Fick and Maxwell-Stefan Diffusion Coefficients in the Ternary Liquid Mixture of Acetone-Methanol-Chloroform

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Fick diffusion coefficients are calculated by means of molecular simulation for liquid mixtures containing acetone, methanol, and chloroform at 1 atm and 298 K for different compositions. For this means, Maxwell-Stefan (MS) diffusion coefficients were calculated using physical properties of the components and thermodynamic factors, Γ, using three different models of Wilson, NRTL, and UNIQUAC. Because of the lack of experimental data for Fick diffusivities for ternary system, the validity of the model was tested by comparing Fick diffusivities obtained for binary subsystems with experimental data for acetone-chloroform system. The results were in good agreement. So the Fick coefficients, Maxwell-Stefan diffusion coefficient, and the thermodynamic factors were predicted for the ternary mixture as well as its binary subsystems by molecular simulation in a consistent manner. The presented ternary diffusion data should facilitate the development of aggregated predictive models for diffusion coefficients of polar and hydrogen-bonding systems and allows for an efficient and consistent prediction of multicomponent Fick diffusion coefficients from molecular models.

Keywords: Fick diffusion coefficient, Maxwell-Stefan, Wilson, NRTL, UNIQUAC

INTRODUCTION

The chemical industry has a need for accurate thermodynamic properties of mixtures in general [1]. Almost all separation processes in chemical engineering, such as distillation, absorption, or extraction, are affected by diffusion in liquids. Diffusion may even be the rate determining process in mass transfer unit operations [2] so that knowledge of the diffusion coefficients is required for their design and optimization [3]. Different theoretical and empirical methods can be used for determination of diffusion coefficients in multicomponent mixtures [1,4-6].

The study of Maxwell-Stefan (MS) diffusivities in multicomponent systems is of great practical and theoretical interest as the MS theory accounts for chemical potential gradients as driving forces for transport diffusion [5,7,8], while Fick's law theory relates a diffusive flux to a gradient of a measurable quantity, *e.g.* a mole fraction [9]. So unlike

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Fick's diffusion coefficients, the MS diffusion coefficients cannot be measured experimentally. Instead, MS diffusivities are obtained from measurable Fick's diffusivities and the matrix of thermodynamic factors [1].

MS diffusivities in binary mixtures can be obtained using measurable quantities like temperature, density, and composition [9-16]. In multicomponent mixtures, the system is much more complicated because of the strong dependence of MS diffusivity to overall composition [15-17]. Extension of techniques proposed for binary systems can lead to the method for estimation of MS diffusivity for multicomponent liquid mixtures [18-22].

Rehfeldt and Stichlmair measured the multicomponent diffusion coefficients for ternary liquid system containing acetone-1-butanol-1-propanol [23]. They obtained the diffusion coefficients for four other ternary liquid systems and calculated the MS diffusion coefficients from Fick diffusivities using thermodynamic correction factor [24]. Janzen and Vrabec measured Fick and MS diffusion coefficients for ternary liquid mixture of cyclohexane-

toluene-methanol [25]. Jamali *et al.* derived a correction term for calculation of the diffusion coefficients of multicomponent mixtures [26]. Guevara-Carrion *et al.* applied molecular dynamics simulation to measure the Fick diffusion coefficients of a quaternary liquid mixture. The mixture contained water-methanol-ethanol-2-propanol [27]. Zhao *et al.* calculated MS and Fick diffusion coefficients for various binary systems of water and H_2, CH_4, CO, O_2 and CO_2. They used molecular dynamics simulation approach by means of thermodynamic factor. The MS coefficients were strongly dependent on composition and temperature [28]. In another study, Liu *et al.* applied molecular dynamic simulation scheme for predicting the MS diffusivities of n-hexane-cyclohexane-toluene system [29]. Liu *et al.* obtained MS and Fick diffusivities for two binary systems, namely, acetone-methanol and acetone-tetrachloromethane. They showed that these diffusivities were in good agreement with experimental data [30].

In this paper, MS diffusion coefficients are estimated by the Vignes equation [18,19] by using diffusivity coefficients at infinite dilution. Diffusivity coefficient at infinite dilution itself can be calculated by different relations [18,19,31,32] that we have used Siddiqi-Lucas relation [22] in this work. The thermodynamic factor serves as a conversion factor between both diffusion coefficient types. Therefore, knowledge of the thermodynamic factor is required to determine the Fick diffusion coefficient using MS diffusion coefficients. It should be noted that the diffusion coefficients and the thermodynamic factor are matrices for mixtures containing three or more components.

The thermodynamic factor is usually estimated from experimental vapor-liquid equilibrium (VLE) or excess enthalpy data [33,34], employing an equation of state, like Soave-Redlich-Kwong or PC-SAFT, or an excess Gibbs energy G^E model, such as Margules, Van Laar, Wilson, NRTL, UNIQUAC or UNIFAC. Here we have used Wilson, NRTL, and UNIQUAC models to determine thermodynamic factor and then by using calculated MS diffusion coefficients, we are able to calculate Fick diffusion coefficients. In addition to ternary liquid mixture of (1) acetone, (2) methanol and (3) chloroform, both diffusion coefficients were also calculated for binary subsystems at T = 298 K and P = 1 atm and were compared with experimental data of Fick coefficients in order to verify the validity of the proposed model.

MATHEMATICAL MODEL

Generalized Fick's law relates the molar flux J_i of component *i* to the Fick diffusivity D_{ij} and its driving force ∇x_j

$$J_i = -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j \tag{1}$$

Here, c_t is the total molar concentration and x_j is the mole fraction of component *j*. There are (*n*-1) independent fluxes and (*n*-1) independent driving forces in an *n*-component system as the net flux of the system is zero in the molar reference frame, *i.e.* $\sum_{i=1}^{n} J_i = 0$. From Eq. (1) it follows directly that the elements of the matrix of Fick diffusivities [*D*] depend on the labeling of the components. The MS formulation uses chemical potential gradients as driving forces for mass transport. For liquid mixtures at constant temperature and pressure, the MS equation equals [34].

$$\sum_{j=1}^{n-1} \Gamma_{ij} \nabla x_j = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i J_i - x_j J_i}{c_t Đ_{ij}} \tag{2}$$

where $Đ_{ij}$ is the MS diffusivity coefficient which describes the interaction or friction between components *i* and *j* due to the difference in their velocities. G_{ij} is the thermodynamic factor which is defined as:

$$\Gamma_{ij} = \delta_{ij} + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,P,\sum} \tag{3}$$

In the above equation δ_{ij} is the Kronecker delta and γ_i is the activity coefficient of component *i* in the mixture. Since generalized Fick's law and the MS approach have the same description for processes, the MS formulation can be related to the Fick formulation by [9]:

$$[D] = [B]^{-1}[\Gamma] \tag{4}$$

In which, [*D*] is the matrix of Fick diffusivities in a molar reference frame and [Γ] is the matrix of thermodynamic factors. The matrix [*B*] elements are defined as follows:

$$B_{ij} = \frac{x_i}{Đ_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{Đ_{ij}} \quad with \ i = 1,2,...(n-1) \tag{5}$$

Table 1. Wilson, NRTL, and UNIQUAC Parameters for Binary Systems

Components	Wilson		NRTL			UNIQUAC	
	$(\lambda_{12} - \lambda_{11})$ (J mol$^-$ K^{-1})	$(\lambda_{21} - \lambda_{22})$ (J mol$^-$ K^{-1})	$(g_{12} - g_{22})$ (J mol$^-$ K^{-1})	$(g_{21} - g_{11})$ (J mol$^-$ K^{-1})	α_{12}	$(u_{12} - u_{22})$ (J mol$^-$ K^{-1})	$(u_{21} - u_{11})$ (J mol$^-$ K^{-1})
(1) Acetone (2) Methanol	-2562.1897	4926.7649	4095.4955	-1665.6244	0.3029	3510.2054	-1420.9118
(1) Acetone (2) Chloroform	839.0968	-2612.2876	-4262.4660	3520.1499	0.287	-2179.0099	1922.1887
(1) Methanol (2) Chloroform	-1513.4945	7086.6110	5708.7525	-562.05861	0.2932	5294.1251	-1147.0709

$$B_{ij} = -x_i \left(\frac{1}{\text{Ð}_{ij}} - \frac{1}{\text{Ð}_{in}} \right) \quad with\ i, j = 1,2,...(n-1)\ and\ i \neq j \quad (6)$$

In order to predict [D] we need the MS diffusivities of each binary pair in the multicomponent mixture. A geometrically consistent generalization of the Vignes equation for ternary mixtures was proposed by Wesselingh and Krishna [18]:

$$\text{Ð}_{ij} = \prod_{k=1}^{n} \left(\text{Ð}_{ij,x_{k \to 1}} \right)^{x_k} \quad (7)$$

where the $\text{Ð}_{ij,x_{k \to 1}}$ are the limiting values of the MS diffusivities in a mixture where component k is present in a very large excess or in other words while both i and j are infinitely diluted in a third component k. The two limiting diffusivities on the i-j face may, therefore, be identified as the binary i-j infinite dilution diffusivities D_{ij}° and D_{ji}° [9].

$$\text{Ð}_{ij,x_{j \to 1}} = \text{Ð}_{ij}^{\circ}$$
$$\text{Ð}_{ij,x_{i \to 1}} = \text{Ð}_{ji}^{\circ} \quad (8)$$

So the binary MS diffusivity in a multicomponent system can be predicted as following equation

$$\text{Ð}_{ij} = \left(\text{Ð}_{ij}^{\circ} \right)^{\frac{1+x_j - x_i}{2}} \left(\text{Ð}_{ji}^{\circ} \right)^{\frac{1+x_i - x_j}{2}} \quad (9)$$

Diffusivity coefficients at infinite dilution were obtained using Siddiqi-Lucas relation [22].

$$\text{Ð}_{12}^{\circ} = 9.89 \times 10^{-8} \mu_2^{-0.907} V_1^{-0.45} V_2^{0.265} T \quad (10)$$

Activity coefficient, γ_i was obtained using Wilson, NRTL, and UNIQUAC models [9]. The term Γ in Eq. (3) has usually large uncertainties. It involves the first derivative of the $\ln\gamma_i$ with respect to composition. Hence, application of excess Gibbs energy models which could be well fitted with vapor-liquid equilibrium data like Wilson, NRTL, and UNIQUAC can provide more accurate approximation with less error for the current system containing polar components of acetone, methanol, and chloroform.

Activity coefficients parameters for Wilson, NRTL and UNIQUAC models for the ternary system (1) acetone, (2) methanol, and (3) Chloroform are given in Table 1 [35]. Also, values of viscosity at 298 K and liquid molar volumes and parameters r_i and q_i for UNIQUAC model for three components are given in Table 2. MATLAB software was used for calculation of the diffusion coefficients based on the mentioned equations. The details could be found in the literature [36].

Table 2. Viscosity, Liquid Molar Volume, and UNIQUAC Parameters for System Components

Component	μ_i @ T = 298 K (cp)	v_i (cm^3 $gmol^{-1}$)	r_i	q_i
(1) Acetone	0.316	74.05	2.57	2.34
(2) Methanol	0.56	40.73	1.43	1.43
(3) Chloroform	0.53	80.67	2.70	2.34

Table 3. MS Diffusion Coefficients of the Binary Subsystems Containing (1) Acetone, (2) Methanol and (3) Chloroform from Simulations at 1 atm and 298 K

x_1	x_2	x_3	Đ (10^{-9} m^2 s^{-1})
(1) Acetone + (2) methanol			
0.0	1.0		1.9193
0.2	0.8		2.3193
0.4	0.6		2.8025
0.6	0.4		3.3865
0.8	0.2		4.0922
1.0	0.0		4.9449
(1) Acetone + (3) chloroform			
0.0		1.0	2.4182
0.2		0.8	2.6237
0.4		0.6	2.8466
0.6		0.4	3.0886
0.8		0.2	3.351
1.0		0.0	3.6358
(2) Methanol + (3) chloroform			
	0.0	1.0	3.1645
	0.2	0.8	2.8414
	0.4	0.6	2.5512
	0.6	0.4	2.2907
	0.8	0.2	2.0568
	1.0	0.0	1.8468

SIMULATION RESULTS

Because of the lack of experimental data for diffusion coefficients in ternary system of acetone-methanol-chloroform, the method was validated for binary mixtures and compared with experimental data of Fick coefficient of the binary system acetone-chloroform and predicted for other binary subsystems acetone-methanol and methanol-chloroform and the ternary system assuming that the quality of the method in ternary mixtures is similar to that of binary systems.

As MS diffusion coefficients are evaluated using the Vignes equation, the results for three binary systems are given in Table 3 at different compositions. It is observed
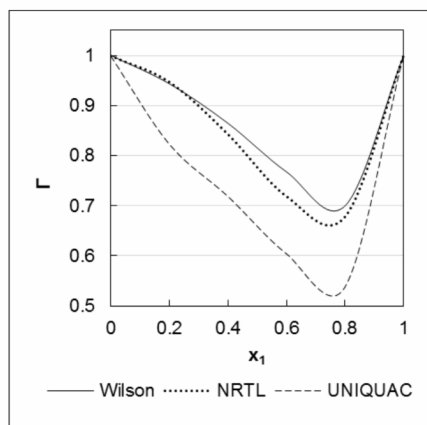
Fig. 1. Thermodynamic factor Γ in the binary system (1) acetone (2) methanol at 298 K, 1 atm.
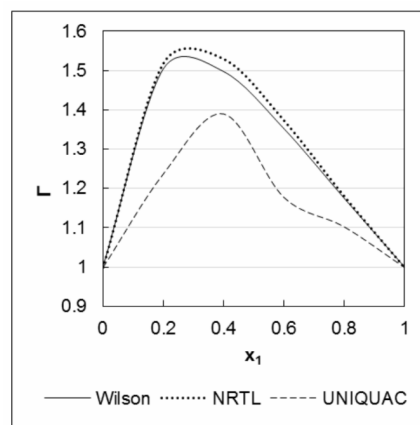

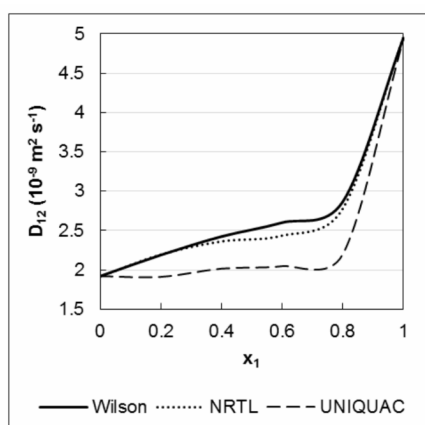**Fig. 3.** Thermodynamic factor Γ in the binary system (1) acetone (3) chloroform at 298 K, 1 atm.

Fig. 2. Fick diffusivity D_{12} in the binary system (1) acetone (2) methanol at 298 K, 1 atm.
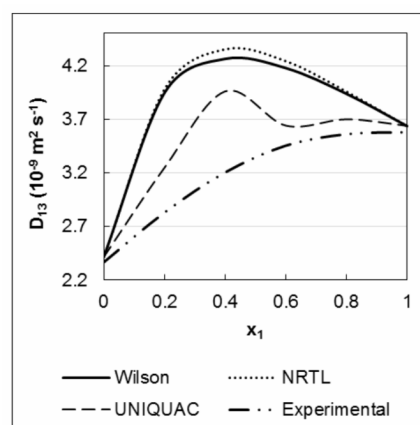

Fig. 4. Fick diffusivity D_{13} in the binary system (1) acetone (3) chloroform at 298 K, 1 atm.

that the MS diffusion coefficient increases by increasing the composition of the more volatile component in the binary mixture. The values of thermodynamic factor, Γ, and Fick coefficients, D_{ij} are obtained using three different models for activity coefficient, Wilson, NRTL, and UNIQUAC and are shown in Figs. 1-6 for three different subsystems.

Figure 1 shows the thermodynamic factor Γ obtained from simulation in the binary mixture acetone-methanol for various compositions. The computed Γ is less than unity suggesting a positive deviation from Raoult's law.

Using the computed MS diffusivity $Đ_{12}$ and

thermodynamic factor Γ, the Fick diffusivity D_{12} was calculated as a function of composition, as shown in Fig. 2. Similar results for other binary systems (1) acetone (3) chloroform and (2) methanol (3) chloroform are shown in Figs. 3-6. The values of Γ for acetone-chloroform and methanol-chloroform binary systems are more and less than unity, respectively indicating negative and positive deviations from Raoult's law, subsequently. A good agreement of Fick diffusivity D between experiments and simulations is seen for the system acetone-chloroform. The Average Absolute Relative Deviation (AARD%) values for
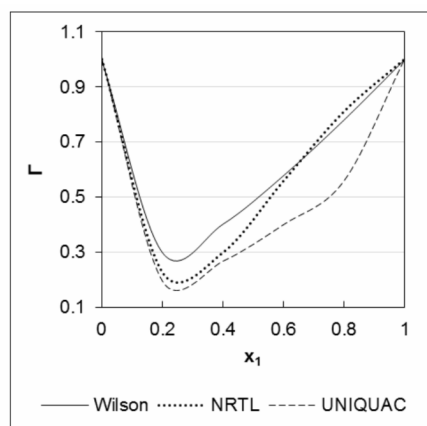
Fig. 5. Thermodynamic factor Γ in the binary system (2) methanol (3) chloroform at 298 K, 1 atm.
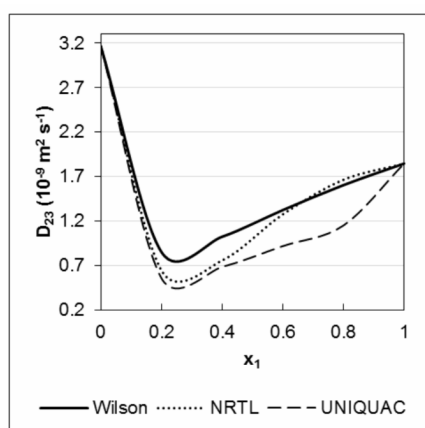

Fig. 6. Fick diffusivity D_{23} in the binary system (2) methanol (3) chloroform at 298 K, 1 atm.

UNIQUAC, Wilson, and NRTL models were 4.2, 8.9, and 9.4%, respectively. It reveals that we can also generalize the simulation to other binary subsystems and trust the calculated results.

For the ternary mixture, the MS diffusion coefficient is given in Table 4 in terms of the B^{-1} matrix, which is identical to the MS diffusion coefficient in case of binary mixtures.

The simulations of ternary diffusion coefficients yield consistent results. The numerical values of thermodynamic factor, Γ, and Fick diffusion coefficient, D, are shown in

Table 4. MS Diffusion Coefficients of the Ternary System Containing (1) Acetone, (2) Methanol and (3) Chloroform from Simulations at 1 atm and 298 K for Three Different Model for Activity Coefficient Calculation

x_1	x_2	x_3	$B^{-1} \times 10^9$ (Wilson, NRTL and UNIQUAC))
0	0.5	0.5	$\begin{bmatrix} 2.549 & 0.0000 \\ -0.007 & 2.417 \end{bmatrix}$
0.2	0.4	0.4	$\begin{bmatrix} 2.828 & 0.008 \\ -0.160 & 2.485 \end{bmatrix}$
0.4	0.3	0.3	$\begin{bmatrix} 3.091 & 0.069 \\ -0.259 & 2.694 \end{bmatrix}$
0.6	0.2	0.2	$\begin{bmatrix} 3.332 & -0.258 \\ -0.296 & 3.084 \end{bmatrix}$
0.8	0.1	0.1	$\begin{bmatrix} 3.530 & -0.622 \\ -0.237 & 3.757 \end{bmatrix}$
1	0	0	$\begin{bmatrix} 3.636 & -1.309 \\ 0.000 & 4.945 \end{bmatrix}$

Tables 5 and 6 for three different models for activity coefficient and fulfill the theoretical restrictions for thermodynamic stability, *i.e.* D has positive and real eigenvalues, positive diagonal elements and a positive determinant. The main term diffusion coefficient D_{ii} is larger than $D_{ij, i \neq j}$ which is expected as the diffusive flow of component i is mainly driven by its own concentration gradient. There is a good agreement between the numerical values of these two parameters for three models. Unfortunately, because of the absence of experimental data on the ternary mixture, it is not possible to compare them to the present simulation results as it was done for the binary mixtures. However, no special changes in the precision of the present results for ternary mixtures when compared to the binary case are expected.

CONCLUSIONS

In this work, a consistent method for computing ternary Fick diffusivities from equilibrium simulations was

Table 5. Thermodynamic Factor Γ of the Ternary System Containing (1) Acetone, (2) Methanol, and (3) Chloroform from Simulations at 1 atm and 298 K for Three Different Models for Activity Coefficient Calculation, x_1 Varies while Keeping $x_2 = x_3$

x_1	x_2	x_3	Γ (Wilson)		Γ (NRTL)		Γ (UNIQUAC)	
0	0.5	0.5	$\begin{bmatrix} 1.0000 & -1.0000 \\ -0.7882 & 0.4852 \end{bmatrix}$		$\begin{bmatrix} 1.0000 & -1.0000 \\ -0.7397 & 0.4223 \end{bmatrix}$		$\begin{bmatrix} 1.0000 & -1.0000 \\ -0.7149 & 0.4889 \end{bmatrix}$	
0.2	0.4	0.4	$\begin{bmatrix} 1.4112 & -0.7439 \\ -1.1167 & 0.4095 \end{bmatrix}$		$\begin{bmatrix} 1.4874 & -0.7035 \\ -1.1201 & 0.3577 \end{bmatrix}$		$\begin{bmatrix} 1.5042 & -0.7126 \\ -1.1100 & 0.4220 \end{bmatrix}$	
0.4	0.3	0.3	$\begin{bmatrix} 1.4444 & -0.6032 \\ -1.1953 & 0.4066 \end{bmatrix}$		$\begin{bmatrix} 1.5161 & -0.5888 \\ -1.2052 & 0.3860 \end{bmatrix}$		$\begin{bmatrix} 1.4959 & -0.5957 \\ -1.1792 & 0.4299 \end{bmatrix}$	
0.6	0.2	0.2	$\begin{bmatrix} 1.3481 & -0.6016 \\ -1.1774 & 0.4621 \end{bmatrix}$		$\begin{bmatrix} 1.3723 & -0.5854 \\ -1.1686 & 0.4823 \end{bmatrix}$		$\begin{bmatrix} 1.3510 & -0.5860 \\ -1.1482 & 0.5026 \end{bmatrix}$	
0.8	0.1	0.1	$\begin{bmatrix} 1.1953 & -0.6793 \\ -1.1102 & 0.6141 \end{bmatrix}$		$\begin{bmatrix} 1.1835 & -0.7005 \\ -1.0894 & 0.6677 \end{bmatrix}$		$\begin{bmatrix} 1.1781 & -0.6992 \\ -1.0841 & 0.6715 \end{bmatrix}$	
1	0	0	$\begin{bmatrix} 1.0000 & -1.0000 \\ -1.0000 & 1.0000 \end{bmatrix}$		$\begin{bmatrix} 1.0000 & -1.0000 \\ -1.0000 & 1.0000 \end{bmatrix}$		$\begin{bmatrix} 1.0000 & -1.0000 \\ -1.0000 & 1.0000 \end{bmatrix}$	

Table 6. Fick Diffusion Coefficient D of the Ternary System Containing (1) Acetone, (2) Methanol, and (3) Chloroform from Simulations at 1 atm and 298 K for Three Different Models for Activity Coefficient Calculation, x_1 Varies while Keeping $x_2 = x_3$

x_1	x_2	x_3	$D \times 10^9$ (m^2 s^{-1}) (Wilson)		$D \times 10^9$ (m^2 s^{-1}) (NRTL)		$D \times 10^9$ (m^2 s^{-1}) (UNIQUAC)	
0	0.5	0.5	$\begin{bmatrix} 2.549 & -2.549 \\ -1.913 & 1.180 \end{bmatrix}$		$\begin{bmatrix} 2.549 & -2.549 \\ -1.796 & 1.028 \end{bmatrix}$		$\begin{bmatrix} 2.549 & -2.549 \\ -1.736 & 1.189 \end{bmatrix}$	
0.2	0.4	0.4	$\begin{bmatrix} 3.983 & -2.101 \\ -3.001 & 1.137 \end{bmatrix}$		$\begin{bmatrix} 4.198 & -1.987 \\ -3.022 & 1.002 \end{bmatrix}$		$\begin{bmatrix} 4.246 & -2.012 \\ -2.999 & 1.163 \end{bmatrix}$	
0.4	0.3	0.3	$\begin{bmatrix} 4.548 & -1.976 \\ -3.594 & 1.259 \end{bmatrix}$		$\begin{bmatrix} 4.770 & -1.847 \\ -3.640 & 1.192 \end{bmatrix}$		$\begin{bmatrix} 4.706 & -1.871 \\ -3.564 & 1.313 \end{bmatrix}$	
0.6	0.2	0.2	$\begin{bmatrix} 4.795 & -2.124 \\ -4.030 & 1.603 \end{bmatrix}$		$\begin{bmatrix} 4.874 & -2.075 \\ -4.010 & 1.661 \end{bmatrix}$		$\begin{bmatrix} 4.798 & -2.082 \\ -3.941 & 1.724 \end{bmatrix}$	
0.8	0.1	0.1	$\begin{bmatrix} 4.910 & -2.780 \\ -4.454 & 2.468 \end{bmatrix}$		$\begin{bmatrix} 4.856 & -2.888 \\ -4.373 & 2.674 \end{bmatrix}$		$\begin{bmatrix} 4.834 & -2.886 \\ -4.352 & 2.688 \end{bmatrix}$	
1	0	0	$\begin{bmatrix} 4.945 & -4.945 \\ -4.945 & 4.945 \end{bmatrix}$		$\begin{bmatrix} 4.945 & -4.945 \\ -4.945 & 4.945 \end{bmatrix}$		$\begin{bmatrix} 4.945 & -4.945 \\ -4.945 & 4.945 \end{bmatrix}$	

presented. For this purpose, MS diffusivities and thermodynamic factors are computed to calculate the matrix of Fick diffusivities. Our approach is applied to a ternary mixture acetone-methanol-chloroform at 1 atm and 298 K. For computation of activity coefficient and so thermodynamic factor three different models of Wilson, NRTL, and UNIQUAC was used and compared with each other. For testing validation of the model because of the lack of experimental data for ternary system, Fick coefficients were obtained for binary subsystems for two models of Wilson and NRTL and were compared with experimental data. Even though a simple molecular model is used, the computed Fick coefficients are in close agreement with experiments. Therefore, we expect that the computed Fick diffusivities for ternary system should also be comparable with experiments. The presented approach allows for an efficient and consistent prediction of multicomponent Fick diffusion coefficients from molecular models.

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