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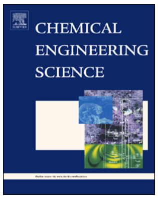

Prediction of mutual diffusion coefficients in binary liquid systems with one self-associating component from viscosity data and intra-diffusion coefficients at infinite dilution

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HIGHLIGHTS

- A prediction model for mutual diffusivities in binary systems was developed.
- The model requires intra-diffusivities 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 cross-associating species.
- The approach is a valid alternative for predicting mutual diffusion from viscosity.

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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 the absence of self-association), the proposed equation was extended to binary liquid systems without significant association. The accuracy of prediction for systems of cross associating species is expected to 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.

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) and so forth. 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

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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:

$$D_{12} = x_2 D_1 + x_1 D_2 \tag{1}$$

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

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

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.

Eq. (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, 2012a, 2012b, 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 (Moggridge, 2012b):

$$D_{12} = \left(2x_2 D_1^* + x_1 D_2^*\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^{\alpha} \tag{3}$$

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). Eq. (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 Eq. (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