

**Prediction of mutual diffusion coefficients in binary liquid systems with one self-associating component
from viscosity data and intra-diffusion coefficients at infinite dilution**

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Abstract

A new model for prediction of mutual diffusion coefficients is proposed over the whole composition range for binary liquid systems of one self-associating component and one non-polar component. The model is based on the Darken equation with the knowledge of intra-diffusion coefficients at infinite dilution of both species and viscosity data for the system, and takes into account the cluster diffusion approach with a scaling power on the thermodynamic correction factor. The model was validated to show good concurrence with the experimental mutual diffusion data. Following the analysis that the mutual diffusion coefficients at infinite dilution can be identified with the molecular intra-diffusion coefficient of the species (i.e., the intra-diffusion coefficient at infinite dilution in absence of self-association), the proposed equation was extended to binary liquid systems without significant association, though the accuracy in prediction for systems of cross associating species may be limited. The model relies on the knowledge of the viscosity of the mixture over the whole composition range and may be used as a valid alternative to models based on measuring intra-diffusion coefficients as a function of composition. Indeed, such data are not always available or are more difficult to obtain whereas viscosity measurements can be readily available and more easily measured.

Keywords: mutual diffusion, intra-diffusion, viscosity, thermodynamics, self-association in liquids

Highlights

- A prediction model for mutual diffusion coefficient in binary systems was developed.
- The model requires intra-diffusion coefficients at infinite dilution and viscosity data.
- The model predicts well mutual diffusion in systems with self-associating species.
- The model was extended to binary systems with no significant associating species, and shown limited accuracy in prediction for system of cross-association between components.
- The approach is a valid alternative for predicting mutual diffusion from viscosity.

1. Introduction

Accurate determination of mutual diffusion coefficients in binary liquid systems is crucial for a proper understanding and design of many unit operations as well as for modelling purposes. Mutual diffusion coefficients can be measured by experimental techniques such as Taylor dispersion (D'Errico et al., 2004), holographic interferometry (Sanchez and Clifton, 1978), light scattering (McKeigue and Gulari, 1984), diaphragm cell (Cain et al., 1995) etc. Due to the complexity of procedures and difficulty in controlling the precision in measurements, reported mutual diffusion coefficients by experiments are often far from adequate for applications. Thus, prediction models become very useful as an alternative to provide mutual diffusion data. A number of models for this purpose have been proposed in the literature. One of the earliest dated back to Darken (1948), who noted that the number of available sites for interchange of one component in a mutual diffusion process is proportional to the mole fraction of the other component, proposing the arithmetic average of two parameters termed intrinsic diffusion coefficients of the components, D_1 and D_2 , in the binary systems:

$$D_{12} = x_2 D_1 + x_1 D_2 \quad (1)$$

where D_{12} is the mutual diffusion coefficient and x is the mole fraction (the subscript denotes component of the system). The intrinsic diffusion coefficients are related to the intra-diffusion coefficients and the thermodynamics of the system (Darken, 1948), giving:

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

where D_1^* and D_2^* are the intra-diffusion coefficients, γ is the activity coefficient in molar fraction scale. The term in the squared bracket is the thermodynamic correction factor.

Equation 2 is known as Darken equation. A similar equation was later formulated by Vignes (1966) as geometric average of two limiting mutual diffusion coefficients at infinite dilution, which was later rationalised from Eyring's absolute reaction rate theory (Cullinan, 1966). For liquid systems with ideal or nearly ideal behaviour, predictions of Darken and Vignes equations were found to be well in agreement with the experimental diffusion data (e.g., Hardt et al., 1959; Vignes, 1966). For systems largely deviating from thermodynamic ideality, the agreement becomes poor and prediction results often significantly under-estimate mutual diffusion coefficients (e.g., Hardt et al., 1959; Bosse and Bart, 2006).

Based on either Darken or Vignes approach, improvements have been attempted to achieve more accurate predictions of mutual diffusion coefficients in various types of binary liquid systems (Caldwell and Babb, 1956; Carman and Stein, 1956; Gainer, 1970; Hartley and Crank, 1949; Oishi et al., 1974; Rathbun and Babb, 1966; Van Geet and Adamson, 1968; Leffler and Cullinan, 1970; Hsu and Chen, 1998; Hsu et al., 2000; Bosse and Bart, 2006; Moggridge, 2012a; Zhou et al., 2013). However, the accuracy of each model in prediction is inevitably reduced when it comes to systems deviating significantly from thermodynamic ideality. A brief review of some of the models can be found in Pertler et al. (1996). More often the infinite dilution diffusion coefficients were used as the starting point for prediction since they are more conveniently measured using conventional techniques.

For those non-ideal systems, Cussler (1980) proposed the cluster diffusion concept highlighting that diffusion occurs through the movement of molecules and clusters formed in the process of removing the concentration fluctuations in non-ideal concentrated solutions which is treated as an analogy of solutions near the consolute temperature or consolute point. Explicit prediction methods have been developed resulting in a scaling power on the thermodynamic correction factor, for binary mixtures near the consolute temperature and consolute point (Clark and Rowley, 1986; D'Agostino et al., 2011; D'Agostino et al., 2012; D'Agostino et al., 2013), and extended for generally non-ideal systems (Rollins and Knaebel, 1991; Cullinan, 1985; Gürkan, 1987; Moggridge, 2012a).

Among the systems, those made of a self-associating component with a non-polar one (e.g., methanol-carbon tetrachloride) are highly non-ideal. The thermodynamic correction factors are very small in both diluted and concentrated solutions and the molecular motions are highly correlated due to strong self-association of the component. This makes difficult the accurate prediction of mutual diffusion coefficients and new models have to be tailored. For example, McKeigue and Gulari (1989) employed the isodesmic association constant of the self-associating component and limits of the diffusivity-viscosity products incorporated in Darken equation to give mutual diffusion coefficient predictions for a series of short-chained alcohols mixed with carbon disulphide or benzene. However, this model cannot be applied in general because of the lack of isodesmic association constant for other systems. Li et al. (2001) assumed linear variation of the association number with composition to formulate intra-diffusion coefficients and replaced the mole fractions with local mole fractions in the Darken equation. Li et al. (2001) model was successfully applied to a wide range of binary non-ideal systems, though the deviation for systems of one strong self-associating and one non-polar component is still inevitably large, up to 20%.

Following the cluster diffusion model with a scaling power on the thermodynamic correction factor, the equation for mutual diffusion coefficient was proposed for four liquid systems of one self-associating and one non-polar component assuming dimerization of the self-associating component, resulting in doubling of its intra-diffusion coefficient (G.D. Moggridge, 2012b):

$$D_{12} = (2x_2D_1^* + x_1D_2^*) \left[1 + \frac{d\ln\gamma_1}{d\ln x_1} \right]^\alpha \quad (3)$$

where the self-associating species is denoted as component 1. The parameter α is the scaling power taken to be 0.64 from the dynamic scaling theory (De et al., 2001). Equation 3 accurately modelled the mutual diffusion coefficients for these systems for mole fractions of the self-associating component (e.g., methanol and ethanol) above 0.2, below which mutual diffusion coefficients are generally over-predicted. Further modification of replacing the mole fractions and the factor 2 in Equation 3 with local compositions (local mole fractions) calculated using Non-Random Two Liquid (NRTL) model has recently

been reported (Zhu et al., 2015). The modified model gives accurate prediction for the whole composition range, and has the important advantage that *a priori* knowledge of the presence of a strongly self-associating component is not necessary to predict the mutual diffusion coefficients for these non-ideal systems. However, the applicability of the models mentioned above is subject to the availability of the composition-dependent intra-diffusion coefficients which are calculated using molecular dynamics simulations (e.g., Krishna and Van Baten, 2005), or measured using a conventional radioactive isotope labelled diffusion set-up (e.g., Pua et al., 1970) or nowadays more routinely by PFG-NMR (e.g., D'Agostino et al., 2013).

In the cases where intra-diffusion coefficient profiles are not available, the mutual diffusion coefficients at infinite dilution for both components in the system are an attracting alternative for the prediction of mutual diffusion coefficients. In this work, a simple model for predicting mutual diffusion coefficients in binary liquid systems will be presented which is based on the combination of the mutual diffusion coefficients at infinite dilution with viscosity correlation data and the Darken equation with the scaling power, 0.64. The accuracy of prediction of this model will be examined with a series of binary liquid systems composed of one self-associating component and one non-polar component., namely, ethanol-carbon disulphide, 1-propanol-carbon disulphide, 1-butanol-carbon disulphide, 1-pentanol-carbon disulphide, methanol-carbon tetrachloride, ethanol-carbon tetrachloride, 1-propanol-carbon tetrachloride, 1-butanol- tetrachloride, methanol-benzene and ethanol-benzene. These are binary liquid systems that are highly non-ideal and the intra-diffusion coefficients cannot be measured by PFG-NMR. The systems are selected on the basis of availability of the experimental mutual diffusion coefficients and vapour-liquid equilibrium profiles. Methanol-carbon disulphide is not studied because methanol is insoluble in carbon disulphide above methanol mole fraction of 0.2 (McKeigue and Gulari, 1986). The applicability of this model will then be extended to non-ideal systems where there is no strong association, showing its limitation in prediction accuracy for systems where cross association occurs between the components. The reason of the model applicability with relation to the molecular diffusion of these types of binary liquid systems will be thoroughly discussed.

2. Model

According to Fick's Law, the flux of a component i (J_i) in a binary liquid mixture is proportional to its concentration gradient along the given axis under isothermal conditions, giving:

$$J_i = -D_i \frac{dC_i}{dz} \quad (4)$$

where C_i is the molar concentration and z is the diffusion coordinate of component i . D_i is a concentration dependent diffusion coefficient and was designated as the intrinsic diffusivity of component i (Darken, 1948; Hartley & Crank, 1949). Using the cluster diffusion approach (Cussler, 1980), the intrinsic diffusion coefficient in non-ideal liquid mixtures can be written as:

$$D_i = \frac{kT}{2\pi\eta\xi_i} \quad (5)$$

where k is the Boltzmann constant, T is absolute temperature and η is the viscosity of the mixture. This equation retains the same temperature and viscosity dependences as the Stokes-Einstein equation:

$$D_i = \frac{kT}{6\pi\eta r_i} \quad (6)$$

where the factor 2π in Equation 5 in place of 6π is originated from the time-integrated velocity correlation function for spherically symmetric molecules (Ferrell, 1970), which is not a major concern. The importance is in the use of the diffusion correlation length (ξ_i) which is an approximate measure of the average size of diffusing clusters and is related to temperature as an analogue of the size of the concentration fluctuations near the consolute point. Thus it is speculated from the critical point theories (Stanley, 1971) that:

$$\xi_i^2 \propto r_i \left[\frac{T-T_c}{T_c} \right]^{-2\alpha} \quad (7)$$

where r_i is molecular radius of the diffusing species, subscript C indicates the consolute value, and α is an exponent calculated empirically to be around two thirds from the dynamic scaling theory (De et al., 2001), being the same as in Equation 3.

If the excess Gibbs energy is independent of temperature (often a reasonable assumption over a small temperature range, since it is usually dominated by the excess enthalpy term), the thermodynamic correction factor can be transformed into terms of the temperature dependence and approximates to that close to the consolute temperature:

$$\left[1 + \frac{d\ln\gamma_i}{d\ln x_i}\right] = \left[\frac{T-T_C}{T}\right] \approx \left[\frac{T-T_C}{T_C}\right] \quad (8)$$

Thus the correlation length is related to the thermodynamic correction factor as:

$$\xi_i \propto r_i \left[1 + \frac{d\ln\gamma_i}{d\ln x_i}\right]^{-\alpha} \quad (9)$$

The chemical potential gradient in the thermodynamic correction factor is related to a change in structure through the transient formation of clusters in the fluid. If the diffusion is truly controlled by the gradient of chemical potential, at any point in a mixture with concentration fluctuations a diffusing species may experience a concentration either higher or lower than the mean concentration. In either case, the result will be that the local influence of the thermodynamic correction factor on diffusion is higher than that would be expected from the mean concentration. This means the scaling law on the thermodynamic correction factor for diffusion can be plausibly extended for mixtures for the whole composition range farther away from the consolute temperature (D'Agostino et al., 2012a). At the consolute point the driving force for the removal of these fluctuations, namely the thermodynamic correction factor, is close to zero, which is similar to what is observed in concentrated mixtures of one self-associating and one non-polar component, which are highly non-ideal. Thus the intrinsic diffusion coefficient for components in these mixtures can be similarly expressed in terms of the scaled thermodynamic correction factor by

substituting Equation 9 into Equation 5 with 2π in Equation 9 replaced with a parameter σ_i to denote the inverse proportionality:

$$D_i = \frac{kT}{\sigma_i \eta r_i} \left[1 + \frac{d \ln y_i}{d \ln x_i} \right]^\alpha \quad (10)$$

Away from the thermodynamic influence, the first part of Equation 10 reveals the molecular mobility of species i in the system, termed as molecular intra-diffusion coefficients (\mathfrak{D}_i):

$$\mathfrak{D}_i = \frac{kT}{\sigma_i \eta r_i} \quad (11)$$

In a previous paper (e.g. Moggridge, 2012a), molecular motions are assumed to be identified from the intra-diffusion coefficients, thus, molecular intra-diffusion coefficients are taken as D_1^* and D_2^* for mutual diffusion coefficient prediction. However, in the concentrated mixtures of one self-associating and one non-polar components, this is only true for the non-polar species. The self-associating species tends to form clusters; consequently, the measured intra-diffusion coefficients are lower than the molecular intra-diffusion ones (i.e., intra-diffusion of molecules in the absence of any self-association). In this case, the molecular intra-diffusion coefficient can only be identified for the mixtures at infinite dilution where both the self-associating and the non-polar components are able to diffuse in monomeric form.

In systems for which cross association between components does not occur, the molecular diffusion is predominantly influenced by the molecular size and viscosity. It is plausible to assume that the **inverse proportionality factor, σ_i , in Equation 11 is independent of composition as this can be thought of a stick-slip parameter, which is an intrinsic property of the type of system.** Thus, the molecular intra-diffusion coefficient at infinite dilution of species i can be found as an analogy of Equation 11 as:

$$\mathfrak{D}_i^\infty = \frac{kT}{\sigma_i \eta_j r_i} \quad (12)$$

where \mathfrak{D}_i^∞ is the molecular intra-diffusion coefficient at infinite dilution of species i , η_j denotes the viscosity of the other component j in pure liquid.

Combining Equations 12 with Equation 11, the molecular diffusion coefficient (\mathfrak{D}_i) becomes:

$$\mathfrak{D}_i = \frac{\eta_j}{\eta} \mathfrak{D}_i^\infty \quad (13)$$

Substituting Equations 13 and 11 into Equation 10 to have the intrinsic diffusion coefficient of species i as:

$$D_i = \frac{\eta_j}{\eta} \mathfrak{D}_i^\infty \left[1 + \frac{d \ln \gamma_i}{d \ln x_i} \right]^\alpha \quad (14)$$

In Equation 14, species i denotes either the self-associating or the non-polar component, since both components are likely to diffuse in monomeric form at infinite dilution conditions.

\mathfrak{D}_i^∞ is identical in value to the mutual diffusion coefficients at infinite dilution (Carman and Stein, 1956; Cussler, 2009), having:

$$\mathfrak{D}_i^\infty = D_{ij}^\infty \quad (15)$$

where D_{ij}^∞ denotes the mutual diffusion coefficient in the mixture of species i infinite diluted in species j .

Incorporating Equations 14 and 15 for both components into the Darken relation of Equation 1, the mutual diffusion coefficient in binary liquid systems of one self-associating component and one non-polar component (deonted components 1 and 2) can be formulated as

$$D_{12} = \frac{1}{\eta} (x_2 \eta_2 D_{12}^\infty + x_1 \eta_1 D_{21}^\infty) \left[1 + \frac{d \ln \gamma_1}{d \ln x_1} \right]^{0.64} \quad (16)$$

with the scaling power in Equation 14, α , equal to 0.64 according to Moggridge (2012a). The application of Equation 16 for prediction of mutual diffusion coefficients will be illustrated.

3. Method

3.1. Chemicals

Carbon disulphide (99.9%) and carbon tetrachloride (99.5%) were purchased from Sigma Aldrich. Methanol (99.9%), ethanol (99.9%), 1-propanol (99.9%), 1-butanol (99.9%) and 1-pentanol (99 %) were purchased from Alfa Aesar. Cyclohexane (99.9%) and acetone (99.8%) were purchased from Fischer Scientific.

3.2. Mutual diffusion coefficients

Mutual diffusion coefficients for alcohol-carbon tetrachloride systems at 20 °C are from Sanchez and Clifton (1978) and Sanchez et al. (1977). The authors gave error of 1.5 % in their measurements. Mutual diffusion coefficients for alcohol-carbon disulphide and alcohol-benzene systems at 20 °C are collected from McKeigue and Gulari (1984) and also from McKeigue and Gulari (1989). The authors reported uncertainty of 1% over most of the concentration range while higher uncertainty of 5% for samples where the mole fraction of either components is less than 0.05. The mutual diffusion coefficient data are summarised in the Supplementary Information (Tables S1-3).

Mutual diffusion coefficients for methanol-water systems at 25 °C are from Derlacki et al. (1985) and Chang et al. (2005) (collected in Table S4). The error in measurements was estimated $\pm 2\%$ by Derlacki et al. (1985) and was not given by Chang et al. (2005). The two sets of mutual diffusion data agree well.

Only one set of mutual diffusion data is available for cyclohexane-acetone from Tasić et al. (1981) at 25 °C. The uncertainty of measurements was not given. To ascertain the accuracy, mutual diffusion coefficients of this system were also measured using the Taylor dispersion method. The relative error of the measurements is approximately 2%. Details of the experiments are described as follows: the apparatus is formed by a 20 m capillary tube with an inner radius of 0.4020 (± 0.0001) mm connected to a metering pump Watson Marlow 403U/VM2 set at the flowing rate of 0.5 mL min⁻¹, the differential refractometer being a Knauer K2301. The inner radius of the tube was determined by calibration of the apparatus at 298.15 K with a 0.2 m KCl solution of which the diffusion coefficient is well-known. The

capillary tube was inserted into a thermostated water bath, while the entire apparatus is once more thermostated by an air bath at $298.15 \text{ K} \pm 0.01 \text{ K}$. The operational equation allows the determination of the mutual diffusion coefficients, D_{12} (Callendar and Leaist, 2006):

$$V_t = V_0 + V_1 t + V_{max} \left(\frac{t_r}{t}\right)^{1/2} \exp\left[-\frac{12D_{12}(t-t_r)^2}{r^2 t}\right] \quad (17)$$

where V_t is the detector output signal, V_0 is the baseline signal, is the signal drift in the detector output, V_{max} is the maximum detector output signal relative to the baseline, t is experiment time, t_r is the retention time and r the inner radius of the bore.

3.3. Intra-diffusion coefficients

PFG-NMR was used to measure the intra-diffusion coefficients for mixture of diluted alcohols in carbon tetrachloride and carbon disulphide, in order to accurately extrapolate the diffusion coefficients at infinite dilution. The uncertainty of the measurements is approximately within 3%. Details on the method have been reported previously by D'Agostino et al. (2011) and are included in the Supplementary Information. Intra-diffusion coefficients for cyclohexane-acetone system at 25°C were also measured using PFG-NMR. Intra-diffusion coefficients for methanol-water system at 25°C were obtained from Derlacki et al. (1985) (Table S4).

3.4. Viscosity

The viscosity data for methanol-benzene at 20°C , cyclohexane-acetone and methanol-water at 25°C were from Mato and Hernandez (1969), González et al. (2005) and Nikam and Nikumbh (2002) respectively. Viscosities of ethanol-benzene at 20°C are linearly extrapolated from the data at 25, 30, 35 $^\circ\text{C}$ from Mato and Coca (1970). González et al. (2005) gave their error estimate of $\pm 0.001 \text{ mPa s}$. The error in the measurements was not given by other authors.

The viscosities of alcohol-carbon disulphide systems are not available in the literature hence they were calculated by measuring the density and kinematic viscosity of the mixtures using glass pycnometer and an Ubbelohde-type suspended-level viscometer respectively. The viscometer was calibrated beforehand

with the already existing viscosity data for water and methanol from Mato and Hernandez (1969). The kinematic viscosity data were calculated with the efflux time in the viscometer measured by observing the passage of the meniscus between two horizontal marks in the upper capillary tube with an electronic stopwatch. The mixture viscosity was calculated as the product of density and the kinematic viscosity. The viscosities were also measured for methanol-carbon tetrachloride, 1-propanol-carbon tetrachloride, 1-butanol-carbon tetrachloride systems at 20 °C. The error in viscosity measurements is estimated $\pm 3\%$.

3.5. VLE data and thermodynamic correction factor

The VLE (Vapour Liquid Equilibrium) data of the studied systems at various temperatures are given in Table 1. The vapour pressures of the pure components, ethanol, 1-propanol, 1-butanol, 1-pentanol and carbon disulphide, were not given by McKeigue (1986), so that they were obtained elsewhere from Zaoui-Djelloul-Daouadji et al. (2014), Villa et al. (2005), Gimeno et al. (2011), Ronc and Ratcliff (1976) and Aracil et al. (1989) respectively VLE data of cyclohexane-acetone at 25 °C from Tasić et al. (1978) is consistent to the data from Puri et al. (1974).

Table 1. Source of VLE data of studied systems

System	Temperature (°C)	Reference
methanol-carbon tetrachloride	20	Wolff and Höpell (1968)
ethanol-carbon tetrachloride	20	Niini (1940)
1-propanol-carbon tetrachloride	35	Paraskevopoulos and Missen (1962)
1-butanol-carbon tetrachloride	35	Paraskevopoulos and Missen (1962)
Ethanol-carbon disulphide	20	Niini (1940)
1-propanol-carbon disulphide	30	McKeigue (1986)
1-butanol-carbon disulphide	30	McKeigue (1986)
1-pentanol-carbon disulphide	30	McKeigue (1986)
methanol-benzene	40	Oracz and Kolasińska (1987)
ethanol-benzene	30	Zielkiewicz et al. (1990)
cyclohexane-acetone	25	Tasić et al. (1978); Puri et al. (1974)
methanol-water	25	Hu et al. (2003)

The thermodynamic correction factors were obtained by extracting activity coefficient profiles from the vapour-liquid equilibrium (VLE) data for the mixtures, using a numerical integration method. The details of the method were given previously in Zhu et al. (2015) and are summarised in Supplementary Information. For those systems where VLE data were given at a different temperature for the corresponding mutual diffusion coefficients, thermodynamic correction factors were extrapolated to the temperature for the mutual diffusion coefficients by assuming the excess Gibbs energy being constant in the temperature range.

4. Results and discussion

4.1. Viscosity measurements

To facilitate the prediction of mutual diffusion coefficients using Equation 15, viscosity data of the mixtures are required to be at the temperature where mutual diffusion coefficients at infinite dilution are available. The mixture viscosity data for cyclohexane-acetone and methanol-water systems at 25 °C and methanol-benzene at 20 °C were directly taken from the literature whereas those for ethanol-benzene system at 20 °C were linearly extrapolated from at 25, 30, 35 °C. The mixture viscosity data for the systems of alcohol-carbon tetrachloride and alcohol-carbon disulphide at 20 °C were measured and are shown in Figure 1. All the viscosity data measured or taken from the literature are summarised in Tables S5-7. The measured viscosity profile of ethanol-carbon tetrachloride systems matched that of Konobeev and Lyapin (1970) in the literature, suggesting the measurements in this work were accurate. From the figure, it is shown that viscosity changes monotonically with composition and increases with the chain length of the alcohols.

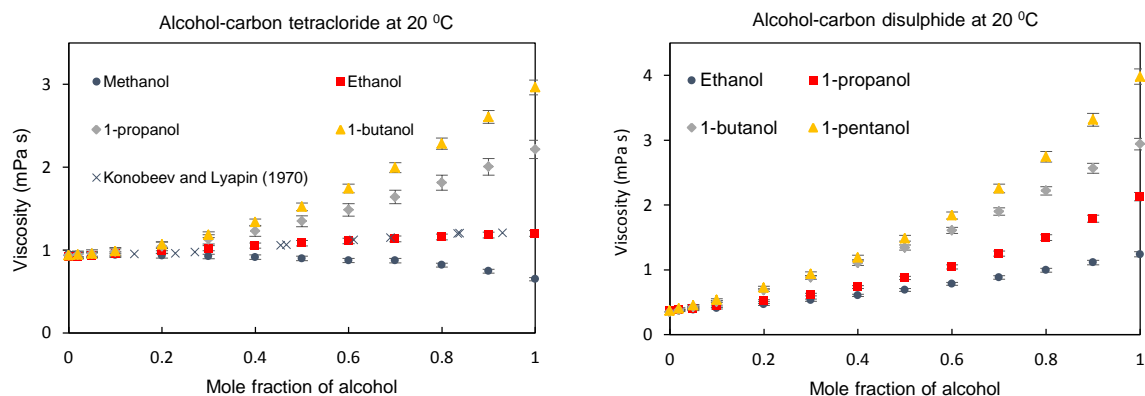


Figure 1. Measured viscosity data of alcohol-carbon tetrachloride and alcohol-carbon disulphide systems at 20 °C. the vertical lines indicate error in the viscosity measurement ($\pm 3\%$). The black cross indicates viscosity of ethanol-carbon tetrachloride at 20 °C from Konobeev and Lyapin (1970).

4.2. Prediction results

The predictions of mutual diffusion coefficients through Equation 16 for alcohol-carbon tetrachloride, alcohol-carbon disulphide and alcohol-benzene systems are shown in Figures 2-4, and compared with the experimental data in the literature. The thermodynamic correction factor profiles calculated for the predictions are summarised in the Supplementary Information (Tables S8-10). To precisely model the mutual diffusion coefficients, accurate mutual diffusion coefficients at infinite dilution are of great importance. First of all, empirical models were employed. However, the model adopted from Wilke and Chang (1955) and some other models gave significant under-estimation of the limiting mutual diffusion coefficient for alcohols. Several other methods have therefore been attempted in order to obtain accurate mutual diffusion coefficients of alcohols at infinite dilution.

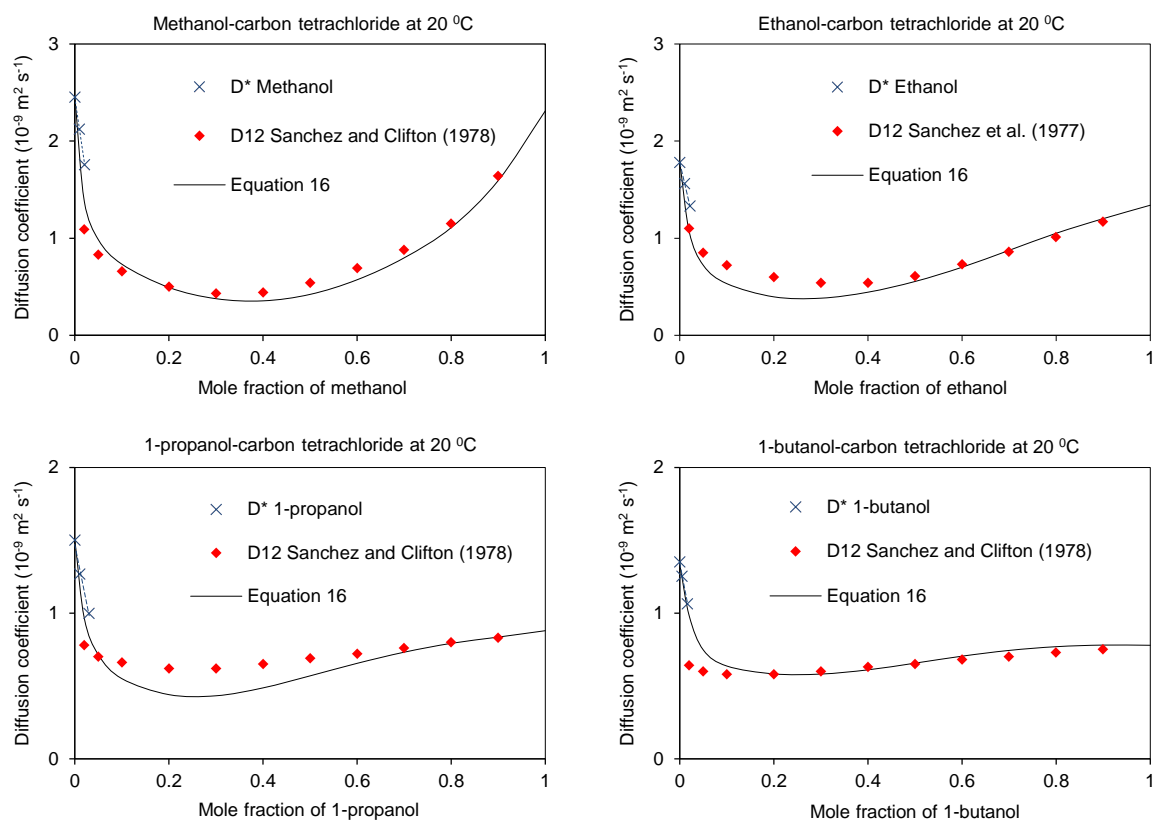


Figure 2. Comparison of mutual diffusion coefficients between experimental results and predictions of Equation 16 for alcohol-carbon tetrachloride systems at 20 °C. The crosses indicate intra-diffusion coefficients for the alcohol. Dashed lines indicate linear extrapolation of intra-diffusion coefficient of alcohols to infinite dilution.

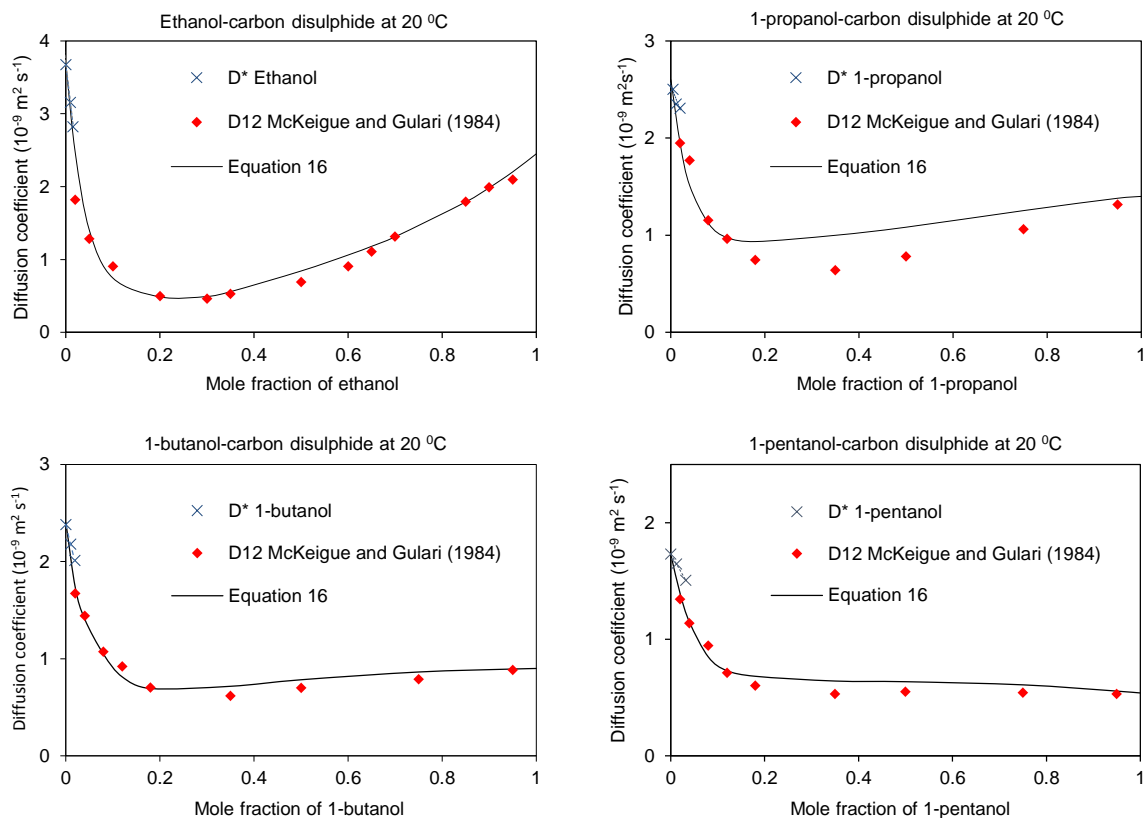


Figure 3. Comparison of mutual diffusion coefficients between experimental results and predictions of Equation 16 for alcohol-carbon disulphide systems at 20 °C. The crosses indicate intra-diffusion coefficients for the alcohol. Dashed lines indicate linear extrapolation of intra-diffusion coefficient of alcohols to infinite dilution.

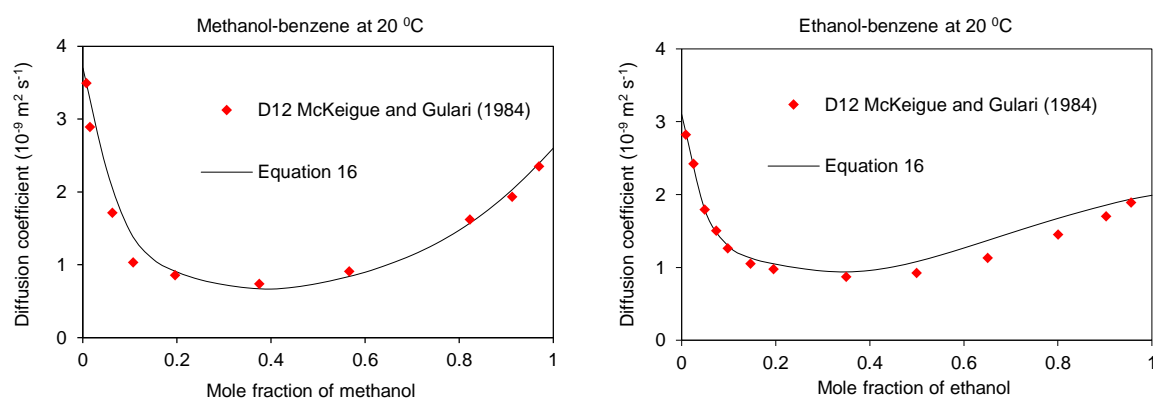


Figure 4. Comparison of mutual diffusion coefficients between experimental results and predictions of Equation 16 for alcohol-benzene systems at 20 °C.

The mutual diffusion coefficients are believed to be continuous and smooth over the whole composition range, thus the values at infinite dilution can be accurately extrapolated using polynomials. Nevertheless, it must be taken into account that these extrapolations may differ greatly depending on the chosen polynomials. Such dependence was minor for the non-polar component present at infinite dilution and methanol or ethanol infinitely diluted in benzene. Thus, mutual diffusion coefficients for infinitely diluted alcohols in benzene and for the infinitely diluted non-polar component, i.e., carbon tetrachloride, carbon disulphide and benzene, were extrapolated directly using the third order polynomials fitted to the mutual diffusion coefficient profiles over a certain composition range (mole fractions of alcohol from 0 to 0.2 or from 0.4 to 1).

Conversely, in our case, the mutual diffusion coefficient profile is greatly influenced by the solution thermodynamics caused mainly by self-association of the alcohols. The mutual diffusion coefficients at infinite dilution of alcohols in a non-polar component may be greatly different from those statistically extrapolated from the bulk profile of mutual diffusion coefficients. A more accurate alternative to extrapolate mutual diffusion coefficient at infinite dilution of alcohols is from profiles of intra-diffusion coefficients in mixtures of dilute alcohols, since the intra-diffusion has a generally weaker dependence on the thermodynamics compared to the mutual diffusion (D'Agostino et al., 2011). Intra-diffusion coefficients can be obtained using PFG-NMR. Thus we performed linear extrapolation using experimental NMR intra-diffusion coefficient data with an alcohol mole fraction less than 0.03 for alcohol-carbon tetrachloride and alcohol disulphide systems, shown in Figures 2 and 3. The PFG-NMR measurements for methanol and ethanol diluted in benzene were not performed due to safety issues; however, the corresponding mutual diffusion coefficients at infinite dilution extrapolated from the available bulk mutual diffusion coefficient profile were used for prediction.

The extrapolated mutual diffusion coefficients at infinite dilution of all components in the studied systems are collected in Table 2. It is interesting to note that the mutual diffusion coefficient at infinite dilution of both the alcohols and the non-polar component decreases with the increasing chain length of

alcohol. This can be explained by Equation 12: as the chain length of the alcohol increases, the mutual diffusion coefficients at infinite dilution for the alcohol and non-polar components decrease as a result of increasing radius and viscosity.

Table 2. Extrapolated mutual diffusion coefficients at infinite dilution.

Systems	T (°C)	D_{12}^{∞} (10^{-9} m ² s ⁻¹)	D_{21}^{∞} (10^{-9} m ² s ⁻¹)
methanol (1)-carbon tetrachloride (2)	20	2.45	2.31
ethanol (1)-carbon tetrachloride (2)	20	1.78	1.34
1-propanol (1)-carbon tetrachloride (2)	20	1.50	0.88
1-butanol (1)-carbon tetrachloride (2)	20	1.33	0.78
ethanol (1)-carbon disulphide (2)	20	3.67	2.44
1-propanol (1)-carbon disulphide (2)	20	2.60	1.41
1-butanol (1)-carbon disulphide (2)	20	2.37	0.90
1-pentanol (1)-carbon disulphide (2)	20	1.73	0.54
methanol (1)-benzene (2)	20	3.70	2.60
ethanol (1)-benzene (2)	20	3.10	1.97

Using the mutual diffusion coefficients at infinite dilution determined, the prediction results of the model show good correlation (shown in Figures 2-4), suggesting that Equation 16 is suitable for modelling the mutual diffusion coefficients for systems of one self-associating and one non-polar component.

The validity of the proposed prediction model is in agreement with the literature data that we assume to be reliable and accurate. Table 3 collects the average relative deviations (ARD) for the prediction results from Equation 16 and the literature mutual diffusion data plotted in Figures 2-4 and compared to that with prediction results from Li et al. (2001) model. It is shown that Equation 16 gives more accurate predictions than Li et al. (2001) for most of the systems studied. Comparing the total average ARD values, Equation 16 gave 10.8% whereas the Li et al. (2001) model gives 18.2% for all the systems studied. The

McKeigue and Gulari (1989) model gives about 15% but only for the systems where the isodesmic association constants are available (i.e. the alcohol-carbon disulphide and alcohol-benzene systems). Equation 16 exhibits the best performance among these models and it is based on knowledge of viscosity data, which can be readily available for many systems.

Table 3. Results of predictions and comparisons in terms of average relative deviations from the experimental mutual diffusion coefficient data.

Systems	No. of points	ARD (%)	
		This work	Li et al. (2001) model
methanol (1)-carbon tetrachloride (2)	11	13.0	20.1
ethanol (1)-carbon tetrachloride (2)	11	13.2	25.6
1-propanol (1)-carbon tetrachloride (2)	11	14.3	27.2
1-butanol (1)-carbon tetrachloride (2)	11	9.5	15.0
ethanol (1)-carbon disulphide (2)	13	8.5	16.5
1-propanol (1)-carbon disulphide (2)	9	15.1	13.3
1-butanol (1)-carbon disulphide (2)	9	10.0	15.6
1-pentanol (1)-carbon disulphide (2)	9	7.8	29.1
methanol (1)-benzene (2)	10	9.6	13.0
ethanol (1)-benzene (2)	13	7.3	6.9
Average		10.8	18.2

a: For McKeigue and Gulari (1989) model, the average relative error is about 15% for the alcohol-carbon disulphide and alcohol-benzene systems.

$$b: \text{ARD (\%)} = \frac{1}{N} \sum_{i=1}^N \frac{|D_{\text{expt}} - D_{\text{cal}}|}{D_{\text{expt}}} \times 100$$

4.3. Relationship between \mathfrak{D}_i and D_i^*

Two fundamental differences of Equation 16 between McKeigue and Gulari (1989) and Li et al. (2001) models are the scaled thermodynamic correction factor and the use of molecular intra-diffusion coefficient (\mathfrak{D}_i) instead of modelling D_i^* for mutual diffusion coefficients. McKeigue and Gulari (1989) and Li et al. (2001) models agreed on the relationship between the intra-diffusion coefficient (D_i^*) and the association number (n_i) that:

$$D_i^* = \frac{kT}{6\pi\eta r_i n_i^\beta} \quad (18)$$

In Equation 18, β is the geometry parameter for self-association of the species. The value of β theoretically ranges from 1/3 to 1/2 depending on the form of self-association from linear to globular.

Recalling the similar relation for the molecular diffusion coefficient in Equation 11, it is plausible to write the ratio of the molecular intra-diffusion to the intra-diffusion coefficients from the ratio between Equations 11 and 18: $\mathfrak{D}_i/D_i^* = 6\pi\eta n_i^\beta/\sigma_i$. However 6π is a generalised factor for slipping condition for intra-diffusion coefficient in Stokes-Einstein equation and may vary with the binary systems in use. From this point of view, the factor 6π is of the similar characteristic to σ_i , hence the ratio $6\pi/\sigma_i$ may be expected to be close to unity. Therefore, one can write:

$$\frac{\mathfrak{D}_i}{D_i^*} \approx n_i^\beta \quad (19)$$

For a non-polar species that does not associate, D_i^* is an approximate to \mathfrak{D}_i in value because the association number is nearly unity. However in the case of self-associating species, D_i^* is expected to be the diffusion coefficient averaging the mobility of all possible polymerised clusters, thus the ratio \mathfrak{D}_i/D_i^* is expected to be greater than unity. For example, in solutions of diphenyl in benzene where diphenyl can be regarded as the linearly dimerised molecule of benzene, Mills (1963) found 1.45 for the intra-diffusion coefficient ratio, $D_{benzene}^*/D_{diphenyl}^*$, independent of composition. This value is close to 1.41 which is $2^{1/2}$ for n_i^β in Equation 19, where the geometry factor β is 1/2.

Equation 19 can be used to explain the mutual diffusion coefficient model where the intra-diffusion coefficient is doubled for the alcohol species. The original explanation was that the alcohols are dimerised in the diffusion process resulting in lowered intra-diffusion coefficient (D_i^*) than the molecular intra-diffusion coefficient (\mathfrak{D}_i). Taking β in the range of 1/3 to 1/2, if the factor 2 in Moggridge (2012b) model (Equation 3) truly represents the effect of self-association on the diffusion coefficients as n_i^β , then the value for the association number n_i results to be between 4 and 8. This range of values may represent a

range of the average number for different types of association of the self-associating species, which is consistent with the molecular simulation studies that the association number could be up to approximately 5 in inert solvents when the majority of alcohol molecules tend to form linear and cyclic clusters (Gómez-Álvarez et al., 2013).

4.4. Extension and limitation of the model applicability

The model (Equation 16) should also be able to accurately predict mutual diffusion coefficients in binary mixtures in which neither species is significantly self-associating, because in such cases the molecular diffusion coefficients (\mathcal{D}_i) of both species can be inferred from the mutual diffusion coefficients at infinite dilution (D_{ij}^∞) and the viscosity correlation. This assumption breaks down if cross-association occurs, in which case the model (Equation 16) may not be able to provide accurate mutual diffusion coefficient predictions, for example for the methanol-water system. To illustrate the range of validity and limitation of the model, mutual diffusion coefficients for cyclohexane-acetone, a system presenting neither strong self- nor cross-association, and methanol-water, a system with strong cross association, were studied. The two sets of mutual diffusion coefficient data for methanol-water at 25 °C in literature were found to agree well with each other, thus confirming the accuracy of these data. In contrast there is only one set of mutual diffusion data available for cyclohexane-acetone from Tasić et al. (1981) at 25 °C. To ascertain the accuracy, mutual diffusion coefficients for cyclohexane-acetone were measured for this work using Taylor dispersion. Table 4 lists the measured mutual diffusion coefficients for the cyclohexane-acetone system at 25 °C and the intra-diffusion coefficients at the same temperature.

Table 4. Mutual diffusion coefficients and intra-diffusion coefficients in cyclohexane (1)-acetone (2) mixtures at 25 °C, by Taylor dispersion method and PFG-NMR respectively. The average relative error on these values is of approximately 3%.

x_1	D_{12} (10^{-9} m s $^{-1}$)	D_1^* (10^{-9} m s $^{-1}$)	D_2^* (10^{-9} m s $^{-1}$)
0	3.99	-	4.83
0.05	3.31	3.98	4.63
0.11	2.50	3.80	4.43
0.20	2.16	3.54	4.28
0.30	b*	3.20	4.03
0.40	1.32	2.77	3.48
0.50	1.14	2.57	3.18
0.60	1.00	2.31	3.15
0.70	1.06	2.09	2.76
0.80	1.23	1.87	2.43
0.90	1.54	1.78	2.24
0.95	1.81	1.52	2.16
1	2.00	1.39	-

b* : This data point cannot be accurately measured, due to difficulties in measuring mutual diffusivity near azeotropic composition.

The mutual diffusion coefficients for cyclohexane-acetone and methanol-water at 25 °C were predicted from Equation 16. The prediction results were compared with experimental mutual diffusion data from the literatures as well as with the measurements carried out in this work, shown in Figure 5. The prediction results from the local composition model (Zhu et al., 2015) are also shown for comparison, with the intra-diffusion coefficients for cyclohexane-acetone from measurement and for methanol-water from Derlacki et al. (1985) respectively. The intra-diffusion coefficient and viscosity data from the literature and thermodynamic correction factor profiles used for prediction of mutual diffusion coefficient in these systems are collected in Tables S4, S7 and S11 respectively.

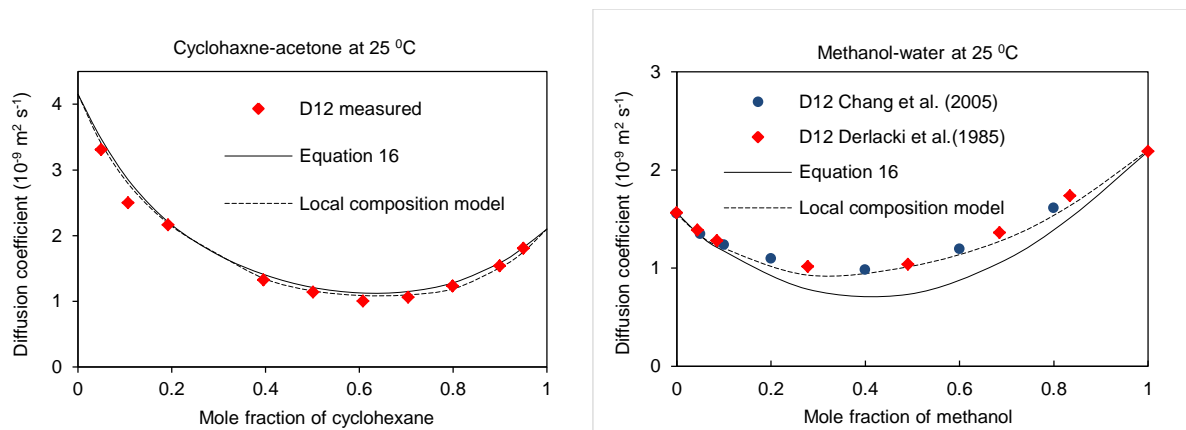


Figure 5. Comparison of experimental results and predictions of mutual diffusion coefficients from Equation 16 and the local composition model for cyclohexane-acetone and methanol-water systems at 25 °C.

It is shown in Figure 5 that both Equation 16 and the local composition model show good concurrence with the measured mutual diffusion coefficients for the cyclohexane-acetone system, for which there is no significant self-association or cross-association within or between components. In the case of the methanol-water system, Equation 16 showed under-prediction over a wide composition range, while the local composition model better describes the experimental behaviour. This is because the two components show cross-association *via* hydrogen bonding, including in diluted solutions (Easteal et al., 1985; Jorgensen and Madura, 1983). The mutual diffusion coefficients at infinite dilution are therefore representative of the diffusion of the fully association species. At intermediate concentrations the species may be only partially associated and so its molecular diffusion will be under-represented by the infinite dilution value. The mutual diffusion coefficients in such cross-associating systems can be accurately predicted by other existing models.

The major advantages of the model (Equation 16) are that it improves the accuracy of mutual diffusion coefficient prediction for binary liquid systems of self-associating component without the need of intra-diffusion coefficient profiles (in contrast to Li et al. (2001) and Moggridge (2012b) models). In addition, the model does not require isodesmic association constant (in contrast to the McKeigue (1984) model)

and it can be extended for to non-ideal systems showing neither significant cross nor self-association, with high accuracy, requiring only easily available viscosity data.

5. Conclusions

In this work, a new equation for prediction of mutual diffusion coefficients is proposed. It is based on Darken equation, with the intrinsic diffusion coefficients correlated with the mutual diffusion coefficients at infinite dilution and viscosities. A scaling power $\alpha = 0.64$ on the thermodynamic correction factor from the Darken diffusion approach is used. This equation was developed for binary liquid systems of one self-associating component and one non-polar component. It fits the experimental mutual diffusion data for a series of systems containing primary alcohols in the presence of a non-polar species i.e. carbon tetrachloride, carbon disulphide or benzene. The proposed equation also well works for binary liquid system without significant association, though the accuracy of prediction for systems of cross association may be limited. the strength of this model essentially consists in the fact that it does not need the knowledge of the intra-diffusion coefficients but only relies on the knowledge of the two limiting mutual diffusion coefficients and easily available viscosity data, .

Nomenclature

C_i Molar concentration of component i [$\text{m}^2 \text{s}^{-1}$].

D_i Intrinsic diffusion coefficient [$\text{m}^2 \text{s}^{-1}$].

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

D_{ij}^∞ Mutual diffusion coefficient species i infinite diluted in species j [dimensionless].

D_i^* Intra-diffusion coefficient of species i [$\text{m}^2 \text{s}^{-1}$].

\mathfrak{D}_i Molecular intra-diffusion coefficient of species i [$\text{m}^2 \text{s}^{-1}$].

- D_i^∞ Molecular intra-diffusion coefficient at infinite dilution [$\text{m}^2 \text{s}^{-1}$].
- n_i Association number of species i [dimensionless].
- r_i Molecular radius of the diffusing species i [m].
- R Universal gas constant [$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$].
- k Boltzmann constant [$1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$]
- T Temperature [K].
- T_C Consolute temperature [K].
- V_t Detector output signal voltage [V].
- V_0 Baseline voltage [V].
- V_1 Voltage drift in the detector signal [V].
- t Time [s].
- V_{max} Maximum voltage relative to the baseline [V].
- t_r Retention time [s].
- r Inner radius of the bore [s].
- x_i Mole fraction of species i in a liquid mixture [dimensionless].
- z Distance in the direction of diffusion [m].
- α A power factor to the thermodynamic correction factor [dimensionless].
- β Geometry parameter for the self-association [dimensionless].
- γ_i Activity coefficient of species i in a liquid mixture [dimensionless].
- η Viscosity of binary liquid mixture [$\text{mPa}\cdot\text{s}$].
- η_i Viscosity of pure liquid [$\text{mPa}\cdot\text{s}$].
- ξ_i Diffusion correlation length [m].
- σ_i Parameter denoting the inverse proportionality in Equation 10 [dimensionless].

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