

# Prediction of Composition-Dependent Self-Diffusion Coefficients in Binary Liquid Mixtures: The Missing Link for Darken-Based Models

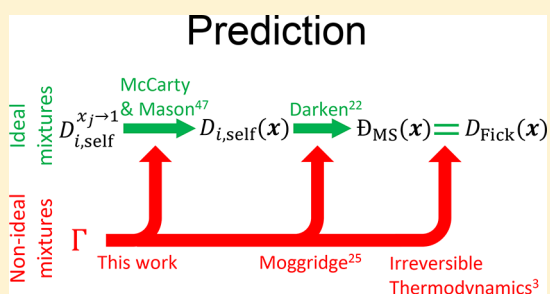
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## Supporting Information

**ABSTRACT:** Mutual diffusion coefficients can be successfully predicted with models based on the Darken equation. However, Darken-based models require composition-dependent self-diffusion coefficients which are rarely available. In this work, we present a predictive model for composition-dependent self-diffusion coefficients (also called tracer diffusion coefficients or intradiffusion coefficients) in nonideal binary liquid mixtures. The model is derived from molecular dynamics simulation data of Lennard-Jones systems. A strong correlation between nonideal diffusion effects and the thermodynamic factor is observed. We extend the model by McCarty and Mason (*Phys. Fluids* 1960, 3, 908–922) for ideal binary gas mixtures to predict the composition-dependent self-diffusion coefficients in nonideal binary liquid mixtures. Our new model is a function of the thermodynamic factor, the self-diffusion coefficients at infinite dilution, and the self-diffusion coefficients of the pure substances, which are readily available. We validate our model with experimental data of 9 systems. For both Lennard-Jones systems and experimental data, the accuracy of the predicted self-diffusion coefficients is improved by a factor of 2 compared to the correlation of McCarty and Mason. Thus, our new model significantly expands the practical applicability of Darken-based models for the prediction of mutual diffusion coefficients.



## 1. INTRODUCTION

Diffusion in liquids plays an important role in many industrial and environmental processes.<sup>1</sup> Engineers are in need of precise diffusion process calculations to design, e.g., separation processes and chemical reactors. The accurate quantitative description of diffusion processes has been a challenge to scientists for decades.<sup>2,3</sup> There is still a continuing demand for diffusion coefficients as input parameters to these models.<sup>4</sup>

Although experimental methods are continuously improving,<sup>5–10</sup> the measurement of diffusion coefficients in liquids is usually time-consuming and expensive.<sup>11,12</sup>

Molecular dynamics (MD) simulations are a powerful tool to complement or even substitute diffusion experiments.<sup>13–15</sup> However, MD simulations are still computationally too expensive to be performed in the framework of process simulations. Therefore, predictive models for diffusion coefficients are needed.<sup>11,16–18</sup> The aim is to reduce the required data to a minimal amount, e.g., to viscosities or diffusion coefficients at infinite dilution.

Most practical applications require the knowledge of *mutual diffusion coefficients*, which describe the net flow of molecules due to a driving force. Numerous models have been proposed to predict the composition dependence of mutual diffusion coefficients in liquids.<sup>11,16–20</sup> Within these models, two main classes can be identified.

The first class of models is based on the Vignes equation:<sup>21</sup>

$$D_{12} = (D_{12}^{x_1 \rightarrow 1})^{x_1} (D_{12}^{x_2 \rightarrow 1})^{x_2} \quad (1)$$

Here,  $D_{12}$  is the (mutual) Maxwell–Stefan (MS) diffusion coefficient,  $x_1$  and  $x_2$  are the mole fractions of components 1 and 2, and  $D_{12}^{x_1 \rightarrow 1}$  and  $D_{12}^{x_2 \rightarrow 1}$  are the MS diffusion coefficients at infinite dilution. The Vignes equation is very popular since it only requires diffusion coefficients at infinite dilution as input for which many predictive models are available, such as the Wilke–Chang equation.<sup>19</sup> The Vignes equation is purely empirical and applicable to binary systems only. However, extensions of the Vignes equation to multicomponent mixtures have been proposed.<sup>16,18</sup>

The second class of models is based on the Darken equation:<sup>22</sup>

$$D_{12} = D_{\text{Darken}} = x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}} \quad (2)$$

Here,  $D_{1,\text{self}}$  and  $D_{2,\text{self}}$  are the composition-dependent *self-diffusion coefficients* (also called tracer diffusion coefficients or

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intradiffusion coefficients) of components 1 and 2 in the mixture, which describe the mean-squared displacements of individual molecules in a mixture. The Darken equation has been extended to multicomponent mixtures by Liu et al.<sup>18,23</sup> In contrast to the Vignes equation (eq 1), the Darken equation has a physical basis and can be derived from statistical-mechanical theory when velocity cross-correlations between the molecules of a mixture are neglected, i.e., when the molecules in the mixture move independently and not in groups or clusters.<sup>18</sup> Hence, the Darken equation is suitable for ideal mixtures, but not for strongly nonideal mixtures.

A modified Darken equation for nonideal binary mixtures has therefore been proposed by D'Agostino et al.<sup>24</sup> and Moggridge<sup>25</sup> which is based on critical point scaling laws:<sup>26–29</sup>

$$D_{12} = D_{\text{Darken}} \Gamma^{-0.36} \quad (3)$$

Here, the Darken equation is corrected by a power function of the thermodynamic factor  $\Gamma$ , which is a measure for the nonideality of the system (cf. eq 8).<sup>3</sup> In the rest of the paper, eq 3 is called the “Moggridge equation”. The Moggridge equation has been tested and successfully validated for a wide range of nonideal liquid mixtures.<sup>15,24,25,30</sup> The Moggridge equation is not applicable to mixtures with dimerizing components. Moggridge<sup>31</sup> proposed a further modification of eq 3 for mixtures with dimerizing components. Zhu et al.<sup>32</sup> introduced local mole fractions into the Moggridge equation. Thereby, mixtures with and without dimerizing species could be successfully described. Recently, Allie-Ebrahim et al.<sup>33</sup> suggested an extension of the Moggridge equation to multicomponent systems.

Despite its sound physical background, the Darken equation (and thereby the Moggridge equation) is generally seen as “of little practical use due to the fact that it relies on the self-diffusion coefficients [ $D_{i,\text{self}}$ ] in the mixture, which are rarely available”.<sup>34</sup> To avoid the use of  $D_{i,\text{self}}$  modifications of the Darken equation have been proposed which use self-diffusion coefficients at infinite dilution  $D_{i,\text{self}}^{x_i \rightarrow 1} = D_{ij}^{x_i \rightarrow 1} = D_{12}^\infty$ <sup>35</sup> include additional, system-dependent modification factors,<sup>36</sup> or incorporate the shear viscosity,<sup>37,38</sup> to name a few. Similar modifications have been applied to the Vignes equation to extend the applicability to a wider range of nonideal systems.<sup>39</sup> However, the applicabilities of the (modified) Vignes equations and of those modified Darken equations that avoid the use of  $D_{i,\text{self}}$  are very case-specific.<sup>3,19</sup> It was concluded that “no single correlation [that avoids the use of composition-dependent self-diffusion coefficients  $D_{i,\text{self}}$ ] is always satisfactory for estimating the concentration effect on liquid diffusion coefficients”.<sup>19</sup> Therefore, the composition-dependent self-diffusion coefficients should preferentially not be replaced in the Darken-based models.

Thus, reliable predictions of composition-dependent self-diffusion coefficients  $D_{i,\text{self}}$  are needed. Existing predictive models for  $D_{i,\text{self}}$  predict  $D_{i,\text{self}}$  from the self-diffusion coefficients at infinite dilution,  $D_{i,\text{self}}^{x_i \rightarrow 1}$ . The self-diffusion coefficients  $D_{i,\text{self}}^{x_i \rightarrow 1}$  can be obtained, e.g., from NMR measurements, diffusion measurements with radioactive tracers, or molecular dynamics simulations. In addition, the self-diffusion coefficients  $D_{i,\text{self}}^{x_i \rightarrow 1}$  can be estimated with predictive models<sup>19,40</sup> or from the binary mutual diffusion coefficients at infinite dilution:<sup>41</sup>  $D_{i,\text{self}}^{x_i \rightarrow 1} = D_{ij}^{x_i \rightarrow 1} = D_{12}^\infty$ . Extensive data sets on experimental self-diffusion coefficients at infinite dilution,  $D_{i,\text{self}}^{x_i \rightarrow 1}$ , do already exist.<sup>42</sup>

Carman and Stein<sup>43</sup> proposed the semiempirical relation

$$D_{i,\text{self,pred}} = \frac{D_{i,\text{self}}^{x_j \rightarrow 1} \eta^{x_j \rightarrow 1}}{\eta} \quad (4)$$

for binary systems, where  $D_{i,\text{self,pred}}$  is the predicted value of  $D_{i,\text{self}}$ ,  $\eta^{x_j \rightarrow 1}$  is the viscosity of pure component  $j$ , and  $\eta$  is the viscosity of the mixture. Equation 4 is based on the Stokes–Einstein equation<sup>19</sup> and works well for ideal mixtures.<sup>43</sup> For nonideal mixtures, large deviations occur.<sup>15</sup>

For nonideal mixtures, Krishna and van Baten<sup>44</sup> suggest the empirical relation

$$D_{i,\text{self,pred}} = \sum_{j=1}^n w_j D_{i,\text{self}}^{x_j \rightarrow 1} \quad (5)$$

where  $w_j$  is the mass fraction of component  $j$ . Equation 5 was successfully tested for linear alkanes<sup>44</sup> and mixtures with thermodynamic factors  $0.55 \leq \Gamma \leq 1$ .<sup>15</sup> For strongly nonideal mixtures with thermodynamic factors  $\Gamma < 0.55$ , large deviations were observed.<sup>15</sup>

Based on derivations of Curtiss and Hirschfelder<sup>45</sup> and Hirschfelder and Curtiss,<sup>46</sup> McCarty and Mason<sup>47</sup> and Miller and Carman<sup>48</sup> derived the relation

$$\frac{1}{D_{i,\text{self,pred}}} = \frac{x_1}{D_{i,\text{self}}^{x_1 \rightarrow 1}} + \frac{x_2}{D_{i,\text{self}}^{x_2 \rightarrow 1}}, \quad i = 1, 2 \quad (6)$$

for binary gas mixtures. In the rest of the paper, eq 6 will be called the “McCarty–Mason equation”. The McCarty–Mason equation is based on the assumption of an approximately constant mutual diffusion coefficient, which is an often valid assumption for gases. It is exact in the limit of infinite dilution.<sup>18</sup> McCarty and Mason<sup>47</sup> and Miller and Carman<sup>48</sup> tested the McCarty–Mason equation successfully with data from gas diffusion experiments. Liu et al.<sup>18</sup> proposed the use of the McCarty–Mason equation for weakly nonideal liquids. Satisfying predictions of self-diffusion coefficients in weakly nonideal liquids were observed.<sup>15,18,23</sup> However, eq 6 performs poorly for strongly nonideal mixtures.<sup>15</sup>

Overall, the predictive models for composition-dependent self-diffusion coefficients (eqs 4, 5, and 6) work well for approximately ideal mixtures, but there is a need for predictive equations for nonideal mixtures. For mutual diffusion coefficients, the successful performance of the Moggridge equation (eq 3) shows that the inclusion of a function of the thermodynamic factor  $\Gamma$  into the ideal mutual diffusion equation (the Darken equation, eq 2) can be a sufficient method to take nonidealities into account. The question arises whether it is also possible to correct the ideal self-diffusion equation (the McCarty–Mason equation, eq 6) with a function of the thermodynamic factor  $\Gamma$  to expand its applicability to nonideal mixtures.

In this work, we study the composition dependence of mutual and self-diffusion coefficients in binary nonideal liquid mixtures. We investigate the correlation of nonideal diffusion effects with the thermodynamic factor. In section 2, we motivate our analysis from a theoretical point of view. Since experimental data rarely provide a full set of transport data and thermodynamic properties, we use MD simulations as the basis for our analysis (section 3). In section 4.1, we assess the performance of the Moggridge equation (eq 3) for the prediction of mutual diffusion coefficients. In section 4.2.1, we analyze the nonideal behavior of self-diffusion coefficients and derive an improved model for the prediction of self-diffusion

coefficients in strongly nonideal binary liquid mixtures. In section 4.2.2, the improved model is tested and validated with experimental data of molecular systems. Conclusions of this study are drawn in section 5.

## 2. THEORY AND METHOD

Commonly, two approaches are used to describe mutual diffusion: Fick's approach and the Maxwell–Stefan (MS) approach.<sup>3,49</sup> Fick's approach is phenomenological and requires the knowledge of Fick diffusion coefficients  $D_{12}$  and of composition gradients. It is therefore often used for practical applications. The MS approach is physically motivated and can be derived from irreversible thermodynamics.<sup>3,50</sup> It requires the knowledge of MS diffusion coefficients  $\mathcal{D}_{12}$  and of chemical potential gradients. Hence, the MS approach separates thermodynamic properties and transport properties. It is therefore often used for predictive modeling of diffusion coefficients.

Since both Fick's and the MS approach describe the same phenomenon, they are linked to each other. For a binary mixture

$$D_{12} = \mathcal{D}_{12}\Gamma \quad (7)$$

holds, where  $\Gamma$  is the thermodynamic factor. The MS diffusion coefficient  $\mathcal{D}_{12}$  describes the molecular friction forces, whereas the thermodynamic factor  $\Gamma$  contains the thermodynamic information.

For a binary mixture, the thermodynamic factor  $\Gamma$  is defined as<sup>3</sup>

$$\Gamma = 1 + x_1 \left. \frac{\partial \ln \gamma_1}{\partial x_1} \right|_{T,p,\Sigma} = 1 + x_1 \left( \left. \frac{\partial \ln \gamma_1}{\partial x_1} - \frac{\partial \ln \gamma_1}{\partial x_2} \right) \right|_{T,p} \quad (8)$$

Here,  $\gamma_1$  is the activity coefficient of component 1,  $T$  and  $p$  denote temperature and pressure, respectively, and  $\Sigma$  indicates that the closing condition  $\sum_i x_i = 1$  has to be considered. For ideal mixtures and pure substances,  $\Gamma = 1$  holds by definition. Thus, MS diffusion coefficients and Fick diffusion coefficients are equal for ideal mixtures, and at infinite dilution. Mixtures with a thermodynamic factor  $0 < \Gamma < 1$  favor attractive interactions between the same species over interactions between different species. If  $\Gamma$  approaches zero, the mixture is approaching phase separation. Mixtures with  $\Gamma > 1$  exhibit associating behavior.

The thermodynamic factor  $\Gamma$  can be calculated from Gibbs energy models<sup>3</sup> or equations of state.<sup>44</sup> In molecular simulations, the thermodynamic factor can be calculated from Kirkwood–Buff integrals<sup>51</sup> or the permuted Widom test particle insertion method.<sup>52</sup> In this work, the thermodynamic factors are calculated from Kirkwood–Buff integrals  $G_{ij}$ :<sup>13</sup>

$$\Gamma = \left( 1 + \frac{1}{V} x_1 x_2 N (G_{11} + G_{22} - 2G_{12}) \right)^{-1} \quad (9)$$

Here,  $V$  is the volume of the simulation box and  $N$  is the total number of particles. For details, the reader is referred to Milzetti et al.,<sup>53</sup> Ben-Naim,<sup>54</sup> and Jamali et al.<sup>55</sup>

The MS diffusion coefficient can be expressed by velocity correlation functions. For a binary mixture, the MS diffusivity  $\mathcal{D}_{12}$  equals<sup>23</sup>

$$\mathcal{D}_{12} = \frac{x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}}}{\mathcal{D}_{\text{Darken}}} + \frac{x_1 x_2 N (CC_{11} + CC_{22} - 2CC_{12})}{\mathcal{D}_{\text{Cross}}} \quad (10)$$

The MS diffusion coefficient  $\mathcal{D}_{12}$  is composed of two parts: an (ideal) Darken diffusion coefficient  $\mathcal{D}_{\text{Darken}}$  containing the self-diffusion coefficients  $D_{i,\text{self}}$  (which are velocity autocorrelations), and a nonideal diffusion coefficient  $\mathcal{D}_{\text{Cross}}$  containing the velocity cross-correlations  $CC_{ij}$  between different particles of components  $i$  and  $j$ . For approximately ideal mixtures with weak molecular interactions, the velocity cross-correlations  $CC_{ij}$  are negligible compared to the self-diffusion coefficients  $D_{i,\text{self}}$  and the MS diffusion coefficient is approximately the Darken diffusion coefficient:  $\mathcal{D}_{12} \approx \mathcal{D}_{\text{Darken}}$ . For nonideal mixtures with strong molecular interactions, the nonideal diffusion coefficient  $\mathcal{D}_{\text{Cross}}$  can be in the same order of magnitude as the Darken diffusion coefficient  $\mathcal{D}_{\text{Darken}}$ . Thus, consideration of  $\mathcal{D}_{\text{Cross}}$  is essential for nonideal mixtures.

A number of works have studied the composition dependence of velocity cross-correlations  $CC_{ij}$ .<sup>56–67</sup> Weingärtner<sup>57</sup> observed that velocity cross-correlations  $CC_{ij}$  show a similar composition dependence as Kirkwood–Buff coefficients  $G_{ij}$ . However, a derivation of a relationship between velocity cross-correlations  $CC_{ij}$  and the thermodynamic factor  $\Gamma$  is not straightforward and no conclusive answer was found. Still, it is interesting to note that Weingärtner's observation in fact suggests a connection between the nonideal diffusion coefficient  $\mathcal{D}_{\text{Cross}}$  and the thermodynamic factor  $\Gamma$ : A comparison of eqs 9 and 10 reveals a structural similarity in the formulations of  $\mathcal{D}_{\text{Cross}}$  and  $\Gamma$ . Similarly, the Moggridge equation (eq 3) also suggests a correlation between the relative nonideality  $\mathcal{D}_{\text{Cross}}/\mathcal{D}_{\text{Darken}}$  and  $\Gamma$ : insertion of the Moggridge equation (eq 3) into eq 10 leads to

$$\frac{\mathcal{D}_{\text{Cross}}}{\mathcal{D}_{\text{Darken}}} = \frac{\mathcal{D}_{12} - \mathcal{D}_{\text{Darken}}}{\mathcal{D}_{\text{Darken}}} \quad (11)$$

$$= \frac{\mathcal{D}_{12}}{\mathcal{D}_{\text{Darken}}} - 1 \quad (12)$$

$$= \Gamma^{-0.36} - 1 \quad (13)$$

Thus, the Moggridge equation (eq 3) in fact relates the nonideal diffusion coefficient  $\mathcal{D}_{\text{Cross}}$  to the ideal Darken diffusion coefficient  $\mathcal{D}_{\text{Darken}}$  and the thermodynamic factor  $\Gamma$ .

The question arises whether the relation between nonideal diffusion effects and the thermodynamic factor can also be observed for self-diffusion coefficients. The McCarty–Mason equation (eq 6) resembles the ideal mixing rule for composition-dependent self-diffusion coefficients. In an analogy to the relative nonideality  $\mathcal{D}_{\text{Cross}}/\mathcal{D}_{\text{Darken}}$  of the mutual diffusion coefficient (eq 11), we define the relative deviation  $\Delta D_{i,\text{self,rel}}$  between the real self-diffusion coefficient  $D_{i,\text{self}}$  and the predicted self-diffusion coefficient  $D_{i,\text{self,pred}}$  by the McCarty–Mason equation (eq 6),

$$\Delta D_{i,\text{self,rel}} = \frac{D_{i,\text{self}} - D_{i,\text{self,pred}}}{D_{i,\text{self}}} \quad (14)$$

which is a measure for nonideal effects of self-diffusion. If the relative deviation  $\Delta D_{i,\text{self,rel}}$  can be described as a function  $f(\Gamma)$  of the thermodynamic factor, predictions of the McCarty–

Mason equation (eq 6) can be corrected to obtain a predictive equation for nonideal mixtures:

$$\Delta D_{i,\text{self,rel}} = \frac{D_{i,\text{self}} - D_{i,\text{self,pred}}}{D_{i,\text{self}}} = f(\Gamma) \quad (15)$$

$$\frac{1}{D_{i,\text{self}}} = \frac{1}{D_{i,\text{self,pred}}} (1 - f(\Gamma)) \quad (16)$$

$$= \left( \frac{x_1}{D_{i,\text{self}}^{x_1 \rightarrow 1}} + \frac{x_2}{D_{i,\text{self}}^{x_2 \rightarrow 1}} \right) (1 - f(\Gamma)) \quad (17)$$

In this work, we investigate correlations between both the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  of mutual diffusion coefficients and the relative deviation  $\Delta D_{i,\text{self,rel}}$  of self-diffusion coefficients with the thermodynamic factor  $\Gamma$ . We expect the thermodynamic factor to cover all nonidealities such that there is no need for further correction factors such as viscosity. To have a full and consistent set of transport data and thermodynamic data, we use MD simulations of Lennard–Jones (LJ) systems for our analysis. The correlations are then tested with experimental data of molecular systems.

### 3. SIMULATION DETAILS

Our analysis is based on MD simulations of LJ systems. In the following, we provide a short overview of the specifications of the simulations. For more details and numeric results, the reader is referred to Jamali et al.<sup>55</sup>

We performed 250 distinct MD simulations of binary LJ systems. All parameters and properties of these simulations are reported in reduced units. The parameters of the first species serve as base units: diameter  $\sigma_1 = \sigma = 1$ , interaction energy  $\epsilon_1 = \epsilon = 1$ , and mass  $m_1 = m = 1$ . The parameters of the second species and the adjustable parameter  $k_{ij}$  of the Lorentz–Berthelot mixing rule are listed in Table 1. To cover a broad

**Table 1. Specifications of the Studied LJ Systems<sup>a</sup>**

specification	values
total number of particles	500, 1000, 2000, 4000
independent simulations	10, 10, 5, 5
$x_1$	0.1, 0.3, 0.5, 0.7, 0.9
$\epsilon_2/\epsilon_1$	1.0, 0.8, 0.6, 0.5
$\sigma_2/\sigma_1$	1.0, 1.2, 1.4, 1.6
$m_2/m_1$	$(\sigma_2/\sigma_1)^3$
$k_{ij}$	0.05, 0.0, -0.3, -0.6

<sup>a</sup>LJ particle of type 1 has  $\sigma_1 = \sigma = 1.0$ ,  $\epsilon_1 = \epsilon = 1.0$ , and mass  $m_1 = 1.0$  in reduced units.<sup>68</sup>  $k_{ij}$  is an adjustable parameter to the Lorentz–Berthelot mixing rule  $\epsilon_{ij} = \sqrt{\epsilon_1 \epsilon_2} (1 - k_{ij})$ , controlling the non-ideality of the systems.

range of nonidealities, the ratios of the parameters of the first and second species are varied over a large range. The reduced temperature  $T$  and pressure  $p$  are  $T = 0.65$  and  $p = 0.05$ . For each specified LJ system, two different types of simulations were performed: simulations to determine transport properties and simulations to determine thermodynamic factors.

Transport properties were calculated from equilibrium MD simulations with 200 million time steps with a time step length of 0.001 in reduced units. The transport coefficients were calculated from time-correlation functions. The Einstein relations were used to sample the time correlations; i.e., the

displacements of particles were sampled over time.<sup>68,69</sup> The self-diffusion coefficients follow from<sup>13</sup>

$$D_{i,\text{self}} = \lim_{t \rightarrow \infty} \frac{1}{6N_i t} \left\langle \sum_{j=1}^{N_i} (\mathbf{r}_{j,i}(t) - \mathbf{r}_{j,i}(0))^2 \right\rangle \quad (18)$$

where  $t$  is the correlation time,  $N_i$  is the number of molecules of species  $i$ , and  $\mathbf{r}_{j,i}$  is the position of the  $j$ th molecule of species  $i$ . The angle brackets denote an ensemble average. The velocity cross-correlations  $CC_{ii}$  and  $CC_{ij}$  follow from<sup>13</sup>

$$CC_{ii} = \lim_{t \rightarrow \infty} \frac{1}{6N_i t} \left\langle \left( \sum_{k=1}^{N_i} (\mathbf{r}_{k,i}(t) - \mathbf{r}_{k,i}(0)) \right) \cdot \left( \sum_{l=1, l \neq k}^{N_i} (\mathbf{r}_{l,i}(t) - \mathbf{r}_{l,i}(0)) \right) \right\rangle \quad (19)$$

$$CC_{ij} = \lim_{t \rightarrow \infty} \frac{1}{6N_i t} \left\langle \left( \sum_{k=1}^{N_i} (\mathbf{r}_{k,i}(t) - \mathbf{r}_{k,i}(0)) \right) \cdot \left( \sum_{l=1}^{N_j} (\mathbf{r}_{l,j}(t) - \mathbf{r}_{l,j}(0)) \right) \right\rangle \quad (20)$$

where  $N$  is the total number of molecules in the mixture.

The values of the transport coefficients depend on the box size of the MD simulations. More precisely, the transport coefficients scale linearly with the inverse of the box size,  $1/L$ . To correct for these finite-size effects, each LJ system was simulated for four different system sizes (500, 1000, 2000, and 4000 particles). Subsequently, the transport coefficients were extrapolated linearly to an infinite box size, i.e.,  $1/L \rightarrow 0$ , to obtain the transport coefficients in the thermodynamic limit. For details on the finite-size corrections with numeric results and a comparison to analytic finite-size corrections, the reader is referred to Jamali et al.<sup>55</sup>

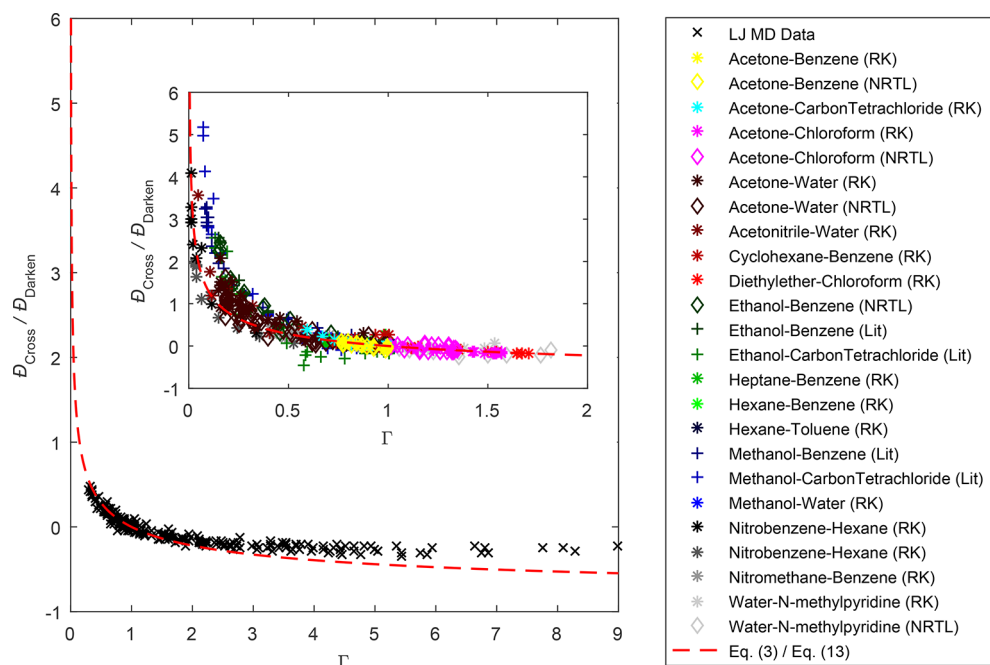
For the calculation of thermodynamic factors, equilibrium MD simulations with large systems consisting of 25 000 particles were performed. The thermodynamic factors were calculated from Kirkwood–Buff coefficients (cf. eq 9). The Kirkwood–Buff coefficients were calculated from integrals of the radial distribution functions (RDFs). Both the RDFs and the Kirkwood–Buff integrals were corrected for finite-size effects using the method of Ganguly and van der Vegt<sup>70</sup> and Milzetti et al.<sup>53</sup> for the RDFs, and the method of Krüger et al.,<sup>51</sup> Dawass et al.,<sup>71</sup> and Krüger and Vlught<sup>72</sup> for the Kirkwood–Buff integrals. Each simulation for the calculation of thermodynamic factors was performed for 10 million time steps with a time step length of 0.001 in reduced units.

All simulations for both transport properties and thermodynamic factors were repeated at least five times with varying seed numbers. Thereby, statistical mean values and 95% confidence intervals were evaluated.

### 4. RESULTS AND DISCUSSION

The MD simulations provide a full set of transport data and thermodynamic properties. Thereby, the MD simulations enable a comprehensive analysis of nonideal effects of mutual and self-diffusion coefficients. In section 4.1, we analyze the correlation between the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  of mutual diffusion coefficients and the thermodynamic factor  $\Gamma$ .





**Figure 1.** Relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  of mutual diffusion coefficients as a function of the thermodynamic factor  $\Gamma$ . Outer figure: Data from MD simulations (black crosses) vs predictive Moggridge equation (eq 3, red dashed line). Inset: Experimental data vs predictive Moggridge equation (eq 3, red dashed line). Stars: Experimental data with thermodynamic factors calculated with Redlich–Kister (RK). Diamonds: Experimental data with thermodynamic factors calculated with NRTL. Plus symbols: Experimental data with thermodynamic factors given in the literature. Statistical uncertainties of the MD data are given in Jamali et al.<sup>55</sup> References for the experimental data are provided in Table S1 in the Supporting Information.

We assess the performance of the Moggridge equation (eq 3) and confirm its validity for a wide range of nonideal mixtures. In section 4.2, we investigate the correlation between the relative deviation  $\Delta D_{i,\text{self,rel}}$  of self-diffusion coefficients with the thermodynamic factor  $\Gamma$ . We derive an improved model for the prediction of composition-dependent self-diffusion coefficients in nonideal binary mixtures (section 4.2.1) and validate our model with experimental data (section 4.2.2).

**4.1. Mutual Diffusion Coefficients.** The nonideality of mutual MS diffusion coefficients  $D_{12}$  is represented by the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  (eq 11). According to eq 13, we can assume a correlation between the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  and the thermodynamic factor  $\Gamma$ . Figure 1 shows the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  as a function of the thermodynamic factor  $\Gamma$ . The data of our MD simulations are a continuous function of the thermodynamic factor  $\Gamma$ . For the considered LJ systems, the thermodynamic factor is in the range  $0.28 < \Gamma < 9$  and the relative nonidealities are in the range  $-0.34 < D_{\text{Cross}}/D_{\text{Darken}} < 0.47$ ; i.e., the MS diffusion coefficient  $D_{12}$  differs from the ideal Darken diffusion coefficient by up to 47%. For ideal mixtures with equal molecular interactions ( $\Gamma = 1$ ), the velocity cross-correlations vanish and thereby the relative nonideality vanishes:  $D_{\text{Cross}}/D_{\text{Darken}} = 0$ . For self-associating mixtures ( $\Gamma < 1$ ), the velocity cross-correlations  $CC_{ii}$  between particles of the same component  $i$  become predominant and the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  is positive. For mixtures with associating behavior between unlike particles of different components  $i$  and  $j$ , the velocity cross-correlations  $CC_{ij}$  become predominant and the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  is negative.

To validate our MD simulation data, we compare it to experimental data from the literature.<sup>15,24,25,32,57,62,66,73–100</sup> Table S1 in the Supporting Information provides a detailed list

of references for the experimental data used in this work. The experimental data sets consist of mutual Fick diffusion coefficients  $D_{12}$ , self-diffusion coefficients  $D_{i,\text{self}}$  and thermodynamic factors  $\Gamma$ . The self-diffusion coefficients  $D_{i,\text{self}}$  originate from NMR measurements or diffusion measurements with radioactive tracers; the thermodynamic factors  $\Gamma$  are either reported directly in the literature or calculated from Redlich–Kister (RK) and/or NRTL parameters reported in the literature. The relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  is calculated from the experimental data sets via combination of eqs 10 and 7:

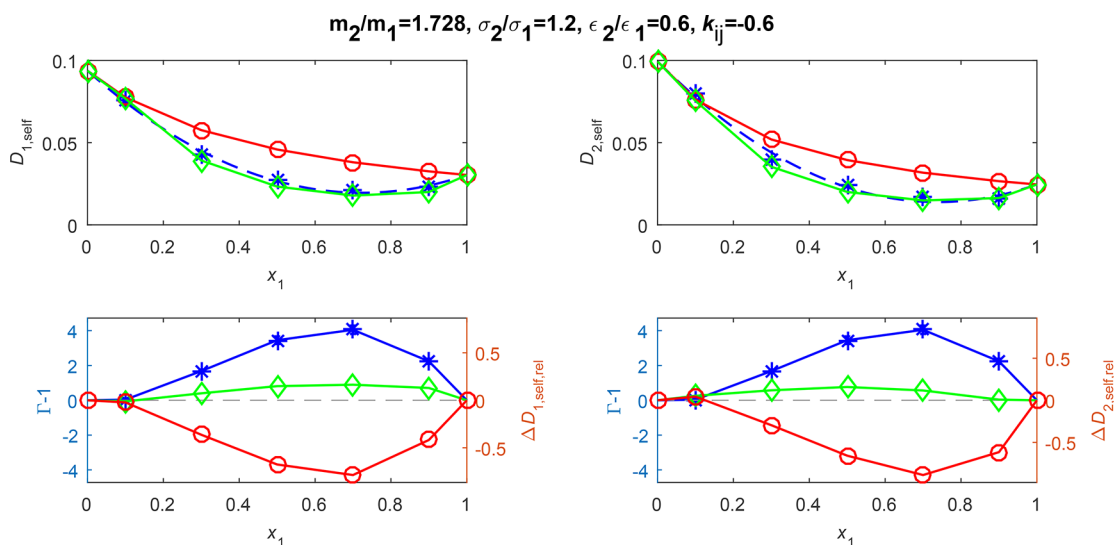
$$\frac{D_{\text{Cross}}}{D_{\text{Darken}}} = \frac{D_{12} - D_{\text{Darken}}}{D_{\text{Darken}}} \quad (21)$$

$$= \frac{D_{12}/\Gamma}{D_{\text{Darken}}} - 1 \quad (22)$$

$$= \frac{D_{12}/\Gamma}{x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}}} - 1 \quad (23)$$

The thermodynamic factors of the experimental data are in the range  $0 < \Gamma < 2$ . Figure 1 provides an inset for the range  $0 < \Gamma < 2$ . Overall, our MD data agree well with the experimental data. Deviations can be observed only for mixtures with dimerizing species, i.e., ethanol and methanol for the current data set. For dimerizing species, the relative nonideality  $D_{\text{Cross}}/D_{\text{Darken}}$  is larger in comparison to nondimerizing species. This special behavior of dimerizing species was also observed by Moggridge<sup>31</sup> and is also observed for self-diffusion coefficients below (cf. section 4.2.2).

Figure 1 also shows the predictions of the Moggridge equation (cf. eqs 3 and 13). In the typical range of thermodynamic factors of molecular systems,  $0 < \Gamma < 2$ , the



**Figure 2.** Composition-dependent self-diffusion coefficients  $D_{i,\text{self}}$ , thermodynamic factors  $\Gamma$ , and relative deviations  $\Delta D_{i,\text{self,rel}}$  of a binary LJ system with specification  $\epsilon_2/\epsilon_1 = 0.6$ ,  $\sigma_2/\sigma_1 = 1.2$ ,  $m_2/m_1 = 1.728$ , and  $k_{ij} = -0.6$ . Left, species 1; right, species 2. Top figures: simulation results of composition-dependent self-diffusion coefficients  $D_{i,\text{self}}$  (blue stars); smoothing fit to the simulation results (blue dashed line); predictions of the McCarty–Mason equation (eq 6) (red circles/line); predictions of the modified McCarty–Mason equation (eq 25) (green diamonds/line). The error bars of  $D_{i,\text{self}}$  are smaller than the symbols. Bottom figures: Composition dependence of the thermodynamic factor  $\Gamma - 1$  (blue stars/line, left axis) and composition dependence of the relative deviation  $\Delta D_{i,\text{self,rel}}$  between the self-diffusion coefficients and the predictions of the McCarty–Mason equation (eq 6) (red circles/line, right axis) and the modified McCarty–Mason equation (eq 25) (green diamonds/line, right axis). A clear correlation between  $\Gamma - 1$  and  $\Delta D_{i,\text{self,rel}}$  can be observed. The error bars of  $\Gamma - 1$  are smaller than the symbols in most cases. A full set of plots for all considered LJ systems is provided in the [Supporting Information](#).

Moggridge equation performs well and agrees with our MD data as well as with most of the experimental data. Again, mixtures with dimerizing species show larger deviations from the Moggridge equation. For large thermodynamic factors  $\Gamma > 2$ , our MD data suggest a different functional relation than the Moggridge equation with less negative relative nonidealities  $\bar{D}_{\text{Cross}}/\bar{D}_{\text{Darken}}$ . To identify possible reasons for the deviations between MD data and the Moggridge equation, we examined the distance of the MD simulations state points to their critical points. Fifteen out of 250 simulations have state points close to their critical points. However, these 15 simulations have thermodynamic factors  $\Gamma < 1$  and their relative nonidealities  $\bar{D}_{\text{Cross}}/\bar{D}_{\text{Darken}}$  are well predicted by the Moggridge equation. In contrast, deviations are observed between the relative nonidealities  $\bar{D}_{\text{Cross}}/\bar{D}_{\text{Darken}}$  of the MD simulations and the Moggridge equation for large thermodynamic factors ( $\Gamma > 5$ ). These systems are far from their critical points. Therefore, the closeness of a system's state point to its critical point can be excluded as a possible reason for the observed deviations between the MD data and the predictions of the Moggridge equation. However, for practical applications with typical thermodynamic factors  $0 < \Gamma < 2$ , the performance of the Moggridge equation is excellent.

**4.2. Self-Diffusion Coefficients.** The nonideality of self-diffusion coefficients  $D_{i,\text{self}}$  is represented by the relative deviation  $\Delta D_{i,\text{self,rel}}$  (eq 14). For ideal mixtures, we expect relative deviations  $\Delta D_{i,\text{self,rel}} = 0$  from the predictions of the McCarty–Mason equation (eq 6). For nonideal mixtures, we assume that a modification of the McCarty–Mason equation with a function of the thermodynamic factor can account for nonideal effects (cf. eq 17). In section 4.2.1, we analyze the correlation between the relative deviation  $\Delta D_{i,\text{self,rel}}$  and the thermodynamic factor  $\Gamma$  in nonideal LJ systems and derive a modified McCarty–Mason equation for nonideal mixtures. In

section 4.2.2, we validate the modified McCarty–Mason equation with experimental data.

**4.2.1. Self-Diffusion Coefficients of LJ Systems.** Figure 2 (top) shows an example of composition-dependent self-diffusion coefficients  $D_{1,\text{self}}$  and  $D_{2,\text{self}}$  of a binary LJ system with pronounced nonideality. The specification of the LJ system is  $\epsilon_2/\epsilon_1 = 0.6$ ,  $\sigma_2/\sigma_1 = 1.2$ ,  $m_2/m_1 = 1.728$ , and  $k_{ij} = -0.6$ . The extreme value of the binary parameter  $k_{ij} = -0.6$  leads to a pronounced nonideal behavior of the mixture. Thereby, a possible relationship between the relative nonideality  $\Delta D_{i,\text{self,rel}}$  and the thermodynamic factor  $\Gamma$  is clearly revealed.

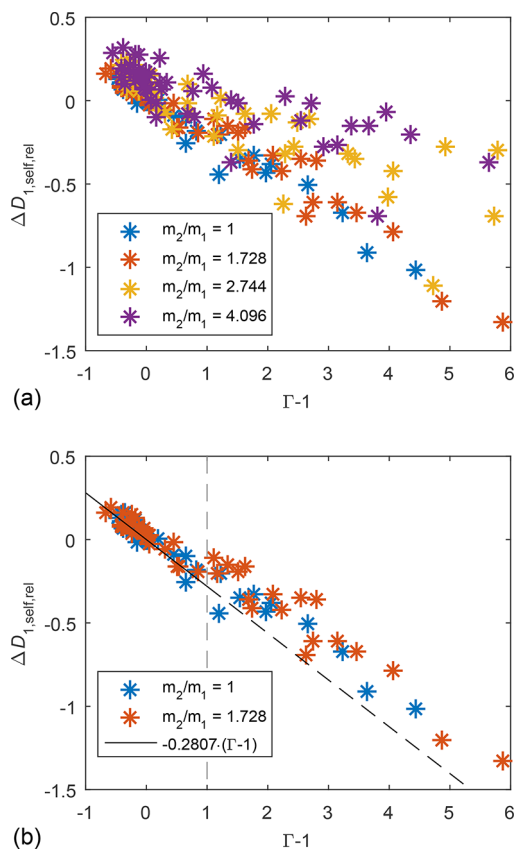
In a first step, we test the performance of the McCarty–Mason equation (eq 6). The McCarty–Mason equation requires the prior knowledge of self-diffusion coefficients  $D_{i,\text{self}}^{x_i \rightarrow 1}$  at infinite dilution and of the pure substances. In MD simulations, statistical uncertainties are very large for mixtures approaching infinite dilution of one of the components. Therefore, the MD simulations have been performed for mixtures with at least 10 mol % of each species, i.e.,  $x_1 = [0.1, 0.3, 0.5, 0.7, 0.9]$ . To obtain the values of  $D_{i,\text{self}}^{x_i \rightarrow 1}$  we performed a smoothing fit with a quadratic polynomial function to the self-diffusion coefficients  $D_{i,\text{self}}$ . Figure 2 (top) shows the smoothing fit as well as the predictions of the McCarty–Mason equation. As expected, the McCarty–Mason prediction shows large deviations. However, the curvature of the composition dependence is retrieved.

Figure 2 (bottom) shows the composition dependence of the relative deviation  $\Delta D_{i,\text{self,rel}}$  (eq 14) of the predictions made by the McCarty–Mason equation. Large relative deviations up to 70% are observed. Figure 2 (bottom) also shows the composition dependence of the thermodynamic factor minus 1,  $\Gamma - 1$ . The term  $\Gamma - 1$  is a measure for the deviation of the mixture from an ideal mixture. In the present

case,  $\Gamma - 1$  takes values of up to 4.2; i.e., the LJ system is highly nonideal.

We can now compare the composition dependencies of  $\Gamma - 1$  and  $\Delta D_{i,\text{self,rel}}$ . Figure 2 (bottom) suggests a strong correlation between  $\Delta D_{i,\text{self,rel}}$  and  $\Gamma - 1$ : Large deviations of a mixture from ideal behavior lead to large relative deviations of the McCarty–Mason prediction.

To study the correlation between  $\Delta D_{i,\text{self,rel}}$  and  $\Gamma - 1$  for the full set of LJ systems, we plot  $\Delta D_{i,\text{self,rel}}$  as a function of  $\Gamma - 1$ . Figure 3a shows the plot for the first species (plots for the



**Figure 3.** Relative deviations  $\Delta D_{i,\text{self,rel}}$  of the McCarty–Mason predictions (eq 6) of self-diffusion coefficients as a function of the thermodynamic factor  $\Gamma$  for LJ systems. (a)  $\Delta D_{i,\text{self,rel}}$  for all LJ systems, color-coded by the molar mass ratios  $m_2/m_1$ . (b)  $\Delta D_{i,\text{self,rel}}$  for LJ systems with molar mass ratios  $m_2/m_1 < 2$  and best fit of eq 15 (black line) for  $0 < \Gamma < 2$  (indicated by the vertical dashed line). Plots for the second species are provided in the Supporting Information.

second species are provided in the Supporting Information). A general trend  $\Delta D_{i,\text{self,rel}} \propto \Gamma - 1$  can be observed. However, the data scatters for molar mass ratios  $m_2/m_1 > 2$ . As a first approximation, we restrict our analysis to systems with molar mass ratios  $m_2/m_1 < 2$ . Figure 3b shows the relative deviation  $\Delta D_{i,\text{self,rel}}$  as a function of  $\Gamma - 1$  for all LJ systems with molar mass ratios  $m_2/m_1 < 2$ . A clear correlation  $\Delta D_{i,\text{self,rel}} \propto \Gamma - 1$  can be observed. For the full range of thermodynamic factors  $0 < \Gamma < 7$ , the McCarty–Mason predictions show large deviations of up to 130%. The root-mean-square error of  $\Delta D_{i,\text{self,rel}}$  is RMSE = 35%; i.e., the McCarty–Mason predictions deviate by 35% on average. However, molecular systems typically have thermodynamic factors in the range  $0 < \Gamma < 2$  (cf. section 4.1). Still, even in this molecular systems

range ( $0 < \Gamma < 2$ ), the McCarty–Mason predictions have an RMSE of 10%.

To improve the McCarty–Mason predictions, we introduce a linear fit of  $\Delta D_{i,\text{self,rel}}$  as a function of  $\Gamma$  following eq 15. Fitting both  $\Delta D_{1,\text{self,rel}}$  and  $\Delta D_{2,\text{self,rel}}$  in the typical range of thermodynamic factors  $0 < \Gamma < 2$  results in the function (cf. Figure 3b)

$$f(\Gamma) = -0.2807(\Gamma - 1) \quad (24)$$

Insertion of eq 24 into eq 17 leads to an improved predictive equation for composition-dependent self-diffusion coefficients:

$$\frac{1}{D_{i,\text{self}}} = \left( \frac{x_1}{D_{i,\text{self}}^{x_1 \rightarrow 1}} + \frac{x_2}{D_{i,\text{self}}^{x_2 \rightarrow 1}} \right) (1 + 0.2807(\Gamma - 1)) \quad (25)$$

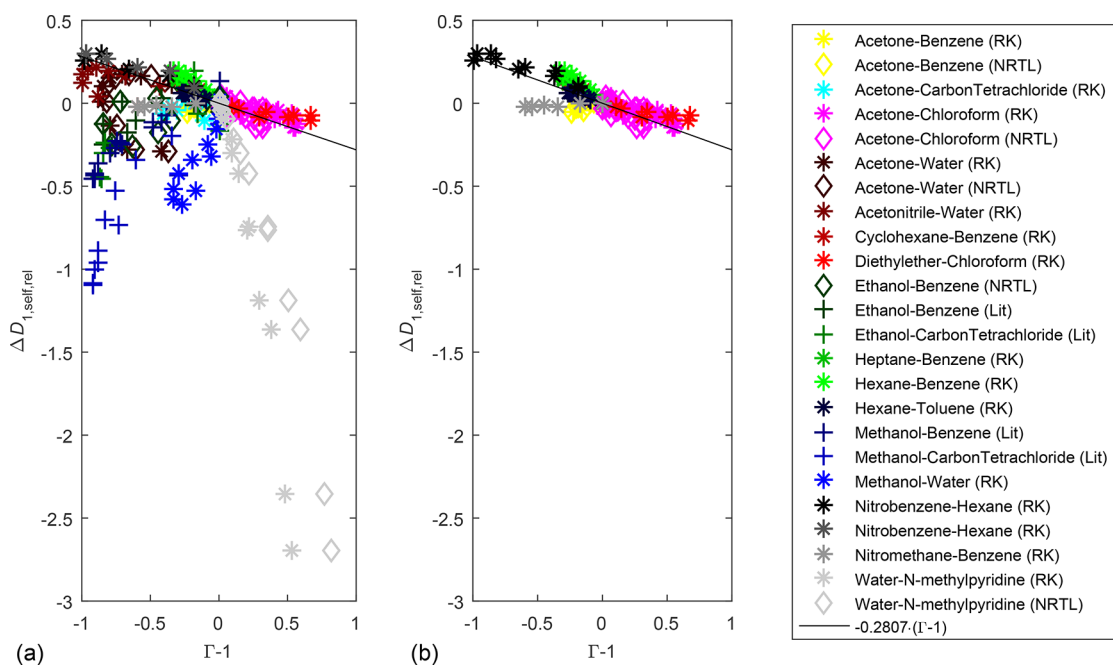
In the rest of the paper, eq 25 will be called the “modified McCarty–Mason equation”. Using the modified McCarty–Mason equation, the accuracy of the predictions is doubled compared to the McCarty–Mason predictions: The RMSE halves from 10 to 5% for  $0 < \Gamma < 2$ .

Figure 2 shows the improved predictions of the modified McCarty–Mason equation for the exemplary LJ system considered above. Since average deviations can be misleading because the error always goes to zero for the pure component limits, it is also important to quantify maximum errors. The maximum relative deviation decreases from  $|\Delta D_{i,\text{self,rel}}| = 70\%$  to  $|\Delta D_{i,\text{self,rel}}| = 12\%$  if the modified McCarty–Mason equation is used; i.e., the predictions are improved by a factor up to  $0.7/0.12 = 5.8$ . A full set of plots for all considered LJ systems is provided in the Supporting Information.

#### 4.2.2. Self-Diffusion Coefficients of Molecular Systems.

The modified McCarty–Mason equation (eq 25) was obtained from MD data of LJ systems. To evaluate the practical performance of the modified McCarty–Mason equation, it has to be tested with experimental data. Figure 4a shows the relative deviation  $\Delta D_{i,\text{self,rel}}$  of the McCarty–Mason equation (eq 6) as a function of  $\Gamma - 1$ . The correlation between  $\Delta D_{i,\text{self,rel}}$  and  $\Gamma - 1$  is not as clear as for LJ systems (cf. Figure 3); even ideal mixtures ( $\Gamma - 1 = 0$ ) have relative deviations  $\Delta D_{i,\text{self,rel}} \neq 0$ . Still, the linear fit (eq 24), which represents the predictions of the modified McCarty–Mason equation, captures a major part of the experimental data, but some molecular systems show large deviations. In particular, the systems water–*N*-methylpyridine and methanol–carbon tetrachloride show large deviations with completely different dependencies of  $\Delta D_{i,\text{self,rel}}$  on  $\Gamma - 1$ . This plot suggests that it may be even impossible to derive a model based on the thermodynamic factor  $\Gamma$  only that can capture all molecular systems.

However, the modified McCarty–Mason equation was derived for systems with molar mass ratios  $M_2/M_1 < 2$ . In addition, it was shown in section 4.1 that mixtures with dimerizing species need a separate analysis. Excluding systems with  $M_2/M_1 > 2$  and systems with dimerizing species results in the remaining data set shown in Figure 4b. For the remaining data set, a clear correlation between  $\Delta D_{i,\text{self,rel}}$  and  $\Gamma - 1$  is observed, which agrees with the linear fit (eq 24) of the modified McCarty–Mason equation. The RMSE of the McCarty–Mason predictions is 11%. If the modified McCarty–Mason equation is used, the RMSE decreases to 5%. Hence, the deviations of the predictions made by the modified McCarty–Mason equation are  $0.11/0.05 > 2$  times lower.



**Figure 4.** Relative deviations  $\Delta D_{1,\text{self,rel}}$  of the McCarty–Mason prediction (eq 6) as a function of the thermodynamic factor  $\Gamma$  for molecular systems (symbols) and linear fit of  $\Delta D_{1,\text{self,rel}}$  derived from LJ systems (black line, cf. eq 24). Stars: Experimental data with thermodynamic factors calculated with Redlich–Kister (RK). Diamonds: Experimental data with thermodynamic factors calculated with NRTL. Plus symbols: Experimental data with thermodynamic factors reported in the literature. (a)  $\Delta D_{1,\text{self,rel}}$  for all considered molecular systems. (b)  $\Delta D_{1,\text{self,rel}}$  for molecular systems with molar mass ratios  $M_2/M_1 < 2$  and without dimerizing species. Plots for the second species are provided in the Supporting Information.

The improvement in the prediction of self-diffusion coefficients can also be visualized in terms of the composition dependence: Figure 5 shows experimental and predicted composition-dependent self-diffusion coefficients of the exemplary systems nitrobenzene–hexane and cyclohexane–benzene (a full set of plots for all considered molecular systems is provided in the Supporting Information). For the system nitrobenzene–hexane, the maximum relative deviation  $|\Delta D_{1,\text{self,rel}}|$  of the McCarty–Mason prediction is  $\approx 30\%$  and the maximum relative deviation  $|\Delta D_{1,\text{self,rel}}|$  of the modified McCarty–Mason prediction is  $\approx 5\%$ . Hence, the deviations of the predictions made by the modified McCarty–Mason equation are  $0.30/0.05 \approx 6$  times lower. For the system cyclohexane–benzene, using the modified version of the McCarty–Mason equation decreases the maximum relative deviation  $|\Delta D_{1,\text{self,rel}}|$  from 10 to 4%, which corresponds to an improvement by a factor of  $0.10/0.04 \approx 2$ .

Hence significant improvements in the prediction of composition-dependent self-diffusion coefficients of nonideal binary liquid mixtures are obtained by use of the modified McCarty–Mason equation. Combining the modified McCarty–Mason equation (eq 6) with the Moggridge equation (eq 3) and eq 7 leads to the following model for the prediction of composition-dependent binary Fick diffusion coefficients:

$$D_{12} = (x_2 D_{1,\text{self}} + x_1 D_{2,\text{self}}) \Gamma^{0.64} \quad (26)$$

$$\frac{1}{D_{i,\text{self}}} = \left( \frac{x_1}{D_{i,\text{self}}^{x_1 \rightarrow 1}} + \frac{x_2}{D_{i,\text{self}}^{x_2 \rightarrow 1}} \right) (1 + 0.2807(\Gamma - 1)), \quad i = 1, 2 \quad (27)$$

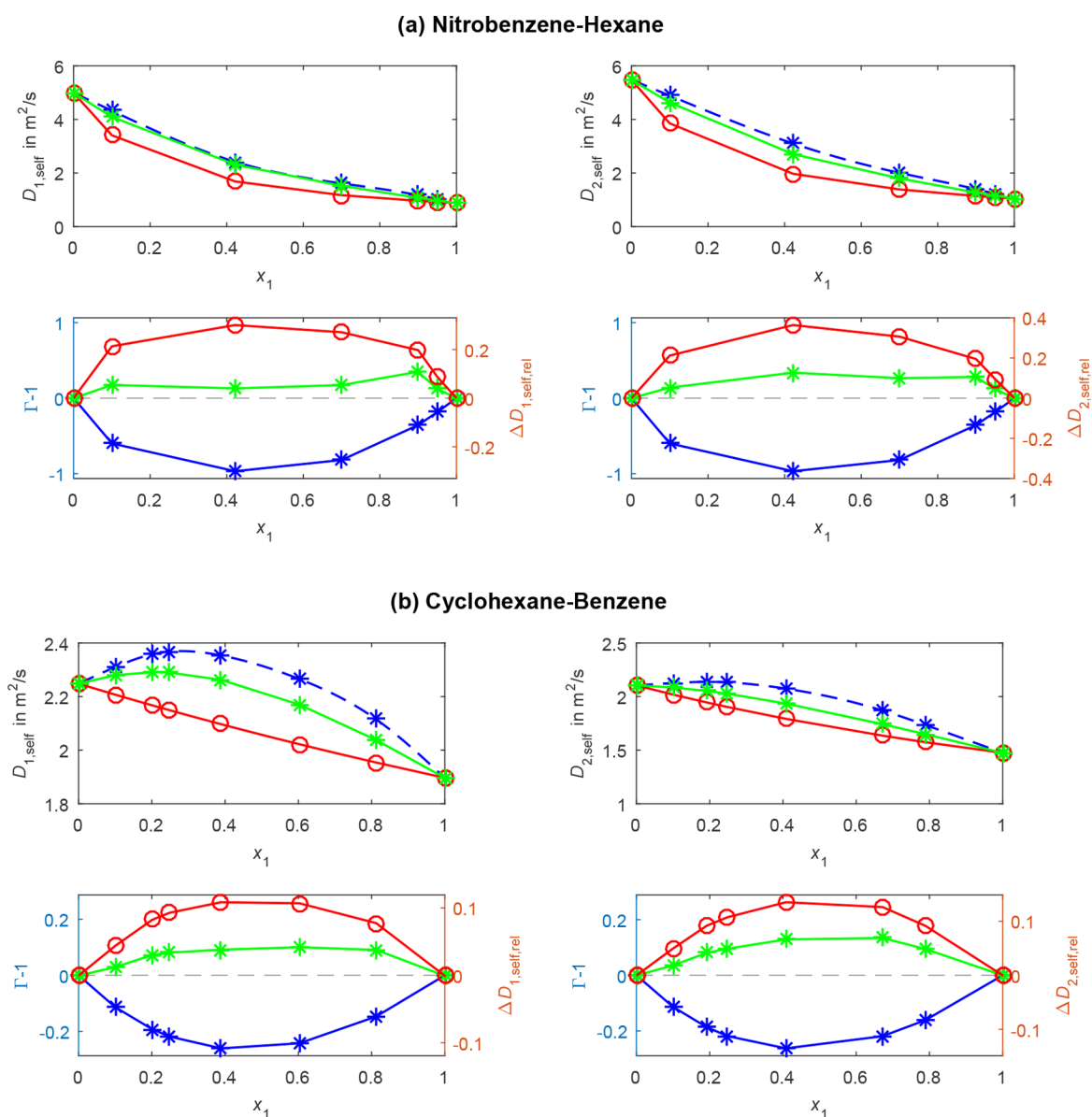
Thus, to predict composition-dependent Fick diffusion coefficients of binary mixtures with molar mass ratios  $M_2/M_1 < 2$  and without dimerizing species, we need only the self-diffusion coefficients at infinite dilution  $D_{i,\text{self}}^{x_i \rightarrow 1} = D_{ij}^{x_i \rightarrow 1} = D_{12}^{\infty}$  and the self-diffusion coefficients of the pure substances  $D_{i,\text{self}}^{x_i \rightarrow 1}$  as well as the thermodynamic factor  $\Gamma$  of the mixture.

## 5. CONCLUSIONS

The reliable prediction of composition-dependent mutual diffusion coefficients has been a challenge to scientists for decades. For ideal mixtures, the physically based Darken equation holds. For nonideal mixtures, semiempirical modifications of the Darken equation have been developed. However, Darken-based models rely on the knowledge of composition-dependent self-diffusion coefficients which are rarely available.

Therefore, predictions of composition-dependent self-diffusion coefficients are needed. In this work, we studied the composition dependence of mutual and self-diffusion coefficients in nonideal binary liquid mixtures. The basis of our analysis were data of Lennard-Jones (LJ) systems from molecular dynamics simulations which provide insight into the full set of transport data and thermodynamic properties. For both mutual and self-diffusion, strong correlations between nonideal diffusion effects and the thermodynamic factor were observed. The existing modification of the Darken equation by D’Agostino et al.<sup>24</sup> and Moggridge<sup>25</sup> was confirmed to accurately predict composition-dependent mutual diffusion coefficients for a wide range of nonideal mixtures with typical thermodynamic factors ( $0 < \Gamma < 2$ ). For mixtures with very large thermodynamic factors ( $\Gamma > 2$ ), the data of the LJ systems suggest deviations.





**Figure 5.** Composition-dependent self-diffusion coefficients  $D_{i,self}$ , thermodynamic factors  $\Gamma$ , and relative deviations  $\Delta D_{i,self,rel}$  for the systems (a) nitrobenzene–hexane and (b) cyclohexane–benzene. Top figures: experimental data of composition-dependent self-diffusion coefficients  $D_{i,self}$  (blue stars); smoothing fit of the experimental self-diffusion coefficients (blue dashed line); predictions of the McCarty–Mason equation (eq 6) (red circles/line); predictions of the modified McCarty–Mason equation (eq 25) (green stars/line). Bottom figures: Composition dependence of the thermodynamic factor  $\Gamma - 1$  (blue stars/line, left axis) and composition dependence of the relative deviation  $\Delta D_{i,self,rel}$  between the experimental self-diffusion coefficients and the predictions of the McCarty–Mason equation (eq 6) (red circles/line, right axis) and the modified McCarty–Mason equation (eq 25) (green stars/line, right axis). The thermodynamic factors are calculated with a Redlich–Kister model.

Based on the predictive model of McCarty and Mason<sup>47</sup> for ideal binary gas mixtures, we developed an improved model for the prediction of composition-dependent self-diffusion coefficients in nonideal binary liquid mixtures. Our new model is a function of the thermodynamic factor, the self-diffusion coefficients at infinite dilution, and the self-diffusion coefficients of the pure substances, which are readily available. Validation was carried out with experimental data of molecular systems. Self-diffusion coefficients of mixtures with typical thermodynamic factors  $\Gamma < 2$ , molar mass ratios  $M_2/M_1 < 2$ , and without dimerizing species are successfully predicted: The relative deviation of the predictions is halved from 10 to 5%. In the future, similar correlations may be derived for systems with dimerizing species and multicomponent mixtures. Our new

model thus provides the missing link to render Darken-based models into practical tools to predict mutual diffusion coefficients.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b03203.

Full set of figures with composition-dependent self-diffusion coefficients of LJ systems and molecular systems (experimental data). Detailed references to the experimental data used in this work (PDF)

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### Notes

The authors declare no competing financial interest.

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## NOTATION

### Latin Symbols

$CC_{ij}$  = velocity cross-correlation function between species  $i$  and  $j$  ( $m^2/s$ )

$D_{12}$  = Fick diffusion coefficient ( $m^2/s$ )

$\mathcal{D}_{12}$  = Maxwell–Stefan (MS) diffusion coefficient ( $m^2/s$ )

$\mathcal{D}_{\text{Darken}}$  = Maxwell–Stefan diffusion coefficient in ideal mixtures computed from the Darken equation ( $m^2/s$ )

$D_{\text{Cross}}$  = nonideal part of the Maxwell–Stefan diffusion coefficient, containing velocity cross-correlation functions ( $m^2/s$ )

$D_{i,\text{self}}$  = composition-dependent self-diffusion coefficient of species  $i$  ( $m^2/s$ )

$D_{i,\text{self,pred}}$  = predicted composition-dependent self-diffusion coefficient of species  $i$  ( $m^2/s$ )

$\Delta D_{i,\text{self,rel}}$  = relative deviation between actual and predicted composition-dependent self-diffusion coefficient of species  $i$

$G_{ij}$  = Kirkwood–Buff coefficient between species  $i$  and  $j$  ( $m^3$ )

$k_{ij}$  = adjustable parameter for the Lorentz–Berthelot mixing rules

$L$  = side length of cubic simulation box (m)

$m_i$  = mass of a Lennard-Jones particle of species  $i$  (m)

$M_i$  = molar mass of species  $i$  (kg/mol)

$N$  = total number of molecules

$N_i$  = number of molecules of species  $i$

$p$  = hydrostatic pressure (Pa)

$r_{ji}$  = position of molecule  $j$  of species  $i$  (m)

$T$  = temperature (K)

$V$  = volume of the simulation box ( $m^3$ )

$w_i$  = weight fraction of species  $i$

$x_i$  = mole fraction of species  $i$

### Greek Symbols

$\gamma_i$  = activity coefficient of species  $i$

$\Gamma$  = thermodynamic factor

$\epsilon_i$  = Lennard-Jones energy parameter for species  $i$  ( $\epsilon$ )

$\eta$  = shear viscosity (Pa·s)

$\sigma_i$  = Lennard-Jones size parameter for species  $i$  ( $\sigma$ )

### Superscripts

$x_i \rightarrow 1$  = mole fraction  $x_i$  of species  $i$  tending toward 1

$\infty$  = infinite dilution

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