Investigation of using different thermodynamic models on prediction ability of mutual diffusion coefficient model

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ABSTRACT

The aim of this study is to improve the new model for prediction of mutual diffusion coefficient in non-ideal, concentrated liquid solutions by applying two thermodynamic models (NRTL and Wilson) to estimate the derivative of activity coefficient logarithm versus the mole fraction ($\frac{d\ln\gamma_1}{d\ln x_1}$). The model which is used in this paper is based on cluster diffusion theory. Unlike, the previous model which was proposed by the authors (Kamgar et al., 2017), this improved one is a predictive model and it does not require any vapor-liquid equilibrium data. It is just function of temperature, mole fraction and viscosity. An optimization approach has been carried out to measure the adjustable parameters of the models. Besides, the results of the improved model are compared with the model in which VLE are used for calculation of $\frac{d\ln\gamma_1}{d\ln x_1}$. Furthermore, to validate the improved model, eleven binary system with more than 130 experimental diffusion coefficient data are used. An acceptable average relative error (ARD %) has been achieved for all the cases. Among investigated thermodynamic models, Wilson gave the best results and the least errors.

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1. Introduction

Mutual diffusion coefficient in binary liquid systems is a very important physical property in different chemical engineering problems, ranging from investigation of unit operation and design to catalysis and soil science [1,2]. Many experimental studies, such as holographic interferometry [3], light scattering [4], and Taylor dispersion [5], have been applied to measure mutual diffusion coefficients. However, most of the times, an experimental approach is very expensive, time consuming, or even not available. Hence, mathematical methods have great importance to predict diffusion coefficient.

The simplest equation for diffusion in binary liquid mixtures was suggested by Schreiner [6], which is presented as follows:

$$D_{12} = D_{12}^* \left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right] \tag{1}$$

where, D_{12}^* represents molecular mobility factor. The term in bracket demonstrates a thermodynamic correction factor, explaining the diffusion due to the chemical potential difference.

Darken [7] proposed one of the most important equations, in which D_{12} was considered to be function of intra-diffusion coefficients of each

component (i.e. D_1^* and D_2^*). Darken equation is shown as follows:

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

Obviously, for applying Darken equation, D_1^* and D_2^* must be obtained, which can be calculated by molecular simulation approach or experimental methods. In order to avoid the need for these parameters, Vignes [8] suggested a geometric average of the diffusion coefficient in the infinite dilute solution to be replaced with the first parenthesis in the Darken equation as the following equation:

$$D_{12} = \left((D_1^\infty)^{x_1} \times (D_2^\infty)^{x_2}\right) \times \left(\frac{d\ln a_1}{d\ln x_1}\right) \tag{3}$$

In this equation, D_1^∞ and D_2^∞ are limiting mutual diffusion coefficients at infinite dilution. It has been proven that Darken and Vignes equations can predict the diffusion coefficient in ideal or nearly ideal solutions relatively well. On the other hand, their prediction of diffusion coefficient in non-ideal solutions is not reliable. Indeed, the results of these equations usually under-predict the experimental data [8–10].

In order to reduce the mentioned problems, Cussler [11] took a considerable step by introducing the concept of cluster diffusion which the diffusion process is controlled by the movement of both single molecules and clusters. This phenomenon mostly takes place in non-ideal, concentrated solutions near the consolute point. Cussler considered a scaling power for the thermodynamic correction factor, which

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accounted for the fluctuation of the local concentration and fluid velocity. Many predictive equations for diffusion coefficient have been developed, based on Cussler theory [4,12–14].

Mixtures of non-polar and self-associating components (e.g., ethanol-benzene) significantly deviate from the thermodynamic ideality. Therefore, the measurement of diffusion coefficient in these systems is more complicated. In this regard, McKeigue and Gulari [12] suggested a new model in which isodesmic association term and viscosity incorporated. Their study focused on different non-ideal systems, including alcohol-benzene and alcohol- carbon disulfide. Although their proposed equation had the ability to predict the binary diffusion coefficient with acceptable accuracy, it required isodesmic association data, which is not available for other systems. In 2001, Li et al. [15] conducted a research to develop a more reliable approach for the estimation of binary diffusion coefficient in non-ideal solutions. They assumed the components' association number was a linear function of composition and formulate intra-diffusion coefficient. Moreover, they replaced the mole fraction in Darken equation with local mole fractions. The model presented a considerable error for a system containing a very self-associating component and a non-polar one.

More recently, D'Agostino et al. [16] considered a scaling power for the thermodynamic factor in Darken equation, explaining the concentration fluctuation close to consolute point. This equation is shown as follows:

$$D_{12} = \left(x_2 D_1^* + x_1 D_2^*\right)\left[1 + \frac{d\,\ln\gamma_1}{d\,\ln x_1}\right]^\alpha \tag{4}$$

Based on the dynamic scaling theory, the value of α is reported 0.64 [17]. Subsequently, the Eq. (4) was improved by Moggride [18]. He considered dimerization of the self-associating component in four liquid systems of self-associating, and non-polar components. Consequently, intra-diffusion coefficient of the self-associating component was doubled in Eq. (4) and can be written in the following format:

$$D_{12} = \left(2x_2 D_1^* + x_1 D_2^*\right)\left[1 + \frac{d\,\ln\gamma_1}{d\,\ln x_1}\right]^\alpha \tag{5}$$

where subscripts 1 and 2 are respectively the self-associating and non-polar components. This model is able to accurately predict the binary diffusion coefficients in solutions in which the mole fraction of the self-associating component is higher than 0.2. Nevertheless, the applicability of the mentioned equations depends on the availability of intra-diffusion coefficients, which does not always have a straightforward estimation process. Indeed, this composition-dependent parameter can be calculated by means of molecular dynamics simulations [19], conventional radio-active isotope labelled diffusion set-up [20], or PFG-NMR [21].

Zhu et al. [1] proposed a new model for diffusion coefficient measurement, in which the intra-diffusion coefficients were replaced with the mutual diffusion coefficient at infinite dilute solutions. However, it is not suitable for predicting mutual diffusion coefficient in a system where cross association occurs between the two components.

Recently, Kamgar et al. [22] have proposed a simple and new equation for prediction of diffusion coefficient in binary non-ideal liquid solutions for the whole range of solute composition. Because of the fact that the VLE and diffusion coefficient data were reported at different temperatures, this method caused some errors in the final equation.

In this study, the previous developed equation is improved by applying NRTL and Wilson thermodynamic models for the estimation of activity coefficient. Taking into account the thermodynamic models, there are 5 adjustable parameters in the final equation for diffusion coefficient prediction. the proposed equations reduce the computation time; and at the same time, provide more reliable results. The outstanding feature of this model is that it does not need intra-diffusion coefficient data. It should be noted that an optimization method was applied to minimize the absolute relative error (ARD %) and estimate the model constants. The two different thermodynamic models and VLE data are used in predicting diffusion coefficient. They are compared with each other and the best thermodynamic model for describing activity coefficient is obtained.

2. Theory

2.1. Model description

According to the cluster diffusion theory, the diffusion coefficient in a dilute solution can be described as a function of velocity correlation [23]. However, in the case of a concentrated solution, both the local concentration and velocity considerably fluctuate the diffusion coefficient can be written as a function of a time-integrated velocity and concentration correlation functions; as shown by the following equation [24–26]:

$$D = \frac{G(r)^* F(r)}{G(r)} \tag{6}$$

where $F(r)$ and $G(r)$ represent the time-integrated velocity and concentration function, respectively. This equation implies that the concentration and velocity fluctuation are statistically independent.

To find diffusivity, the functions $F(r)$ and $G(r)$ must be estimated. Ferrell [27] obtained the following format for $F(r)$:

$$F(r) = \frac{KT}{2\pi\eta}\frac{1}{r} \tag{7}$$

where K, T, and η are Boltzmann number, temperature, and dynamic viscosity, respectively. Eq. (7) provides a microscopic definition for velocity and implies that an increase in temperature contributes to more fluctuations in velocity.

Different form for $G(r)$ could be defined depending on the solute concentration. For a significantly dilute solution, concentration function takes large and zero values for distances smaller than the molecular size and larger than that, respectively. Combining this function with Eqs. (6) and (7), results in the Stokes-Einstein equation which is shown in Eq. (8). On the other hand, the focus of this study is on concentrated solutions; and therefore, the Ornstein-Zernike form for concentration function is applied (Eq. (9)) [28]:

$$D = \frac{KT}{6\pi\eta r} \tag{8}$$

$$G(r) = \frac{R^2}{r}\,\exp\left(-\frac{r}{\xi}\right) \tag{9}$$

where R^2 is a factor of length with order of molecular size, and ξ presents the characteristic size of the concentration fluctuations. In other words, it gives a rough estimation of the average size of diffusing clusters.

Eq. (9) is derived based on some assumptions; and therefore, it introduces some errors in the final equation. In order to reduce the error, a modification can be considered for the concentration fluctuation function, as follows [22]:

$$G(r) = \frac{a}{r^n}\,\exp\left(-\frac{r}{\xi}\right) \tag{10}$$

In Eq. (10), n, is added as an adjustable parameter; and as a result it is able to reduce the final error of Eq. (9). The relation for prediction of mutual diffusion coefficient is derived by combining Eqs. (6), (7), (10):

$$D = \frac{4\pi\int_0^\infty \frac{a}{r^n}\,\exp\left(-\frac{r}{\xi}\right)^* \frac{kT}{2\pi\eta}\frac{1}{r}r^2 dr}{4\pi\int_0^\infty \frac{a}{r^n}\,\exp\left(-\frac{r}{\xi}\right)^* r^2 dr} = \frac{kT}{2\pi\eta\xi(2-n)} \tag{11}$$

where K, T, η, and $\xi(2-n)$ represent the Boltzmann constant, temperature, dynamic viscosity, and corrected length, respectively. This