculated from the VLE data at 20°C and 30°C. The thermodynamic correction factors and interaction parameters used for calculating the local mole fractions for ethanol-benzene are extrapolated from the thermodynamic correction factors and

interaction parameters calculated by fitting the VLE data at 30°C and 40°C based on the same assumptions.

The predicted mutual diffusion data is compared to the experimental mutual diffusion data available in the literature. In order to achieve predictions of mutual diffusivity values at compositions different from those at which tracer diffusivity values are available, the tracer diffusion data are interpolated with best-fit polynomials (of order one to four). It is reasonable to assume that tracer diffusion coefficients vary rather smoothly, though there can be significant changes as a function of composition. In cases where there is significant noise in tracer diffusion data, the polynomial interpolation also has the effect of smoothing the data. Some of the interpolated curves are shown in Figures 2-9.

2.2.   Local mole fractions

Li *et al*. (2001) obtained the local mole fractions from local volume fractions calculated from the parameters of the Wilson model, obtained by fitting to the VLE data of the binary mixture. In this paper, the NRTL model will be used as the local mole fractions (x_{11} and x_{22}) can be straightforwardly obtained using the two interaction parameters (G_{21} and G_{12}):

$$x_{11} = \frac{x_1}{x_1 + x_2 G_{21}}, \qquad x_{22} = \frac{x_2}{x_2 + x_1 G_{12}} \qquad (14)$$

given $$G_{12} = exp(-\varepsilon_{12}\tau_{12}), \qquad G_{21} = exp(-\varepsilon_{12}\tau_{21}) \qquad (15)$$

and $$\tau_{12} = \frac{g_{12} - g_{22}}{RT}, \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (16)$$

ε_{12} is the   non-randomness term; larger values indicate higher non-randomness of the mixture. Renon and Prausnitz (1969) suggested that the value of ε_{12} is characteristic of the nature of the pure components of 1 and 2, varying from 0.2 - 0.55, and is independent of temperature. The NRTL interaction parameters necessary to calculate local mole fractions were obtained by fitting to VLE data. Following Renon and Prausnitz (1969)'s recommendation, the value of ε_{12} was set at 0.47 for the mixtures of higher non-randomness in which there is one self-associating species with one non-polar substance (i.e. methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride and ethanol-carbon tetrachloride), while an ε_{12} of 0.30 was used for other non-ideal binary mixtures. With the pre-determined ε_{12} value, G_{12} and G_{21} are determined by making a least squares fit of pressure to literature VLE data with $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$ as floating parameters, using:

$$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat} \tag{17}$$

where P is the total vapour pressure of the mixture, P^{sat} is saturated pressure of each component. The activity coefficients (γ_1 and γ_2) are expressed as:

$$ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right] \tag{18}$$

$$ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{19}$$

The local mole fractions for acetonitrile-water at 25°C are calculated from the excess Gibbs energy data given by French (1977). A least squares fit is made to the excess Gibbs energy data (G^E), expressed in NRTL parameters as:

$$\frac{G^E}{RT} = x_1 x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1 G_{12}}\right) \tag{20}$$

2.3. Thermodynamic correction factor

The thermodynamic correction factors are calculated from VLE data available in the literature. Numerical integration is used to extract the values of activity coefficients as a function of composition. Using the Gibbs-Duhem equation and assuming the vapour phase to be ideal, the vapour phase mole fraction (y_i) can be calculated from:

$$dy_i = \frac{y_i(1 - y_i)}{(y_i - x_i)P}dP \tag{21}$$

The activity coefficients can be obtained from:

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}} \tag{22}$$

The VLE data are smoothed using second to fourth order polynomials. In regions of VLE profile that cannot be satisfactorily fit with polynomials, the following function is used to describe the total vapour pressure in the composition region:

$$P = P_j^{sat} + \{[A + Bx_i][1 - exp(Cx_i)]\} \tag{23}$$

where A, B and C are adjustable parameters to be optimised via least squares fit to the VLE data. This is similar to the piecewise fitting method of Bollen (1999).

Each integration was carried out using the fourth order Runge-Kutta method using a composition increment of Δx_1=0.005. Starting points for the integration are obtained at the most dilute points by assuming that the dilute component obeys Henry's law and the concentrated component obeys Raoult's law. Values of dlnγ_1/dlnx_1 are calculated for each increment of mole fraction by linear interpolation. The increments are sufficiently small so that the error introduced by the linear interpolation is negligible.

It has been argued by Van Ness (1970) that the numerical integration of the coexistence equation must proceed in the direction of increasing pressure. Thus, in the mixtures of methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride and ethanol-carbon tetrachloride where the VLE profile shows a positive boiling pressure azeotrope, integrations are carried out separately from both x_1=0 and x_1=1 to the azeotrope. In the mixture of acetone-chloroform and acetone-diethyl ether where the VLE profile shows a negative boiling pressure azeotrope, there is no way to start the integration from the azeotrope with the same assumptions. In this case, the thermodynamic correction factors are calculated using the NRTL model with the same parameters used for calculating the local mole fractions. The thermodynamic correction factors for acetonitrile-water at 25°C are calculated directly from the activity coefficients reported by French (1987). The gradient of lnγ_i versus lnx_i at each composition is obtained by fitting a series of quadratics to a rolling set of five points. The thermodynamic correction factors calculated from this method are in agreement with those extrapolated by numerically integrating French's VLE data at 35°C, assuming that the excess Gibbs energy is independent of temperature between 25°C and 35°C.

Instead of the numerical integration method used, NRTL, Wilson or UNIQUAC models could have been used to calculate the thermodynamic correction factor, again by fitting to the VLE data. We have tested each of these methods for each mixture studied. In most cases, NRTL, Wilson and UNIQUAC yield similar thermodynamic correction factors to those obtained by numerical integration. Greater discrepancy may be encountered for highly non-ideal mixtures, such as methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride or ethanol-carbon tetrachloride, which the activity coefficient models are unable to accurately describe. For this reason, we have preferred to use the numerical integration method to obtain the thermodynamic correction factors for all mixtures, since it gives reliable results for all systems, as long as good quality VLE data is available. It has been observed that different models can provide estimates of $ln\gamma_i$ that give equally good fits of the vapour-liquid equilibrium data, but have significantly different first derivatives of $ln\gamma_i$ (and hence

thermodynamic correction factors) (Taylor and Kooijman, 1991); this is particularly true for highly non-ideal mixtures and when the VLE data is "thin" across the composition range. This is another reason to consider numerical integration a more reliable method to calculate thermodynamic correction factors, as $ln\gamma_i$ is calculated from VLE point by point without fitting the range of VLE data as a whole. Thus the uncertainty of the results is entirely a consequence of the quality of VLE data being used.

3. Results and discussion

Table 1 shows the calculated NRTL parameters for the binary mixtures considered. The average relative deviations (ARDs) from the experimental pressure data are in the range of 0.05-2.8%. The fitting of VLE data for methanol-benzene mixtures at 25°C is shown in Figure 1, giving an ARD of 1.47%. We conclude that the NRTL model can reasonably describe the total vapour pressure of the mixtures studied; thus the results of G_{12} and G_{21} should be sufficiently reliable to calculate the local mole fractions.
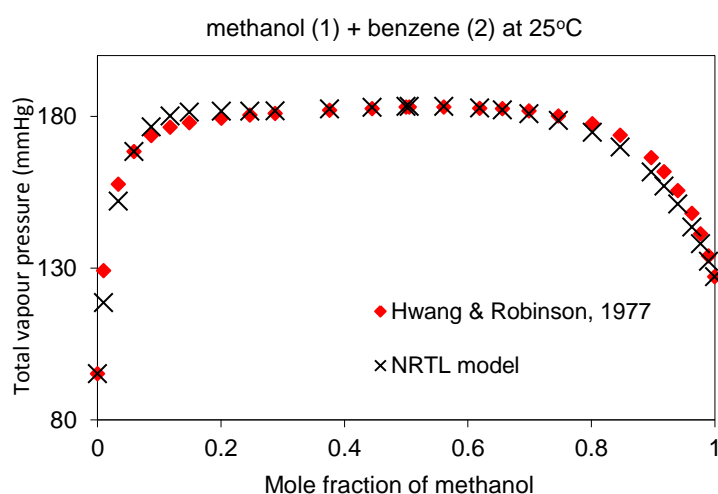

Figure 1. Fit of NRTL model to the experimental total vapour pressure of methanol-benzene mixture at 25°C from Hwang and Robinson (1977).

The minimum/maximum thermodynamic correction factors, calculated from numerical integration, or using the NRTL model for acetone-chloroform and diethyl ether-chloroform, are shown in Table 1, to give an indication of the extent of non-ideality for each mixture. Most of the mixtures exhibit positive deviation from Raoult's law (thermodynamic correction

factors less than one); mixtures of octamethylcyclotetrasiloxane-carbon tetrachloride, acetone-chloroform, water- N-methylpyrrolidone and diethyl ether-chloroform show negative deviations from Raoult's law (thermodynamic correction factors higher than one). The four mixtures (methanol-benzene, ethanol-benzene, methanol-carbon tetrachloride and ethanol-carbon tetrachloride) where there is one self-associating species fall into the category of the most non-ideal mixtures, corresponding to the value of G_{21} for the alcohol component being relatively low.

Table 1. NRTL interaction parameters and average relative deviation (ARD) of prediction of total vapour pressure.

Comp. 1	Comp. 2	G_{21}	G_{12}	ARD ΔP/P (%)	Min/max correction factor
methanol	benzene	0.320	0.582	1.47	0.07
ethanol	benzene	0.452	0.650	1.45[a]	0.14
methanol	CT	0.289	0.547	2.01[b]	0.08
ethanol	CT	0.252	0.755	1.39	0.13
acetonitrile	water	0.627	0.693	0.34[c]	0.05
acetone	water	0.687	0.757	1.28	0.16
acetone	CT	0.732	1.029	0.23	0.60
heptane	benzene	0.682	1.136	0.08	0.69
hexane	benzene	0.740	1.069	0.05	0.67
methanol	water	1.100	0.868	0.05	0.74
acetone	benzene	0.824	1.036	0.13	0.78
OMCTS	benzene	0.820	0.969	2.22	0.79
OMCTS	CT	0.955	1.110	0.11	1.12[d]
acetone	chloroform	0.936	1.358	0.11	1.49[d]
water	NMP	1.793	0.677	2.80	1.54[d]
diethyl ether	chloroform	1.159	1.206	0.82	1.60[d]

a: the averaged value of ARD of predicted VLE data at 30°C and 40°C;
b: the averaged value of ARD of predicted VLE data at 20°C and 30°C;
c: the fitting is made to excess Gibbs energy data.
d: numbers larger than 1 indicate maximum correction factor, otherwise indicate minimum correction factor.
CT: carbon tetrachloride;
OMCTS: octamethylcyclotetrasiloxane;
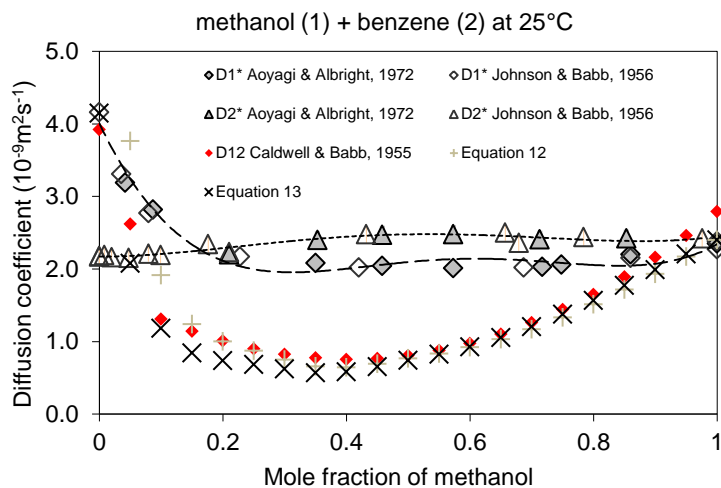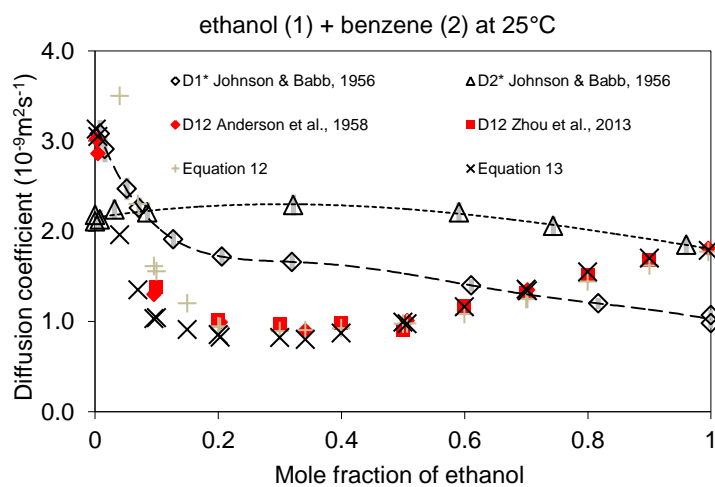NMP: N-methylpyrrolidone.

Figure 2. Prediction of mutual diffusion coefficients of methanol-benzene at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Estimation of errors in the measurements of tracer diffusion coefficients are shown as vertical bars (Aoyagi and Albright, 1972: $\pm$0.2%; Johnson and Babb, 1956: $\pm$5%). Mutual diffusion coefficients are interpolated from Caldwell and Babb, 1955 at 27.06°C and Lemonde, 1938 at 11 $^{\circ}$C.

Figure 3. Prediction of mutual diffusion coefficients of ethanol-benzene at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Estimation of errors in the measurements of tracer diffusion coefficients are shown as vertical bars (Johnson and Babb, 1956: $\pm$5%). Error estimates of mutual diffusion data are not given by the authors.
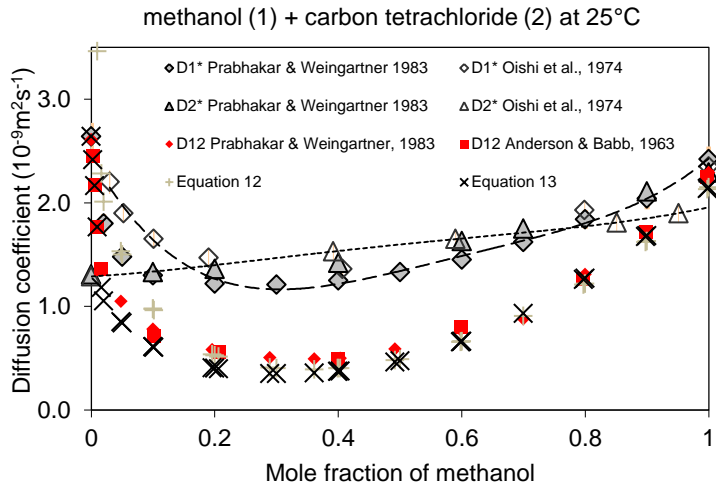
Figure 4. Prediction of mutual diffusion coefficients of methanol-carbon tetrachloride at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Estimation of errors in the measurements of tracer diffusion coefficients are shown as vertical bars (Prabhakar and Weingärtner, 1983: $\pm$1-2%; Oishi *et al.*, 1974: $\pm$5%). Error estimate of mutual diffusion data (Prabhakar and Weingärtner, 1983: $\pm$1%; the rest are not given).
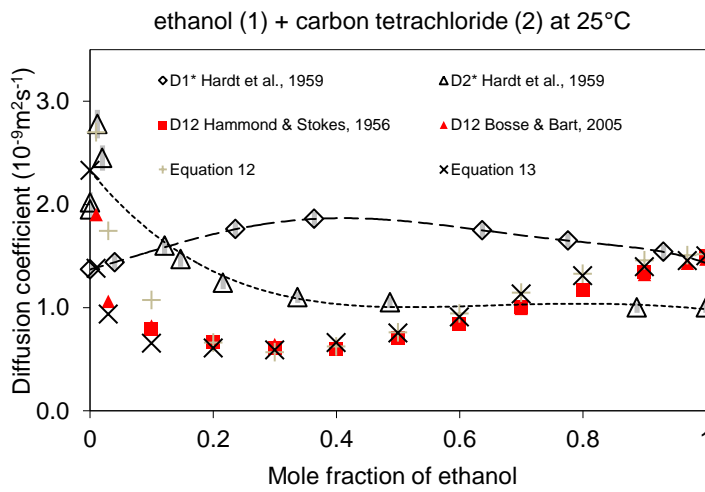

Figure 5. Prediction of mutual diffusion coefficients of ethanol-carbon tetrachloride at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Estimation of errors in the measurements of tracer diffusion coefficients are shown as vertical bars (Hardt *et al.*, 1959: $\pm$5%). Error estimate of mutual diffusion data (Hammond and Stokes, 1956: ±1.5%; Bosse and Bart, 2005: 3×10^{-11} m^{2}s^{-1}).

Figures 2-9 show comparisons of experimental and predicted mutual diffusion coefficients, for a selection of the mixtures studied. The α value used in Equations 11, 12 and 13 is taken to be 0.64 in all cases. The tracer diffusion coefficients used for the prediction are also

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indicated for each mixture. The quality of the tracer diffusion data can be assessed on the basis of the error estimation given by the original authors and the fluctuation of the data from a smooth curve. Systematic errors can be identified from the discrepancy of mutual diffusion data and tracer diffusion data at infinite dilution of both components. As the relevant data are measured by different authors, such discrepancies are most likely caused by small differences in experimental conditions, notably temperature.

For the four mixtures of one self-associating and one non-polar component, resulting in strongly correlated movement, prediction from Equation 12 (the self-associating species assumed to be a dimer) with α=0.64 is shown for comparison. As shown in Figure 2-5, the new equation (Equation 13) describes better the full composition range of mutual diffusion coefficients for these mixtures. Introducing the local composition calculated from a thermodynamic model allows the size of diffusing cluster to be successfully estimated over the full range of composition without *a priori* assumptions. The Darken expression for average molecular mobility assumes that the number of available sites for the molecular movement of one component in a mutual diffusion process is proportional to the mole fraction of the other component. In non-ideal mixtures, where self-association occurs, the mole fractions of each species in the local environment are not the same as those in the bulk liquid. Given that the molecular interchanges must initially occur into the immediate vicinity of the diffusing molecule, it seems plausible that the effect of self-association on mutual diffusion may be accounted for by the local mole fraction of each species.
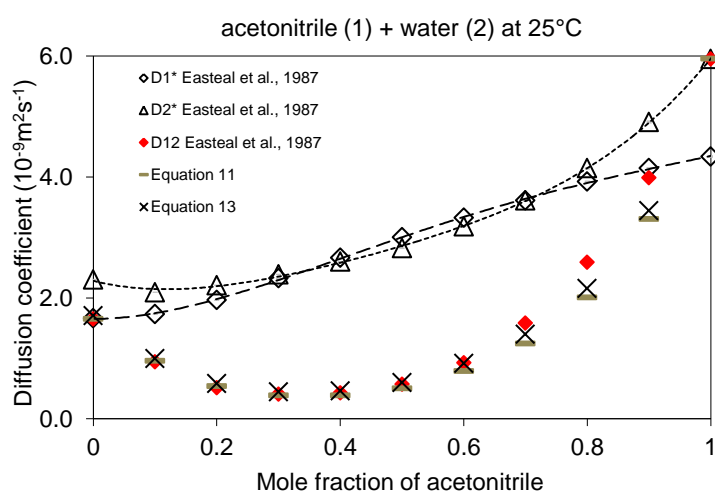

Figure 6. Prediction of mutual diffusion coefficients of acetonitrile-water at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Estimation of errors in the measurements of tracer diffusion coefficients are shown as vertical bars. Errors for tracer and mutual diffusion data are reported to be ±0.5% and ±1% by the authors, respectively.

Figure 7. Prediction of mutual diffusion coefficients of acetone-benzene at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Vertical bars on tracer diffusion coefficients are shown as estimation of errors in the measurements (Kamei and Oishi, 1972: ±5%). Error of mutual diffusion coefficients is ±1.5% given by Cullinan and Toor (1965).
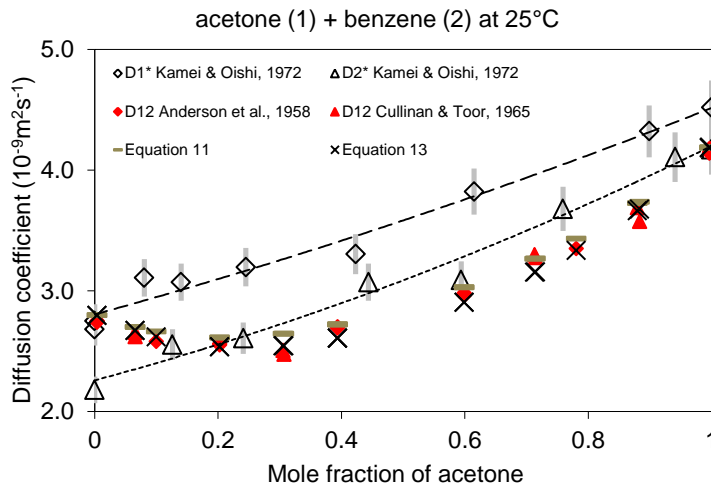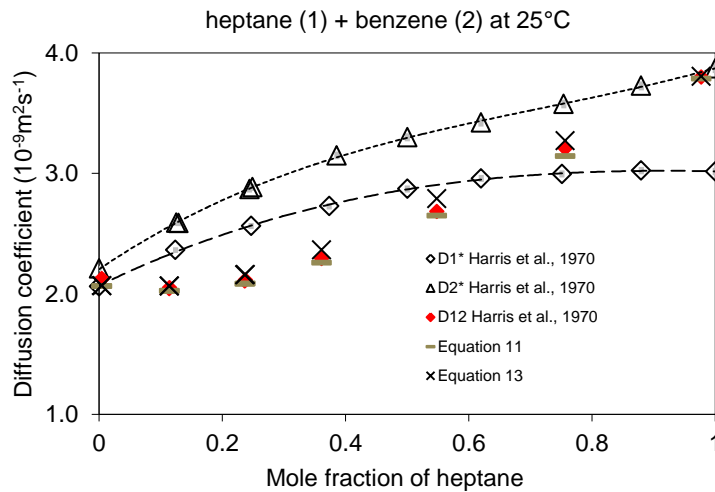

Figure 8. Prediction of mutual diffusion coefficients of heptane-benzene at 25°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Error in the measurements of tracer and mutual diffusion data is reported to be around ±1%. Vertical bars are shown for error estimate of tracer diffusion data.
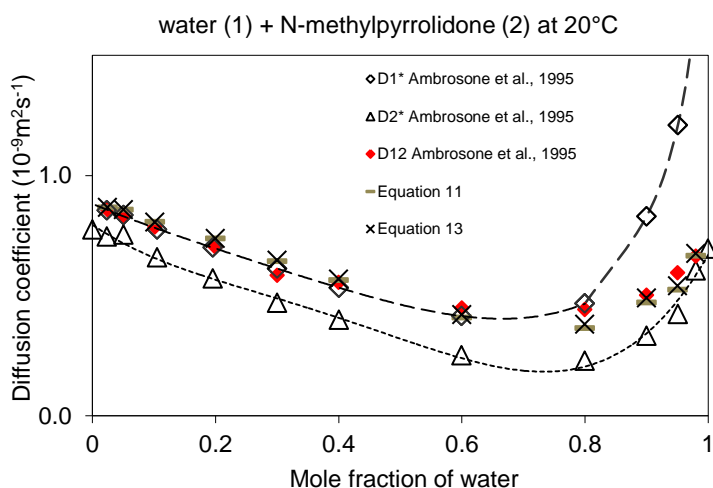
Figure 9. Prediction of mutual diffusion coefficients of water-N-methylpyrrolidone at 20°C. The broken lines on tracer diffusion data indicate best-fit polynomials. Error estimate of tracer and mutual diffusion data are not given by the authors.

Figures 6-9 show comparisons of mutual diffusion coefficients, predicted using Equations 11 and 13, to experimental mutual diffusion values taken from the literature. These mixtures show various extents of non-ideality, and exhibit either positive (acetone-benzene, heptane-benzene, and acetonitrile-water) or negative deviations (water-N-methylpyrrolidone) from Raoult's law. Equations 11 and 13 (both with α=0.64) perform almost equally well in terms of the concurrence with the literature mutual diffusion data. Indeed, in these cases, the values of local mole fractions do not differ greatly from the bulk mole fractions, as is indicated by the values of G_{12} and G_{21} (unlike for the cases of the four mixtures discussed above). It is expected that in a relatively ideal mixture, both G_{12} and G_{21} approach unity, hence Equation 13 reduces to Equation 11.

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Table 2. Comparison of the prediction of mutual diffusion coefficients with different models.

Comp. 1	Comp. 2	Average relative deviation $\Delta D_{12}/D_{12}$ (%)				Value of optimised α
		Eq. 11 α=0.64	Eq. 13 α=1	Eq. 13 α=0.64	Eq. 13 optimised α	
methanol	benzene	30.0	27.6	13.2	8.0	0.57
ethanol	benzene	26.4	30.9	9.1	7.3	0.58
methanol	CT	25.7	24.9	12.5	7.3	0.55
ethanol	CT	18.9	22.3	9.9	9.6	0.66
acetonitrile	water	9.9	27.3	7.8	6.7	0.67
acetone	water	8.3	20.0	15.0	2.8	0.42
acetone	CT	3.5	4.3	5.6	2.0	0.34
heptane	benzene	1.5	2.1	2.1	1.1	0.71
hexane	benzene	0.4	2.6	2.2	0.5	0.74
methanol	water	3.3	2.6	4.2	2.7	0.41
acetone	benzene	1.9	4.2	1.7	1.7	0.56
OMCTS	benzene	6.4	5.4	5.7	2.7	0.27
OMCTS	CT	4.2	5.9	4.2	0.4	1.32
acetone	chloroform	2.2	5.6	2.8	1.5	0.77
water	NMP	7.6	7.8	6.3	5.0	0.71
diethyl ether	chloroform	2.7	5.3	5.7	2.7	0.89
Average		9.6	12.4	6.8	3.9	0.64

Thermodynamic correction factors for acetone-chloroform and diethyl ether-chloroform are calculated using NRTL model with the same parameters used for the local mole fractions.
CT: carbon tetrachloride;
OCTMS: Octamethylcyclotetrasiloxane;
NMP: N-methylpyrrolidone.

Table 2 lists the average relative deviations of the three models in predicting mutual diffusion data compared to the literature data for the all the mixtures studied. The mixtures from methanol-benzene to acetone-water mixtures are highly non-ideal, and the thermodynamic correction factors and local mole fractions are calculated from extrapolated or interpolated values in the cases of methanol-carbon tetrachloride and ethanol-benzene; so it is unsurprising that the predictions for these mixtures show larger deviations from the experimental data than those for other mixtures, with all the three prediction models. The new model (Equation 13 with α=0.64), on average, gives the best predictions of mutual diffusion coefficients amongst the three models. The relative deviation results for Equation 12 (with α=0.64) are not less meaningful to shown as this equation is to explicitly predict of the composition range for the mixtures of methanol-benzene, ethanol-benzene, methanol-

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carbon tetrachloride and ethanol-carbon tetrachloride. Comparisons to other models can be seen in Figures 2-5.

It is interesting to note that using α=1 (Equation 13) fails for the most non-ideal mixtures, from methanol-benzene to acetone-water, with average relative deviations all above 20%, while the prediction with Equation 13 (α=0.64) remains good in these cases. Optimised values of α, obtained by least squares fit of Equation 13 to the literature mutual diffusion coefficients, with α as the only variable, are also given in Table 2, along with the resulting average relative deviations. The averaged value of optimised α is also 0.64; and in the majority of cases it is close to 0.64.This suggests that the use of the constant scaling factor of 0.64, a value consistent with critical point scaling laws theory (Cussler, 1980), is appropriate for the prediction of mutual diffusion coefficients for non-ideal binary liquid mixtures. Even in the mixtures of octamethylcyclotetrasiloxane-benzene and octamethylcyclotetrasiloxane-carbon tetrachloride where the optimised α can be as small as 0.27 or as large as 1.32, the use of 0.64 do not significant reduce the accuracy of predictions.

Table 3: Average relative deviations of mutual diffusion coefficient prediction using Equation 13 with α=0.64 in which the local mole fractions are calculated using NRTL, Wilson and UNIQUAC models.

Comp. 1	Comp. 2	Average relative deviation $\Delta D_{12}/D_{12}$ (%)			
		NRTL	NRTL[a]	Wilson	UNIQUAC
methanol	benzene	13.2	9.4	27.6	6.4
ethanol	benzene	9.1	9.1	9.6	16.3
methanol	CT	12.5	12.0	26.6	14.6
ethanol	CT	9.9	9.6	25.8	11.0
acetonitrile	water	7.8	8.0	37.2	7.3
acetone	water	15.0	14.6	7.9	12.0
acetone	CT	5.6	5.6	6.4	3.1
heptane	benzene	2.1	1.9	9.1	2.7
hexane	benzene	2.2	2.3	10.5	3.6
methanol	water	4.2	3.4	3.8	2.6
acetone	benzene	1.7	2.0	9.6	4.2
OMCTS	benzene	5.7	6.2	7.6	2.3
OMCTS	CT	4.2	4.6	3.5	2.7
water	NMP	6.3	5.9	7.4	12.2
Average		7.1	6.8	13.8	7.2

Equation 11 with α=0.64 gives poor predictions for mixtures of one self-associating and one non-polar component. In these cases, substantial improvement is achieved by using local mole fractions, calculated from the NRTL model, in place of bulk mole fractions (Equation 13); on the assumption that the probability of the molecular interchange in a mutual diffusion process is related to the local surroundings of the diffusing molecules. In order to calculate the local mole fractions for these mixtures using NRTL model, a value of non-randomness parameter (ε_{12}) must be assumed, based on the recommendations of Renon and Prausnitz (1969). The choice of ε_{12} values for different type of mixtures may be called in question. Since the original authors of the NRTL model stated that appropriate values of the non-randomness parameter, ε_{12} were based on fitting a large number of systems (Renon and Prausnitz, 1969), it is possible that ε_{12} could effectively also be treated as a variable parameter to be optimised, along with $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$; this is indeed fairly common practise in using the NRTL model, although it is important to ensure that the optimized value of ε_{12} is not outside the expected range given by Renon and Prausnitz (1969). Local mole fractions can also be calculated using other local composition models. Using two adjustable energy parameters, the Wilson and UNIQUAC models can give local volume fractions and local area fractions, respectively, by fitting to the VLE data of a liquid mixture. The local mole fractions are calculated from local volume/area fractions by multiplying the ratio of total molar volume/surface area of the mixture to the molar volume/area of each component.

Table 3 summarises the average relative deviation of mutual diffusion coefficient prediction from Equation 13 (α=0.64) with the local mole fractions calculated using different methods. In order to check the differences in prediction only as a consequence of the different models for the calculation of local mole fractions, comparison is limited to those mixtures for which the thermodynamic correction factors are calculated using numerical integration (i.e. acetone-chloroform and diethyl ether-chloroform, for which numerical integration is not possible due to the presence of minimum boiling pressure azeotropes, are excluded). Using the NRTL model for local mole fraction gives a better fit to the literature mutual diffusion coefficients than using the Wilson model, especially for highly non-ideal mixtures of one self-associating and one non-polar component. When the non-randomness factor (ε_{12}) in NRTL

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model is treated as a floating variable, the accuracy of prediction is improved in some cases. This may be because the use of three variable parameters allows a more accurate description of the VLE compared to a two parameters model. The use of UNIQUAC for local mole fractions also gives good correspondence to the mutual diffusion data in most cases, although the deviation becomes unexpectedly large in the case of water-NMP. Equation 13 (α=0.64) using the NRTL model (with the recommended values of ε_{12}) to calculate the local mole fractions appears to be satisfactory, and slightly superior to the use of other activity coefficient models; and is capable of predicting mutual diffusion coefficients over the full composition range for mixtures of one self-associating and one non-polar components, which results in correlated movement, as well as for other non-ideal mixtures studied here.

4. Conclusion

In a recent publication (Moggridge, 2012a), a simple equation was shown to accurately predict the mutual diffusion coefficients for a wide range of non-ideal binary mixtures, from the tracer diffusion coefficients and thermodynamic correction factor, on the physical basis that the dynamic concentration fluctuations in the liquid mixture result in a reduction of the mean thermodynamic correction factor relative to the hypothetical case in which no such fluctuation occurs. The analysis was extended to cases where strong molecular association was hypothesised to occur in the form of dimerization of a polar species mixed with a non-polar one. This required modification of the average molecular mobility in the form of doubling the tracer diffusivity of the dimerized species (Moggridge, 2012b). The difficulty with this approach is that it is an *a posteriori* correction: there is no *a priori* way of knowing whether strong cluster formation influences the observed molecular mobility, or what the appropriate size of the cluster is.

In this work, a modification is made to the average molecular mobility in the original equation by replacing each bulk mole fraction with the local mole fraction to take account of the effect of strong molecular association that results in correlated movement during a diffusion process. Some deviations are observed in the prediction of mutual diffusion coefficients with local compositions calculated using various thermodynamic models. NRTL model results in more accurate predictions in general, so it is preferable. The factor α of 0.64 is retained for moderating the thermodynamic correction factor, given the deviations of prediction using α of 0.64 are well in the range of error compared to using optimised α value. The new modelis shown to enable accurate description of mutual diffusion coefficients for

mixtures of one strongly self-associating species and one non-polar species, as well as for non-ideal, non-associating mixtures. This result is significant, because there is no need of any prior knowledge of the degree of molecular association in the mixture for the prediction of mutual diffusion coefficients from tracer diffusivities.

Acknowledgements

Nomenclature

A, B, C Adjustable parameters to fit VLE data of a binary mixture [mmHg].

D_0 Temperature independent part of abinary diffusion coefficient [m^2s^{-1}].

D_{12} Mutual diffusion coefficient in a liquid mixture of species 1 and 2 [m^2s^{-1}].

D_i^* Tracer diffusion coefficient of species i [m^2s^{-1}].

D_{ij}^* Average mobility of a liquid mixture of species i and j [m^2s^{-1}].

$g_{ji} - g_{ii}$ Energy parameter in NRTL model.

G_{ij} Interaction parameter of a binary mixture of species i and j in NRTL model.

G^E Molar excess Gibbs energy of a mixture [$Jmol^{-1}$].

P Total vapour pressure of a binary mixture [mmHg].

P_i^{sat} Saturated vapour pressure of species i at the specified temperature [mmHg].

R Universal gas constant [8.314 $Jmol^{-1}K^{-1}$].

T Temperature [K].

T_C Consolute temperature [K].

x_i Mole fraction of species i in a liquid mixture [dimensionless].

x_{ii} Local mole fraction of component i at the surrounding of i [dimensionless].

z Distance in the direction of diffusion [m].

α A power factor to the thermodynamic correction factor [dimensionless].

ε_{ij} Nonrandomness parameter in NRTL model [dimensionless].

τ_{ij} Parameter in NRTL model [dimensionless].

γ_i Activity coefficient of species i in a liquid mixture [dimensionless].

μ_1 Chemical potential of species 1 in a liquid mixture [Jmol^{-1}].

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