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Unified Model for Nonideal Multicomponent Molecular Diffusion Coefficients

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Multicomponent diffusion is important in a variety of applications. In order to calculate diffusion flux, molecular diffusion coefficients are required, where fluid nonideality and the multicomponent nature of the mixture have a significant effect. A unified model for the calculation of diffusion coefficients of gas, liquid and supercritical states of nonpolar multicomponent mixtures is presented. A new correlation is proposed for the binary infinite dilution-diffusion coefficients. The generalized Vignes relation is used in multicomponent mixtures. Nonideality is rigorously described by the fugacity derivatives evaluated by the volume-translated Peng-Robinson equation of state. Predictions for highly nonideal gas and liquid multicomponent mixtures demonstrate the reliability of the proposed methodology. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2932–2939, 2007

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Introduction

Molecular diffusion describes the passive movement of molecules, due to random motion (Brownian motion), or to a composition gradient in a mixture, and is quantified by molecular diffusion coefficients, generally represented by *D*. Binary and multicomponent molecular diffusion is a fundamental process in a wide range of disciplines, including polymer science,[1] isotope separation,[2] combustion,[3] heterogeneous catalysis[4] and petroleum engineering.[5–8]

There is currently no general reliable theoretical framework to accurately predict *D* in nonideal gas and liquid multicomponent mixtures. The Chapman-Enskog theory[9] adequately accounts for diffusion in low-pressure binary-gas mixtures, but fails for liquids. The Stokes-Einstein theory[10] provides an estimate of *D* in ideal liquid mixtures, but is not applicable to real liquids. Various correlations have been developed to estimate *D* in specific conditions, with varying degrees of success.[11] However, to the best of our knowledge, there is no unique method that is reliably applicable to nonideal gas and liquid multicomponent mixtures.

In this work, we present a unified model to determine *D* for nonideal and nonpolar multicomponent mixtures. We develop a new correlation to predict binary infinite-dilution diffusion coefficients for gas, liquid and supercritical nonpolar mixtures. The new correlation is then used to calculate the dependency of molecular diffusion coefficients on composition, pressure and temperature for multicomponent mixtures, using the generalized Vignes relation and a rigorous description of mixture nonideality in the framework of irreversible thermodynamics.

Molecular Diffusion Flux

The most commonly used forms of expressing *D* are based on Stefan-Maxwell (SM) and Fickian diffusive fluxes. For a nonideal *n*-component mixture, the mole-based SM diffusive flux $\boldsymbol{J}^{\boldsymbol{M}}$ ($n-1$ element vector) is given by[11]

$$\boldsymbol{J}^{\boldsymbol{M}} = -c\left(\boldsymbol{B}^{\boldsymbol{M}}\right)^{-1}\cdot\Gamma\cdot\nabla x, \tag{1}$$

where c is the molar density of the mixture, and ∇x is the vector of composition gradients. The elements of the $(n-1)$ square matrix $\boldsymbol{B}^{\boldsymbol{M}}$ in Eq. 1 are given by

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$$B_{ii}^{M} = \frac{x_i}{\mathcal{D}_{in}} + \sum_{\substack{k=1 \\ i \neq k}}^{n} \frac{x_k}{\mathcal{D}_{ik}}, \qquad i = 1, \ldots, n-1 \tag{2}$$

$$B_{ij}^{M} = -x_i \left(\frac{1}{\mathcal{D}_{ij}} - \frac{1}{\mathcal{D}_{in}} \right), \qquad i,j = 1, \ldots, n-1, i \neq j \tag{3}$$

where $\mathcal{D}_{ij}$ are the SM diffusion coefficients for each i-j binary pair in the mixture, and x_i is the mole fraction of component i. Note that in the SM domain $\mathcal{D}_{ij}$'s do not form a square matrix, and that $\mathcal{D}_{ij} = \mathcal{D}_{ji}$. In Eq. 1., Γ is the matrix of thermodynamic factors with elements[12]

$$\Gamma_{ij} = x_i \left. \frac{\partial \ln f_i}{\partial x_j} \right|_{x_j, T, P}, \qquad i,j = 1, \ldots, n-1 \tag{4}$$

where f_i is the fugacity of component i. In Eq. 1, Γ represents fluid mixture nonideality[13] at the given conditions, and its elements can be calculated using activity coefficient or an equation of state. Many authors calculate Γ from activity coefficients, which can accurately describe the composition dependency of Γ, but fail to represent the system nonideality dependency on pressure. In this work, we choose to calculate Γ from the Peng-Robinson equation of state (PR-EOS),[14] for nonpolar mixtures. This EOS has a high accuracy for describing nonideality for hydrocarbon mixtures (see Figure 3.41 of Ref. 13). For polar mixtures, other equations of state can be used to accurately describe fugacity and nonideality.

The mole-based multicomponent Fickian diffusive flux is described as

$$\boldsymbol{J^M} = -c\boldsymbol{D^M} \cdot \nabla x, \tag{5}$$

where $\boldsymbol{D^M}$ is a square matrix (of order $n - 1$) of mole-based Fickian diffusion coefficients D^M. The Fickian diffusion in a nonideal multicomponent mixture has a solid foundation in thermodynamics of irreversible processes. Comparison of Eqs. 1 and 5 yields the following relationship[11] between $\boldsymbol{B^M}$ and $\boldsymbol{D^M}$

$$\boldsymbol{D^M} = \left(\boldsymbol{B^M}\right)^{-1} \Gamma. \tag{6}$$

For an n-component mixture, there are $n(n - 1)/2$ SM diffusion coefficients and $(n - 1)^2$ Fickian diffusion coefficients. For a ternary mixture, the SM diffusion coefficients are $\mathcal{D}_{12}, \mathcal{D}_{13}$ and $\mathcal{D}_{23}$; the mole-based Fickian diffusion coefficients are D_{11}^M, D_{12}^M, D_{21}^M and D_{22}^M.

Reference frames

The four most commonly used set of fluxes[15,16] are calculated from the mole-, mass-, volume- and solvent-based average reference velocity. The diffusive flux and diffusion coefficients in Eqs. 1 and 5 are relative to the mole-average reference velocity. For practical applications, we need to transform the mole-based diffusion coefficients D^M, to mass-based diffusion coefficients D^m. The transformation is given by[11]

$$\boldsymbol{D^m} = \boldsymbol{K^M} w x^{-1} \boldsymbol{D^M} x w^{-1} \left(\boldsymbol{K^M}\right)^{-1}, \tag{7}$$

where w and x are $(n - 1)$ vectors of mass and mole fractions, respectively. The elements of matrix $\boldsymbol{K^M}$ are given by:

$$K_{ij}^{M} = \delta_{ij} - w_i \left(1 - \frac{w_n x_j}{x_n w_j} \right), \qquad i,j = 1, \ldots, n-1 \tag{8}$$

where δ_{ij} is the Kronecker delta. The transformation from D^M to volume-based molecular diffusion coefficients D^V, is given by[11]

$$\boldsymbol{D^V} = \boldsymbol{K^V} \boldsymbol{D^M} \left(\boldsymbol{K^V}\right)^{-1}. \tag{9}$$

The elements of $\boldsymbol{K^V}$ are

$$K_{ij}^{V} = \delta_{ij} - x_i\left(\overline{V}_j - \overline{V}_n\right)/V, \qquad i,j = 1, \ldots, n-1. \tag{10}$$

where $\overline{V}_i$ is the partial molar volume of component i, and V is the molar volume of the mixture.

Infinite dilution coefficients

At the infinite dilution limit, all molecular diffusion coefficients $\left(\mathcal{D}, D^M, D^m \text{ and } D^V\right)$ become equal (for a given binary pair i-j in a multicomponent mixture), and receive a different notation D^∞. There are a number of relationships[11] that can be used to determine D^m in concentrated mixtures, based on D^∞ and other parameters, such as composition, viscosity, volume fraction, excess Gibbs energy. One of the most widely used correlations to estimate $\mathcal{D}$ for concentrated liquid mixtures is the Vignes relation[17]

$$\mathcal{D}_{12} = \left(D_{12}^{\infty}\right)^{x_2} \left(D_{21}^{\infty}\right)^{x_1}, \tag{11}$$

where $\mathcal{D}_{12}$ is the SM molecular diffusion coefficient of the mixture 1-2 with x_1 mole fraction of component 1 (and x_2 mole fraction of component 2), D_{21}^{∞} is the molecular diffusion coefficient of component 2 infinitely diluted in component 1, and D_{12}^{∞} is the molecular diffusion coefficient of component 1 infinitely diluted in component 2. In this work, we have selected to work with the Vignes relation, even though there are alternative suggestions. Recently, Bosse and Bart[18] proposed a relationship that incorporates nonideality in Eq.11, and showed results with apparent improvement. We have examined the work in Ref. 18 and found that the suggestion might in fact result in larger deviation between data and predictions. Krishna and van Baten[19] have proposed an extension of the Darken relation to multicomponent alkane mixtures, based on molecular simulation studies. In their work, both D^∞ and self-diffusion coefficient are needed to calculate $\mathcal{D}$ of all binary pairs in the mixture. We tested their proposed extension to the Darken relation, and obtained similar results as with the generalized Vignes relation. We opted for the latter since there are less coefficients needed in the Vignes relation. The generalized Vignes relation to multicomponent mixtures is given by[20]

$$\mathcal{D}_{ij} = \left(D_{ij}^{\infty}\right)^{x_j} \left(D_{ji}^{\infty}\right)^{x_i} \prod_{\substack{k=1 \\ k \neq i,j}}^{n} \left(D_{ik}^{\infty} D_{jk}^{\infty}\right)^{x_k/2}, \qquad i,j = 1, \ldots, n, i \neq j \tag{12}$$

where $\mathcal{D}_{ij}$ is the SM molecular diffusion coefficient of the binary pair i-j, D_{ij}^{∞} is the molecular diffusion coefficients of component i infinitely diluted in component j, and x_{i} is the mole fraction of component i. Once all $\mathcal{D}_{ij}$ are found, $\boldsymbol{D^M}$ and $\boldsymbol{D^m}$ can be calculated from Eqs. 6 and 7, respectively.

Table 1. Summary of Data Used in Development of Infinite Dilution Diffusion Coefficient Correlation

State	Solvents	No. Data Points	Solutes	Range of Conditions
Liquid	Alkanes, alkyl halides, aromatics gases	420	Alkanes, alkyl halides, aromatics gases	T: 273 − 567 K P: 0.10 − 922 MPa μ: 0.04 − 5.09 mPa.s D^{∞}: 0.46 − 118 × 10^{-9} m^2/s
Gas	Alkanes, alkyl halides, gases	353	Alkanes, alkyl halides, gases	T: 154 − 958K P: 0.1 − 138 MPa μ: 0.01 − 0.60 mPa.s D^{∞}: 9.7 × 10^{-9} − 6.8 × 10^{-4} m^2/s
Supercritical	Carbon dioxide	116	Alkanes, aromatics	T: 299 − 333K P: 9.0 − 26.5 MPa μ: 0.03 − 0.66 mPas D^{∞}: 8.2 − 25.8 × 10^{-9} m^2/s

Previous Correlations

In the past, empirical relations have been developed with varying degrees of success, particularly for D^{∞}. Taylor and Krishna[11] provide a comprehensive review of correlations for low-pressure liquid systems, their accuracies and limitations. Here we list only the ones most pertinent to our work. The most widely used correlation to calculate D^{∞} is that of Wilke and Chang[21]; they express D^{∞} in terms of temperature, solution viscosity, solute molar volume at normal boiling point, and obtain an absolute average deviation (AAD) of 10% for 285 data points. Their correlation is valid for liquid mixtures at atmospheric pressure only. Kooijman[22] developed a correlation for D^{∞}, based on the Stokes-Einstein relation, and using UNIFAC parameters to correct for particle roundness and size, and valid only for liquid mixtures at atmospheric pressure. He obtains an AAD of 10% for 245 data points. Hayduk and Minhas[23] developed a set of correlations, specific to certain types of mixtures (alkanes, nonpolar mixtures and mixtures with water as solvent). For normal alkanes, they calculate D^{∞} from temperature, solvent viscosity at normal boiling point and solute molar volume at normal boiling point, finding an AAD of 3.4% (for 58 data points). Their correlation is only applicable to liquid alkane mixtures at atmospheric pressures. Sigmund[24] developed a correlation for high-pressure gas and liquid binary mixtures. He finds D^m from an expression that relates the reduced density-diffusion coefficient product $cD/(cD)^0$ to a third-degree polynomial function of reduced densities c/c^0, and yields AADs of 10% for gas mixtures, and 40% for liquid mixtures (for 344 data points and 52 data points, respectively). His correlation is intended for binary mixtures only. Riazi and Whitson[25] developed a correlation to predict gas and liquid D^m for nonideal binary mixtures. They relate reduced density-diffusion coefficient product $cD/(cD^0)$ to reduced viscosity μ/μ^0, component reduced pressures and component acentric factors. They report AADs of 8% for gas mixtures (for 140 data points), and 15% for liquid mixtures (for 163 data points). The main limitation of their work is that it cannot be extended to multicomponent mixtures, although the authors suggest an extension of their method to ternary mixtures (by treating them as pseudo-binary mixtures). Their expression cannot be used in a way similar to ours; according to their model, D^{∞} has very similar values for all mixtures with a similar dominant component, regardless of the component at infinite dilution, which may not be justifiable. We tested their correlation and found it to be very sensitive to the viscosity model chosen, especially for the composition dependency of D, and, therefore, we do not compare their model to ours. We use the Wilke-Chang method as a base comparison; we compare our work to the Kooijman and the Hayduk-Minhas methods because all can be used for multicomponent mixtures. We compare our work with Sigmund's because, like ours, his method can also be used for binary mixtures at high-pressures.

Proposed Correlation

Experimental data used

We have developed a new correlation based on 889 experimental data of D^{∞} for nonpolar mixtures from literature. The data used in our work are given in Tables 1, 2 and 3 of the supplementary material. We do not include polar components, but include data for very light to heavy gases, aromatics and polyaromatics, normal and branched alkanes. For the sake of brevity, normal alkanes are referred to as nC_i (i = number of carbon atoms) from here on. Table 1 summarizes mixtures and experimental conditions. We include self-diffusion coefficients and binary D^{∞}, aiming at a general correlation for all types of nonpolar mixtures, in gas, liquid and supercritical states. When available, we used experimental values of solvent density and viscosity. When not available, we calculated density and viscosity according to the

Table 2. Comparison of D^{∞} Model Performance

	AAD (%)*				
Mixture Type	This Work	Wilke-Chang[21]	Kooijman[22]	Hayduk Minhas [23]	Sigmund[24]
All	12.1	181.8	74.2	95.7	40.9
Gas	11.5	71.1	79.8	83.5	11.8
Liquid	13.2	156.9	54.7	116.0	72.8
Supercritical	10.3	605.9	127.0	60.1	14.4
Data not used in correlation	16.4	227.8	977.6	136.8	70.3

*AAD stands for absolute average deviation, which is defined as:

$$\mathrm{AAD}(\%) = 1/n\left(\sum_{n=1}^{n}\left|\left(D^{\infty}_{\mathrm{reg}} - D^{\infty}_{\mathrm{exp}}\right)\Big/D^{\infty}_{\mathrm{exp}}\right|\right) \times 100.$$

Table 3. Comparison of our Model Results with Experimental Data for Ternary Mixtures

	$D^m_{ij}(10^{-9}\text{m}^2/\text{s})$			$D^V_{ij}(10^{-9}\text{m}^2/\text{s})$		
Subscripts *ij*	Mixture 1[39] nC_8 (1), nC_{10} (2), and MN (3)			Mixture 2[38] nC_{12} (1), nC_{16} (2) and nC_6 (3)		
	Exp.	This work	Δ (%)	Exp.	This work	Δ (%)
1 1	1.99	1.30	35	0.968	1.04	7
1 2	−0.93	−0.11	88	0.226	0.42	57
2 1	−0.42	−0.46	10	0.225	0.27	19
2 2	2.40	0.87	65	1.031	1.12	8

Mixture 1 consists of normal octane (nC_8), normal decane (nC_{10} and 1- methylnaphthalene (MN) at 295.65K and 0.1 MPa. The symbols nC_8, nC_{10} and MN stand for normal octane, normal decane and 1-methylnaphthalene, respectively. Mixture 2 is at 298.15K and 0.1 MPa; it consists of normal dodecane (nC_{12}), normal hexadecane (nC_{16}) and normal hexane (nC_6). Numbering of each component is in parenthesis after name of component. Δ(%) is defined as $|D_{\text{exp}} - D_{\text{reg}}|/D_{\text{exp}} \times 100$.

most reliable method: for hydrocarbons, we calculated viscosity using the corresponding state theory,[26] and density using the PR-EOS,[14] corrected by the volume shift parameter;[13] for other components, we used specific correlations for density and viscosity based on experimental data.[27–29]

Resulting correlation

In the development of our correlation, we performed nonlinear least-squares minimization on various relationships of the general functional form

$$\frac{cD^\infty}{(cD)^0} = f\left(\frac{\mu}{\mu^0}, T_r, P_r, \omega\right), \tag{13}$$

and found the following expression to best describe the experimental data

$$\frac{cD^\infty_{21}}{(cD)^0} = A_0\left(\frac{T_{r,1}P_{r,2}}{T_{r,2}P_{r,1}}\right)^{A_1}\left(\frac{\mu}{\mu^0}\right)^{\left[A_2\left(\omega_1,\omega_2\right)+A_3\left(P_r,T_r\right)\right]} \tag{14}$$

The constants A_0 to A_3 are given by

$$\begin{aligned}
A_0 &= e^{a_1},\\
A_1 &= 10a_2,\\
A_2 &= a_3(1 + 10\omega_1 - \omega_2 + 10\omega_1\omega_2),\\
A_3 &= a_4\left(P_{r,1}^{3a_5} - 6P_{r,2}^{a_5} + 6T_{r,1}^{10a_6}\right) + a_7T_{r,2}^{-a_6} + a_2\left(\frac{T_{r,1}P_{r,2}}{T_{r,2}P_{r,1}}\right)
\end{aligned} \tag{15}$$

where

$$\begin{aligned}
a_1 &= -0.0472,\\
a_2 &= 0.0103,\\
a_3 &= -0.0147,\\
a_4 &= -0.0053,\\
a_5 &= -0.3370,\\
a_6 &= -0.1852,\\
a_7 &= -0.1914
\end{aligned}$$

In Eq. 14, c is the molar density (mol/m^3) of component 1, μ is the viscosity (Pa.s) of component 1, $(cD)^0$ and μ^0 are the dilute gas density-diffusion coefficient product (mol/m.s) and viscosity (Pa.s), respectively, $T_{r,i}$ and $P_{r,i}$ are the reduced temperature and pressure ($T/T_{c,i}$ and $P/P_{c,i}$), respectively, of component i and ω_i is the acentric factor of component i. Subscript 1 indicates the concentrated component, subscript 2 indicates the component at infinite dilution. We calculate $(cD)^0$ using the approach by Fuller et al.,[30,31] and use the correlation by Stiel and Thodos[32] to calculate μ^0. Details are given in appendix A. For an n-component mixture, we calculate the $(n - 1)^2$ D^m from binary pairs D^∞ by the following steps:

1. For each binary pair *i-j*, find D^∞_{ij} from Eq. 14;
2. Calculate $Ɖ_{ij}$ from Eq. 12;
3. Calculate $\boldsymbol{B^M}$, using Eqs. 2 and 3;
4. Calculate $\boldsymbol{D^M}$, using Eqs. 4 and 6.
5. Transform $\boldsymbol{D^M}$ to $\boldsymbol{D^m}$ (using Eqs. 7 and 8), or to $\boldsymbol{D^V}$ (using Eqs. 9 and 10).

Results

Figure 1 shows that our correlation fits very well to the experimental data. The ADD of Eq. 14 is 12.1% for all mix-

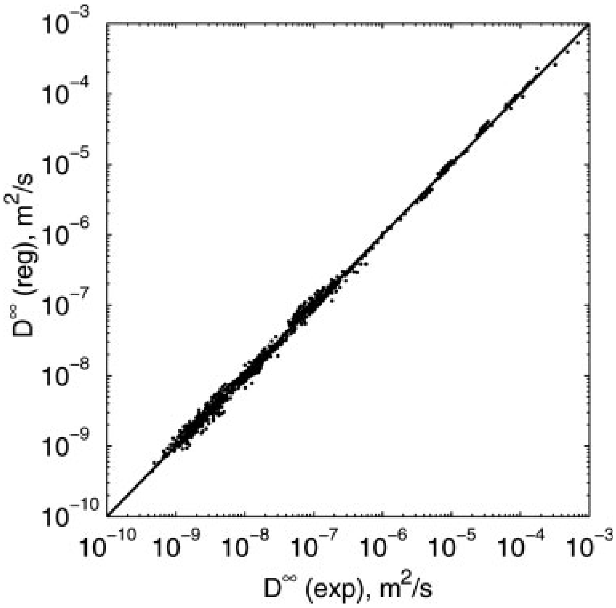

Figure 1. Infinite dilution diffusion coefficient: experimental (dots) values vs. values obtained from Eq. 14 (solid line).

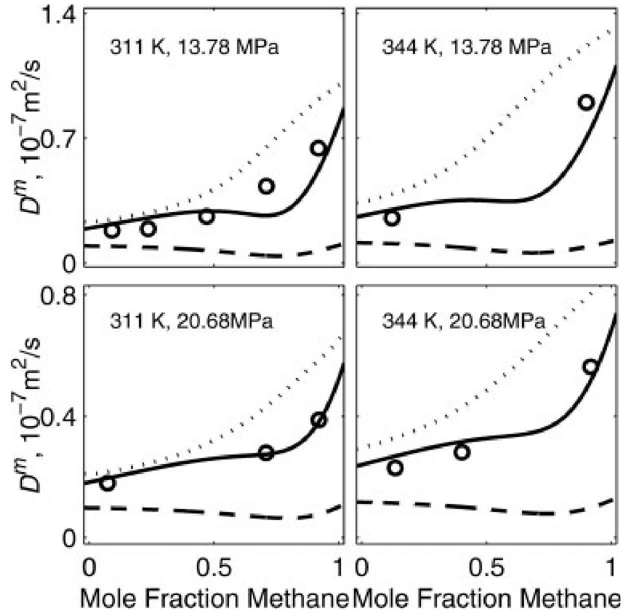

Figure 2. Variation of D^m with composition for methane-propane mixtures,[24] at various pressures and temperatures (indicated in each plot).

Plots show experimental data (○), this work (—), Hayduk-Minhas correlation (– –), Sigmund correlation (. . .).

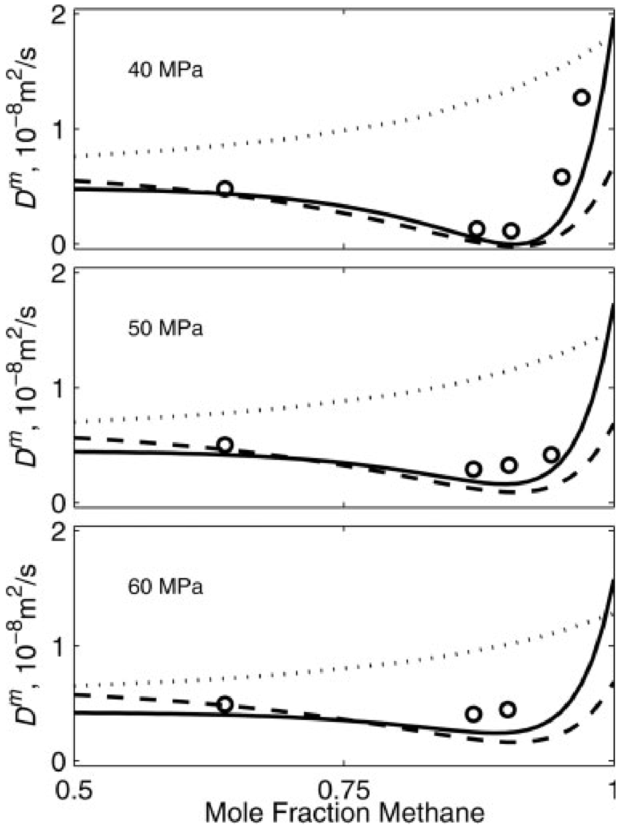

Figure 3. Variation of D^m with composition for methane-normal decane,[33] at 303K and different pressures (shown in plots).

Plots show experimental data (○), this work (—), Hayduk-Minhas correlation (– –), and Sigmund correlation (. . .)

tures, 11.5% for gases, 13.2% for liquids and 10.3% for mixtures close to or above their critical point. Table 2 compares results from our correlation with those by Wilke-Chang[21], Kooijman[22], Hayduk-Minhas,[23] and Sigmund,[24] for the experimental data used in this work. Our correlation performs better than all other we compared it to, for all types of mixtures. We tested Eq. 14 with 368 experimental data not used in the development of the correlation (Tables 4, 5 and 6 of supplementary material). For such data, our correlation also performs better when compared to others, as shown in the last row of Table 2. The data not included in the correlation consist mostly of slightly polar or polar components and very light gases.

We compare our model to Sigmund and Hayduk-Minhas models for specific mixtures. Figures 2 and 3 show compositional variation of D for binary mixtures C_1-C_3[24] and C_1-nC_{10},[33] at different temperatures and pressures. Our model accurately predicts the change of D^m with mixture composition for alkane mixtures, close and far from the critical point. Note that the nonideality in a binary mixture is explicitly represented by $\partial \ln f_1/\partial \ln x_1$ which we calculate from the PR-EOS. It is interesting to note that D^m of C_1-nC_{10} is one-order of magnitude lower than that of C_1-C_3 for the data conditions. Based on the criteria of stability and criticality, binary D's approach zero as the mixture approaches the critical point. Some of the correlations in the literature, including that of Riazi-Whitson and Sigmund may not represent this behavior.

In Figure 4, we compare our model predictions to experimental results for six equimolar binary mixtures of alkane gases (C_1-C_3, C_1-iC_4, C_1-iC_5 and C_2-C_3, C_2-iC_4, C_2-iC_5; where iC_4 is methylpropane, and nC_5 is dimethylpropane), at 0.1 MPa and various temperatures.[34] Results from our model are in accordance with experimental data and trends, for all tested mixtures. Note that there is a three-order of magnitude increase in D^m for the gas mixtures of Figure 4 compared to results in Figure 3.

Figure 5 compares model results to experimental data for four binary mixtures (nC_7-nC_{10}, nC_7-nC_{12}, nC_7-nC_{14}, and nC_8-nC_{14}) at 298.15K, 0.1MPa and varying composition.[35] Our model shows the smallest deviation from experimental data, and agrees best with experimental trends.

In Figure 6, we compare model results to experimental data for the following systems of binary mixtures: 1-methylnaphthalene-normal alkanes,[36] benzene-normal alkanes,[37] and nC_{10}-normal alkanes,[36] at 298.15K, 0.1MPa, and 50 wt % of each component (50 mole % for mixtures with benzene). Our model predicts very well the experimental data for all mixtures.

There are very few experimental data on molecular diffusion coefficient of ternary mixtures. To the best of our knowledge, the only two ternary liquid mixtures available in the literature consisting of nonpolar or only slightly polar molecules are nC_6 (33.3 mole %), nC_{12} (35 mole %) and nC_{16} (31.7 mole %), at 298.15 K and 0.1 MPa;[38] and nC_8-nC_{10}-1-methylnaphthalene, with 33 wt % each component, at 296.65 K and 0.1 MPa.[39] In Table 3 we compare

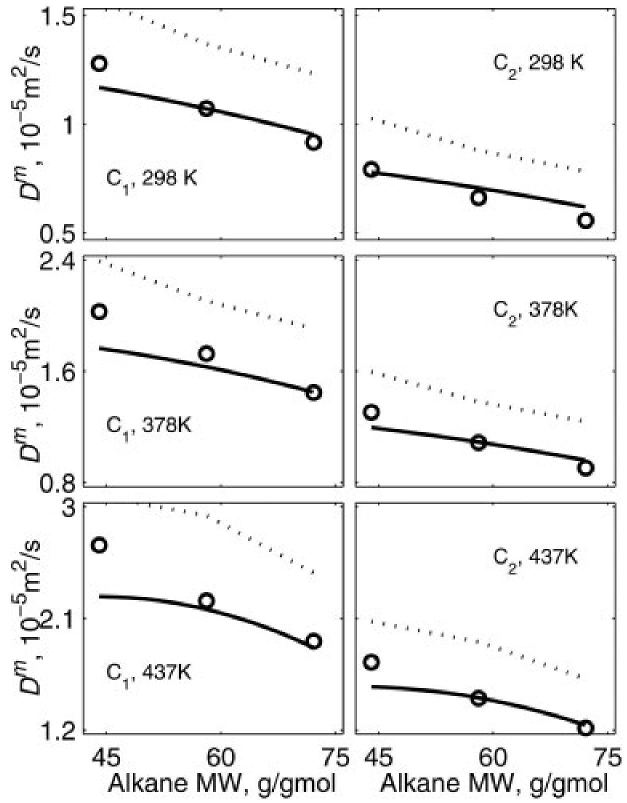

Figure 4. D^m vs. alkane molecular mass of binary gas mixtures of alkanes, at atmospheric pressure and different temperatures.[34]

For each plot, we show either C_1 or C_2, and the temperature. The other alkanes used are propane, methylpropane and dimethylpropane. Results are for experimental data (○), this work (—), and Sigmund correlation (…). The results for Hayduk-Minhas correlation are much lower than the scale in the plot, and are not shown.

our results for the two ternary mixtures to the experimental data. Our model shows a deviation from experimental results comparable to reported errors for cross-diagonal molecular diffusion coefficients D_{12}^M and D_{21}^M. Given the limited available literature data, and the high inaccuracy of experimental ternary molecular diffusion coefficients (especially for cross-diffusion coefficients), our model works well for slightly polar ternary mixtures. For the nonpolar mixture nC_6-nC_{12}-nC_{16}, our predicted values are very close to experimental results.

Concluding Remarks

We have developed a method to calculate diffusion coefficients for nonideal binary and multicomponent mixtures in a unified framework. The proposed methodology is based on accurate estimation of binary infinite dilution-diffusion coefficients D^∞. We used an extensive set of data for various nonpolar mixtures to develop a new correlation to determine D^∞ in gas, liquid and supercritical states, using the same correlating parameters. The data included hydrocarbons from C_1 to nC_{32} and nonhydrocarbons, such as N_2, CO_2 and He. The predicted results are in agreement with measured data. In addition to the results presented in the figures and tables in the article, we have also tested our model with additional

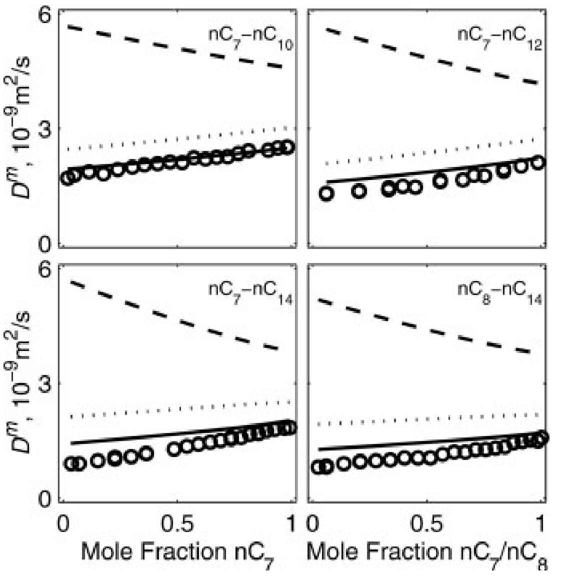

Figure 5. D^m vs. composition for binary liquid mixtures of normal alkanes[35], at 298.15 K and 0.1 MPa.

The components of each mixture are indicated in the graph. Results are for experimental data (○), this work (—), Hayduk-Minhas correlation (– –), and Sigmund correlation (…).

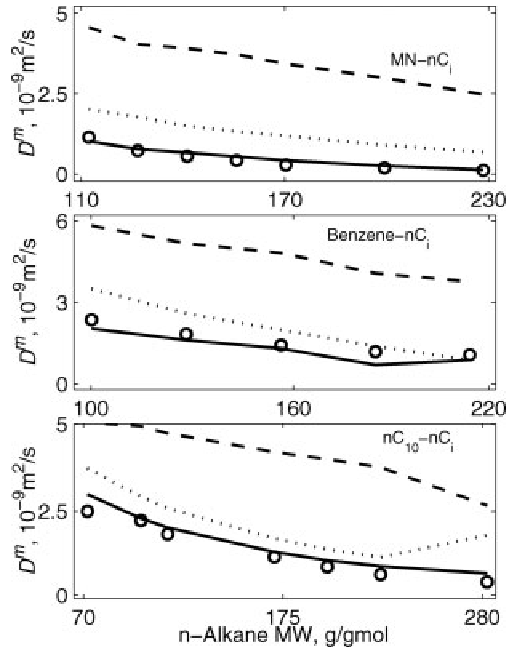

Figure 6. D^m vs. normal alkane molecular mass for 1-methylnaphthalene (MN) — normal alkanes, benzene — normal alkanes, and normal decane — normal alkanes, at 298.15 K and 0.1 MPa.[36,37]

Results are for experimental data (○), this work (—), Hayduk-Minhas correlation (– –), and Sigmund correlation (…).

binary and ternary mixtures. The agreement between measured data and predictions are similar to what we have reported in the article.

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Notation

a_1-a_6 = constants of Eq. 15
A_0-A_3 = coefficients of Eq. 14
$\boldsymbol{B^M}$ = $(n - 1)$ mole-based square matrix, s/m^2
c = total and pure component mixture molar density at T and P, mol/m^3
D = general form of molecular diffusion coefficient, m^2/s
D_{ij}^{∞} = infinite dilution-diffusion coefficient of component i infinitely diluted in component j, m^2/s
$Đ_{ij}$ = Stefan-Maxwell diffusion coefficient of binary pair i-j, m^2/s
$\boldsymbol{D^M}$ = $(n - 1)$ square matrix of mole-based Fickian diffusion coefficients, m^2/s
$\boldsymbol{D^m}$ = $(n - 1)$ square matrix of mass-based Fickian diffusion coefficients, m^2/s
$\boldsymbol{D^V}$ = $(n - 1)$ square matrix of volume-based Fickian diffusion coefficients, m^2/s
f_i = fugacity of component i, Pa
$\boldsymbol{J^M}$ = molar diffusive flux, mol/m^2.s
$\boldsymbol{K^M}$ = conversion matrix for mass-mole conversion of diffusion coefficients
$\boldsymbol{K^V}$ = conversion matrix for volume-mole conversion of diffusion coefficients
M_1, M_2 = molecular mass of components 1 and 2, g/mol
n = number of components in a mixture
P = pressure, Pa
$P_{c,i}$ = critical pressure of component i, Pa
$P_{r,i}$ = reduced pressure of component i
T = temperature of system, K
$T_{c,i}$ = critical temperature of component i, K
$T_{r,i}$ = reduced temperature of component i
$\underline{V}$ = molar volume of mixture, m^3/mol
$\overline{V}_i$ = partial molar volume of component i, m^3/mol
w_i = mass fraction of component i
x_i = mole fraction of component i

Greek letters and other symbols

δ_{ij} = Kronecker delta
$\sum v_i$ = sum of atomic diffusion volumes of component i, used in Eq. A1
Γ = matrix of thermodynamic factors
∇x = molar composition gradient, 1/m
μ = viscosity of mixture at T and P, Pa.s
μ^0 = dilute-gas viscosity, Pa.s
ξ_i = parameter used in Eqs. A2 and A3 to calculate μ^0
$(cD)^0$ = dilute gas density-diffusion product, mol/m.s
ω_i = acentric factor of component i

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Appendix A

We use the Fuller et al. approach[30,31] to calculate the dilute gas density-diffusion coefficient product, as recommended by Poling, Prausnitz and O'Connell[40]

$$(cD)^0 = 1.01 \times 10^{-2} T^{0.75} \frac{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{0.5}}{R\left[\left(\sum v_1\right)^{1/3} + \left(\sum v_2\right)^{1/3}\right]^2} \tag{A1}$$

where $(cD)^0$ is given in mol/m.s; M_1, M_2 are the molecular masses (g/mol) of components 1 and 2, respectively; T is the absolute temperature (K), and $\sum v_i$ is the so-called "diffusion volume increments" of component i, and is calculated by summing the atomic diffusion volumes given in their work (Table 11-1 in Ref. 40). It is also possible to calculate the dilute gas density-diffusion coefficient product theoretically;[9] we found that the Fuller et al. approach yielded smaller errors in the calculations.

We tested various methods to calculate low-pressure viscosity[9,42,43] for pure components and mixtures. The correlation by Stiel and Thodos[32] gave the most reliable result for nonpolar mixtures, with no need for extra parameters. The low-pressure viscosity for each component is given by[32]

$$\begin{aligned} \mu_i^0 \xi_i &= 34 \times 10^{-8} \left(T_{r,i}\right)^{0.94} & \left(T_{r,i} < 1.5\right) \\ \mu_i^0 \xi_i &= 17.78 \times 10^{-8} \left(4.58 T_{r,i} - 1.67\right)^{5/8} & \left(T_{r,i} > 1.5\right), \end{aligned} \tag{A2}$$

where $T_{r,i}$ is the reduced temperature of component i ($T/T_{c,i}$) and

$$\xi_i = \frac{T_{c,i}^{1/6}}{M_i^{1/2} \left(0.987 \times 10^{-5} P_{c,i}\right)^{2/3}}. \tag{A3}$$

We consider that the dilute gas viscosity of the mixture is a weighted average of dilute gas viscosity of the components, given by

$$\mu^0 = \frac{\mu_1^0 M_1^{1/2} + \mu_2^0 M_2^{1/2}}{M_1^{1/2} + M_2^{1/2}}. \tag{A4}$$

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