

Phenomenological Models of Diffusivities Based on Local Composition

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Abstract: In phenomenological models, diffusivity is at least a function of composition and the diffusivities at infinite dilution. An additional parameter Ξ , which can be determined by diffusivity in midpoint, are specially brought forward as token of fractional friction related with the interactions of same molecules in this paper, to extrapolate a new correlative equation for the mutual Maxwell-Stefan diffusivities. Furthermore, the correlative equation can be extended to calculate diffusivities in multicomponent mixtures based on binary data alone. The rate of random motion of molecule i , which determine diffusional behavior, consider to be depended on the local composition (x_{ji}), comparatively on the average mole fraction (x_i and x_j), and local composition is calculated by binary thermodynamic parameters available, such as Wilson and NRTL parameters. The theoretical calculations are evaluated with published experimental data. The total average relative deviation of predicted values with respect to experimental data is 4.43% for 17 binary systems. And the M-S diffusivities in a three-component liquid system are regarded as binary coefficients, the predictive results also agree with the experimental data. Results indicate that the model with additional coefficients is superior to currently used Darken methods, especially for systems of polar organic-water and those containing associative component.

Key words: diffusivity; diffusion; phenomenological models; Maxwell-Stefan's law

1. INTRODUCTION

The knowledge of diffusion is crucial in many processes because reactions and separations are often limited by a diffusional process. Historically there have been two major formulations for the mass-flux relations in liquid diffusion. One is the Maxwell-Stefan's expression. And the other one is the generalization of Fick's law in which the mass flux is written as a linear combination of concentration gradients

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$$j_i = \sum_{j=1}^{n-1} D_{ij} \nabla c_j \quad (1)$$

The physical significance of Fick's law is easier to visualize than that of M-S form, and Fick's equations can be directly combined with continuity equation and solved in most practical situations. So they are more the values first calculated from experimental data. Nevertheless, while their utility is unquestionable, they are subjected to some potentially serious restrictions. First, the diffusion coefficient can be strong functions of concentration. This would not be a serious limitation by introduce the thermodynamic factor, and the application of local composition conception is now mostly limited for such purpose. Second, Fick's law implies that one species must be chosen as "solvent", or species "n" in equation (1), this is a serious restriction. The third restriction, more greatly, it is very difficult to determine the relation between multicomponent diffusion coefficient D_{ij} and the binary values. Because the required thermodynamic information detail is rarely available, the restraints to reduce the number of diffusion coefficient are frequently impossible to apply. So for an n -component system, Fick's equations contain $(n-1)^2$ diffusion coefficient. Only few sets of experimental data on the ternary mixtures have been reported in the literature, and it is unpractical to search for experimental data on diffusion coefficients in the mixtures with a higher number of components.

Maxwell suggested the M-S equations for binary mixture on the basis of kinetic theory, and Stefan generalized them to describe the diffusion in a gas mixture with n components. For dense gases and liquids, it has been shown that the M-S equations are still valid, but the strongly concentration-dependent D_{ij} appearing therein are not binary diffusivities. M-S approach separates thermodynamics and mass transfer while the Fick diffusivity accounts for both effects in one coefficient and this makes the M-S diffusivity simpler to model.

There has been no general framework available for the quantitative explanation of diffusion coefficient. Series of models for the estimation of diffusion coefficients are based on the concepts of free volume and activation energy. However, all the variations of this approach operate in term of self-diffusion coefficients. The approach of molecular dynamics simulation is developing, and widely used for the estimation of self-diffusion, but it is still difficult to estimate the mutual diffusion coefficients with good accuracy in a reasonable time. The phenomenological approach is still capable of the most widely applied modeling variations of diffusion coefficients with molar fraction. With Vignes relation as a simple approximation, M-S equations had been used in the calculation of process engineering, and the model is able to simulate the measured component trajectory more accurately than the equilibrium stage model for some process^[1]. However, as the Vignes or Darken mixing rule, liquid mixtures would be with a monotonous concentration behavior of M-S diffusivities. In fact, monotonous behavior is not always observed, even for mixtures which are close to ideal solutions, and non-monotonous behavior is typical for mixtures of polar and associating components^[2]. For highly non-ideal systems, the various kinds of molecular interaction are often not appropriately accounted for, and chemical theories that were developed for molecular association often lack the required equilibrium constants.

Due to the system-specific nature of interactions, local composition is some different with the average composition in liquid mixtures. With local compositions for presentation of excess Gibbs energies of liquid mixtures, equilibrium data for a wide variety of liquid mixtures can be correctly predicted based on **binary** data alone^[3]. As fundamental principle based on irreversible thermodynamics, a basic postulate states that thermodynamic variables, such as entropy and chemical potential, can in fact be correctly defined in differential volume of a system that is not equilibrium, like a diffusional liquid mixture. In this work, M-S equations are renewedly surveyed in local composition point of view, to meet a multicomponent mass transfer problem just by binary diffusivities and other binary parameters available.

2. MODEL DEVELOPMENT

Molecules in liquid participate in chaotic random Brownian motion, and tend to evenly distribute the concentrations, which is referred as diffusion. The rate of random motion depends upon the temperature and molecular interactions. In the following, special respect paid to the influence on diffusion of molecular interactions.

The physical significance of M-S equations shows the balance between driving force and friction force of a component in a diffusional liquid mixture. For binary system

$$\frac{1}{RT} \frac{d\mu_1}{dz} = \frac{x_2}{\mathfrak{D}} (v_1 - v_2) \quad \text{or} \quad \frac{1}{RT} \frac{d\mu_2}{dz} = \frac{x_1}{\mathfrak{D}} (v_2 - v_1) \quad (2)$$

When chemical potential gradient is regarded as the only driving forces for a species, the friction exerted 1 on 2 is proportional to the fraction of 1 in the mixture, and also to the difference in velocity between 1 and 2.

The friction force of a molecule i , which determine diffusional behavior, should depend on the local composition of this molecule i at center (x_{ii} and x_{ji}), but not to the average mole fraction (x_i and x_j). Previous studies proposed, for diffusion in multicomponent solutions, volume fractions should be used instead of mole fractions in setting up the M-S equations^[4]. This approach is especially needed when the species have wide differences in molecular weights. So M-S model for binary solutions could be given by

$$\frac{1}{RT} \frac{d\mu_1}{dz} = \frac{\phi_{21}}{\mathfrak{D}_{12}} (v_2 - v_1) \quad \text{and} \quad \frac{1}{RT} \frac{d\mu_2}{dz} = \frac{\phi_{12}}{\mathfrak{D}_{21}} (v_2 - v_1) \quad (3)$$

Local volume composition above can be calculated by binary thermodynamic parameters available, such as Wilson and NRTL parameters. However, eq. (3) is not consistent with restrictions given by Gibbs-Duhem equation and by Onsager's reciprocity relations. The right side of eq. (3) does not sum to zero when the \mathfrak{D} values are taken to be symmetric ($\mathfrak{D}_{12} = \mathfrak{D}_{21}$).

The deviation to Gibbs-Duhem equation is associated with reference diffusional velocity frame. The M-S equations do not determine the absolute values of velocities, are reference frame independent. But the absolute diffusional velocities of components are needed to determine the diffusional flux, and the common bootstrap relations (such as bulk stagnant) are reference frame dependent. When Navier-Stokes equation and continuity equation act as bootstrap relations, the absolute diffusional velocities of every component can also be calculated in same Lagrangian coordinate^[5]. However, the related calculation overloaded with many details for theoretical strictness.

The binary pair \mathfrak{D} diffusivities in eq. (2) should be equal to one another ($=\mathfrak{D}$) according to the physical significance of M-S equation. But in Lagrangian coordinate, binary pair \mathfrak{D} can be an inverse coefficient only when the volume changes in mixing are negligible. However, volume change does exist for all non-ideal solution mixtures according to thermodynamics of fluid. And so, the volume average velocity is not zero in Lagrangian coordinates, which mean a bulk motion do exist in Lagrangian coordinates when volume average velocity is zero. In this case, binary pair \mathfrak{D} can not be an inverse coefficient to answer for the restrictions given by Gibbs-Duhem equation.

The difference between binary pair \mathfrak{D} in eq. (3) should come down to the fluctuation of local composition besides the volume changes in mixing. The fluctuation of local compositions can be converted into fluctuation of diffusional velocities, and the average difference in velocity between 1 and 2 should be

$$(v_1 - v_2)_{av} = \frac{\phi_{21}}{\phi_{21} + \phi_{12}} (v_1 - v_2)_2 + \frac{\phi_{12}}{\phi_{21} + \phi_{12}} (v_1 - v_2)_1$$

Where $(v_1 - v_2)_{i1}$ and $(v_1 - v_2)_{i2}$ are the difference in diffusional velocity in local of molecule 1 or 2 at center, and naturally associate with binary diffusivities at infinite dilution. So with the interpolation rule

$$\mathcal{D} = \frac{\phi_{21}}{\phi_{21} + \phi_{12}} \mathcal{D}_{x_2 \rightarrow 1}^* + \frac{\phi_{12}}{\phi_{21} + \phi_{12}} \mathcal{D}_{x_1 \rightarrow 1}^* \quad (4)$$

The binary pair \mathcal{D} diffusivities values are taken to be symmetric and used in eq. (2). In this way, eq. (2) is inconsistent with the Gibbs-Duhem equation and with Onsager's reciprocity relations when the volume changes in mixing are negligible.

The local compositions in eq. (4) can be calculated by

$$\phi_{21} = \frac{x_2 \Lambda_{12}}{x_1 + x_2 \Lambda_{12}} \quad \phi_{12} = \frac{x_1 \Lambda_{21}}{x_2 + x_1 \Lambda_{21}}$$

According to Wilson

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad \Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right)$$

NRTL equation contains a non-randomness parameter α_{12}

$$\Lambda_{12} = \exp[-\alpha_{12}(g_{12} - g_{11})/RT] \quad \Lambda_{21} = \exp[-\alpha_{12}(g_{21} - g_{22})/RT]$$

Eq. (4) is some similar in shape with Darken equation. For mixtures which close to ideal from thermodynamic point of view and molecules similar in size, eq. (4) transform to Darken equation. Furthermore, \mathcal{D}^* appearing therein are binary diffusivities, can be directly extend to multicomponent liquid mixtures as

$$\mathcal{D}_{ij}^* = \frac{\phi_{ij}}{\phi_{ij} + \phi_{ji}} \mathcal{D}_{x_i \rightarrow 1}^* + \frac{\phi_{ji}}{\phi_{ij} + \phi_{ji}} \mathcal{D}_{x_j \rightarrow 1}^* \quad (4a)$$

And when the local compositions replaced with macro compositions, eq. (4a) transform into the Darken relation for multicomponent diffusion, which has been used for liquid mixtures of linear alkanes^[6].

$$\mathcal{D}_{ij}^* = \frac{x_i}{x_i + x_j} \mathcal{D}_{x_i \rightarrow 1}^* + \frac{x_j}{x_i + x_j} \mathcal{D}_{x_j \rightarrow 1}^* \quad (4b)$$

However, monotonous behavior is always observed by eq. (4) also similar with Darken equation. This is still a serious restriction.

The rate of diffusion in liquid mixture can be described in terms of three factors^[7]: *the thermodynamic factor*; *the kinetic factor*; or the rate of the molecular motion; and *the resistance factor*. To consider more about the obstacles on the way of a given molecule in diffusion, we should find the resistance may be served not only by other molecules but also by the same molecules. The resistance by other molecules could be embodied by diffusivities in infinite dilution, but the resistance by same molecules has not been denoted well in common phenomenological models, such the Vignes or Darken mixing rule.

If the resistance served by other molecules could be correctly expressed by diffusivities in infinite dilution, self-diffusivities should be the proper indication for the obstacles on the way of a given molecule by same molecules. In a binary mixture, the apparent friction coefficient for species 1 and species 2 defined as

$$\zeta_1 \propto \frac{\phi_{21}}{D_{x_2 \rightarrow 1}^*} + \frac{\phi_{11}}{D_1^s} \quad \zeta_2 \propto \frac{\phi_{12}}{D_{x_1 \rightarrow 1}^*} + \frac{\phi_{22}}{D_2^s}$$

The interpolation rule for mutual diffusivity could be ascertained by end values as

$$\frac{1}{\mathcal{D}_{12}} = x_2 \left(\frac{\phi_{21}}{D_{x_2 \rightarrow 1}^*} + \frac{\phi_{11}}{D_1^s} \right) + x_1 \left(\frac{\phi_{12}}{D_{x_1 \rightarrow 1}^*} + \frac{\phi_{22}}{D_2^s} \right) \quad (5)$$

The resistance by same molecules is of great influence in dense solutions. Therefore, an additional coefficient Ξ is specially brought forward as token of fractional friction related with the interactions of same molecules instead of self-diffusivities. Coefficient Ξ is set to be a constant for every binary liquid mixture, and with the same dimension as diffusivity. So

$$\frac{1}{\mathcal{D}_{12}} = x_2 \left(\frac{\phi_{21}}{D_{x_2 \rightarrow 1}^*} + \frac{\phi_{11}}{\Xi} \right) + x_1 \left(\frac{\phi_{12}}{D_{x_1 \rightarrow 1}^*} + \frac{\phi_{22}}{\Xi} \right) \quad (6)$$

The reciprocal format is also used for comparison

$$\mathcal{D}_{12} = x_2 (\phi_{21} D_{x_2 \rightarrow 1}^* + \phi_{11} \Xi) + x_1 (\phi_{12} D_{x_1 \rightarrow 1}^* + \phi_{22} \Xi) \quad (7)$$

The structure of liquid mixture, or the difference between local and macro compositions, may be determined only by thermodynamic factor. In this case, local compositions in eq. (6) should be replaced with macro compositions, so

$$\frac{1}{\mathcal{D}_{12}} = \frac{x_2^2}{D_{x_2 \rightarrow 1}^*} + \frac{x_1^2}{D_{x_1 \rightarrow 1}^*} + \frac{2x_1x_2}{\Xi} \quad (6a)$$

And extend to multicomponent liquid mixtures as

$$\frac{(x_i + x_j)^2}{\mathcal{D}_{ij}} = \frac{x_j^2}{D_{x_j \rightarrow 1}^*} + \frac{x_i^2}{D_{x_i \rightarrow 1}^*} + \frac{2x_ix_j}{\Xi} \quad (6b)$$

To compare with experimental data of Fick diffusion coefficient, a thermodynamic correction factor is required for estimation of the compositional derivative of the activity coefficient, to achieve the transformation of the M-S binary diffusion coefficient by eq. (4), (5), (6), (7) to Fick diffusion coefficient

$$\Gamma = \frac{D}{\mathcal{D}} = \frac{d \ln \alpha_1}{d \ln x_1} = 1 + x_1 \frac{d(\ln \gamma_1)}{dx_1} \quad (8)$$

For multicomponent systems, eq. (4a), (5a) or (6b) can be directly used to calculate the elements of the square matrix of inverted M-S diffusivities

$$B_{ii} = \frac{x_i}{\mathcal{D}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^n \frac{x_k}{\mathcal{D}_{ik}} \quad B_{ij(i \neq j)} = -x_i \left(\frac{1}{\mathcal{D}_{ij}} - \frac{1}{\mathcal{D}_{in}} \right) \quad i, j = 1, 2, \dots, n-1$$

It is common to define a matrix of Fick diffusivities analogous to binary case [cf. eq.(8)]. For ternary systems, Fick diffusivities constitute 2×2 matrix notation

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \quad (9)$$

Wilson or NRTL model is used for the evaluation of thermodynamic correction factor Γ in this paper, corresponding with the way for calculation of local compositions. And the processes of calculating Γ are discussed at length in refer [8].

RESULTS AND DISCUSSION

Altogether 17 binary systems and one ternary mixture are selected to test the predictive equations in this work. Diffusivities in infinite dilution are taken from experimental data or calculated by the way from [9], and self-diffusivities are from [10, 11]. Table 1 list these self- diffusivities, diffusivities in infinite dilution and other parameters used in this work. The parameters of Wilson and NRTL are regressed from vapor-liquid equilibrium data [12] at the nearest temperature because the needed temperature is sometime unavailable.

PARAMETER Ξ

The values of parameter Ξ are firstly determined by published experimental data of diffusion coefficient. To minimize the average error between the theoretical computed values and the experimental data, the optimum values for equation (6), (6a), (7) are listed in table 2.

Table 1. Parameters of Binary Solutions in 298.15 K

No.	Systems ^a 1-2	self-diffusivities of pure component		diffusivities of infinite dilution	
		D_1^s $\text{m}^2/\text{s} \times 10^9$	D_2^s $\text{m}^2/\text{s} \times 10^9$	$D_{x_2 \rightarrow 1}^*$ $\text{m}^2/\text{s} \times 10^9$	$D_{x_1 \rightarrow 2}^*$ $\text{m}^2/\text{s} \times 10^9$
1	methanol-water	2.32	2.51	1.56	2.19
2	ethanol-water	1.01	2.51	1.25	1.22
3	acetone-water	4.835	2.51	1.3	5.22
4	acetone -CT	4.835	1.32	1.71	3.57
5	hexane-CT	4.21	1.32	1.47	3.87
6	bezene-CT	2.22	1.32	1.41	1.92
7	Chloroform-CT	2.58	1.32	1.50	2.03
8	methanol-benzene	2.32	2.22	3.82	2.66
9	ethanol-benzene	1.01	2.22	3.17	1.82
10	acetone-benzene	4.835	2.22	2.76	4.20
11	toluene-benzene	2.27	2.22	1.83	2.55
12	chloroform -bezene	2.58	2.22	2.25	2.88
13	Chlorobenzene-benzene	1.76	2.22	1.85	2.12
14	cyclohexane-benzene	1.39	2.22	2.1	1.89
15	cyclohexane-toluene	1.39	2.27	2.42	1.57
16	acetone-chloroform	4.835	2.58	2.33	3.62
17	acetone-cyclohexane	4.835	1.39	2.22	4.06

To be continue

continued

No.	Wilson		NRTL			molar volume	
	$\lambda_{12}-\lambda_{21}$	$\lambda_{21}-\lambda_{22}$	$g_{12}-g_{11}$	$g_{21}-g_{22}$	α	V_1 ml/mol	V_2 ml/mol
1	271.1382	433.0681	-306.155	998.5807	0.3012	40.73	18.07
2	177.7372	1102.1827	21.6167	1192.753	0.3015	58.68	18.07
3	344.3346	1482.2133	656.6727	1197.444	0.5103	74.05	18.07
4	539.7984	81.9142	211.0539	380.6299	0.2993	74.05	97.09
5	151.8605	40.234	-292.236	499.1284	0.2931	131.61	97.09
6	355.2046	-252.1256	-296.653	410.7374	0.3052	89.41	97.09
7	-409.8965	831.8887	976.0567	-662.83	0.304	80.67	97.09
8	1658.987	137.872	1108.98	588.616	0.40209	40.73	89.41
9	1274.342	126.48	897.278	332.862	0.38506	58.68	89.41
10	809.0284	-342.9787	-396.494	886.5703	0.2971	74.05	89.41
11	579.9992	-333.9041	-51.0865	60.198	0.3019	106.85	89.41
12	-191.709	96.328	-381.258	318.405	0.39884	80.67	89.41
13	19.0041	14.4852	1.3739	24.5239	0.3033	102.24	89.41
14	-70.4353	346.0688	245.301	26.6575	0.3025	108.75	89.41
15	-279.2808	623.0145	797.4637	-429.427	0.3036	108.75	106.85
16	28.8819	-484.3856	-643.277	228.4574	0.3043	74.05	80.67
17	1054.0376	267.1229	385.4843	771.1362	0.2921	74.05	108.75

CT: carbon tetrachloride

Table 2. Data of Parameter Ξ ($m^2/s \times 10^9$, 298.15K)

No.	optimum values by eq. (7)		optimum values by eq. (6)		optimum values by eq. (6a)		values by eq. (10)		Data source (Refs)
	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	
1	0.45	0.68	0.85	1.02	0.81	1.02	0.71	0.88	13
2	-0.26	-0.37	0.28	0.34	0.24	0.28	0.36	0.51	14
3	-0.64	-0.47	0.56	0.78	0.50	0.77	0.50	0.87	14, 15
4	1.49	1.53	1.72	1.77	1.67	1.71	2.01	2.03	16
5	2.17	2.35	2.74	2.94	2.96	3.13	2.85	3.04	17
6	1.67	1.70	1.72	1.75	1.73	1.73	1.75	1.75	18
7	1.68	1.62	1.72	1.67	1.66	1.66	1.70	1.74	18
8	-0.36	-0.62	0.65	0.67	0.60	0.68	0.74	0.82	19
9	-0.67	-1.17	0.71	0.64	0.66	0.65	0.95	0.92	15
10	2.73	2.79	2.86	2.96	2.86	2.85	2.95	2.93	15
11	2.1	2.09	2.16	2.15	2.22	2.18	2.21	2.15	20
12	2.25	2.30	2.31	2.35	2.29	2.33	2.28	2.32	20
13	1.91	1.95	1.93	1.95	1.92	1.94	1.90	1.94	21
14	1.81	1.82	1.82	1.83	1.81	1.82	1.81	1.82	20
15	1.93	2.01	2.03	2.11	2.07	2.08	2.07	2.08	20
16	3.19	3.25	3.32	3.40	3.30	3.33	3.30	3.33	14
17	1.15	0.76	1.56	1.52	1.46	1.46	1.57	1.55	22

The local compositions and thermodynamic correction factors in above equations are respectively

calculated by Wilson and NRTL equation, and the two ways give different result of parameter Ξ . The result of Ξ values is so analogous in eq. (6) and eq. (6a), that the structure of liquid mixture should be determined mostly by thermodynamic factor. Or it can be postulated that *the resistance factor* is independent of the difference between local and macro compositions.

Particularly, the discrepancy of Ξ in two ways is not negligible in eq. (7). And also in this equation, negative together with positive values of Ξ appear, which is questionable for the physical significance of parameter Ξ .

Farther research is needed for the physical significance of parameter Ξ . The reciprocal of M-S diffusivity shows the friction force between two species of molecules. If the resistance served by other molecules could be correctly expressed by diffusivities in infinite dilution, self-diffusivities should be the proper indication for the obstacles on the way of a given molecule by same molecules, and is subjected to a transformation of eq. (5).

The self-diffusivities of components are listed in table 1, those data are obvious different with the result of Ξ values in table 2. And eq. (5) predicts all binary systems with monotonous concentration behavior of M-S diffusivities, clearly deviates from experimental data of diffusion coefficient, especially for mixtures with polar component, e.g. water, methanol and ethanol.

Just as diffusion coefficient, parameter Ξ increase with temperature. For example, values of Ξ in 298.15 K for acetone-water (No. 3) are shown in table 2 as 0.50 and 0.77 respectively by Wilson and NRTL. Correspondingly, the data of Ξ become 0.65 and 0.94 in 308.15 K, and 0.82 and 1.27 in 318.15K.

It is a worthwhile work to determine the values of Ξ in a simple and feasible way. And in the following, parameter Ξ are evaluate by diffusivity in midpoint when eq. (6) convert to

$$\frac{4}{D_{12}|_{x_1=0.5}} = \frac{1}{D_{x_2 \rightarrow 1}^*} + \frac{1}{D_{x_1 \rightarrow 1}^*} + \frac{2}{\Xi} \quad (10)$$

The result of parameter Ξ by eq. (9) is also listed in table 2, all the values are in agreement with the optimum values by equation (5) and (6).

BINARY LIQUID MIXTURES

Besides this work, Darken equation is also used for comparison. The form of Darken equation is similar with eq. (3), and they are equivalent when the difference between local and macro compositions is neglectable. Simultaneously, Darken equation show qualitatively same behavior of the MS diffusion coefficient with that observed in the molecular dynamics simulations^[23]. The Vignes model has recently been shown to give a good fit of experimental multicomponent diffusivities. However, to consider the strongly concentration-dependent appearing, M-S diffusivities by Vignes model are not regarded as binary diffusivities in publications^[8]. So the relevant calculations are not comparable here.

The average relative deviations of the predicted results with respect to experimental data and Darken model are listed in table 3. The average relative deviation is given by

$$A.R.D.(%) = \frac{100\%}{N_p} \sum_{n=1}^{N_p} \frac{|D_{\text{exp}(i)} - D_{\text{cal}(i)}|}{D_{\text{cal}(i)}} \quad (10)$$

The predicted results by eq. (4) are close to that of Darken equation, and results by eq. (6) are approximately equal with that of eq. (6a). So it could be assumed that the structure of liquid mixture has scarcely influence on the resistance factor. And in setting up the phenomenological models on mutual diffusivities, the local compositions could be replaced with macro compositions.

From the data in table 3, it can be concluded eq. (6) (6a) are superior to eq. (4) and Darken equation, especially for mixtures with polar or associating component, e.g. water, acetone, methanol and ethanol. In a non-ideal diffusion system of acetone-chloroform with cross association, this work makes an excellent prediction while Darken's model overestimates the minimum as shown in Fig. 1. And the most predicted results in this work are satisfactory with respect to experimental data, for the influence of interactions between same molecules on diffusion behavior, it is then appropriate to represent by parameter Ξ in eq. (6) (6a). Fig. 2 shows results for acetone-water at different temperatures, which again indicates that eq. (6a) behaves better than the Darken's model.

Table 3 Results of predictions and comparisons

No.	N _p	A.R.D. (%)								Data source (Refs)
		Darken eq.		eq.(3)		eq.(5)		eq.(6)		
		Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	
1	8	27.12	22.64	13.70	15.10	6.29	13.71	11.21	15.59	13
2	17	20.60	16.68	10.68	7.80	9.88	6.85	9.37	8.15	14
3	26	27.53	25.26	12.93	13.70	6.75	9.71	12.21	14.96	14, 15
4	9	5.18	5.21	5.14	7.21	1.49	2.02	1.70	1.91	16
5	6	4.37	4.99	2.03	2.64	2.05	3.14	3.51	3.52	17
6	5	1.28	1.38	0.84	2.31	0.69	1.11	0.93	0.99	18
7	8	6.80	4.97	4.35	5.72	5.23	2.71	4.19	2.84	18
8	11	24.65	29.06	16.90	18.88	4.35	3.85	4.63	4.64	19
9	8	14.93	17.34	10.72	11.13	6.50	7.24	5.70	6.21	15
10	8	5.14	5.49	5.93	5.88	4.33	5.40	5.16	5.50	15
11	11	3.02	0.80	7.13	1.56	1.35	0.27	1.26	0.27	20
12	11	9.59	10.35	8.18	8.93	0.84	1.67	1.29	1.18	20
13	5	5.74	6.27	5.11	5.60	0.79	1.46	1.06	1.16	21
14	11	7.38	7.60	7.15	7.95	1.60	2.04	1.93	1.66	20
15	11	4.27	4.31	2.72	6.21	2.01	4.02	3.31	3.78	20
16	16	17.02	16.99	15.80	14.64	2.32	4.24	3.17	3.74	14
17	11	3.32	3.65	2.93	2.82	2.25	3.19	7.86	11.68	22
average		13.48	12.88	8.96	9.09	4.00	4.86	5.53	6.22	

Fig. 3 indicate the prediction for cyclohexane-benzene system, the result by eq. (6) or (6a) is more satisfactory than that of eq. (4) and Darken's model. However, bias error went without saying in this result by eq. (6) (6a), and the results bears an analogy problem in several other systems, such as acetone-water and ethanol-water. In case that the values are assuredly exact of Wilson parameters and diffusivities of infinite dilution in both ends, the way to determine the value of parameter Ξ should be improved.

As a possible method for binary systems, parameter Ξ is considered to be variable with concentration, in the first instance to associate with partial molar volume and intra-diffusion coefficient ^[24]. Nevertheless, value of parameter Ξ for a binary system should remain as constant so that eq. (6) or (6a) can be expediently extended to multicomponent systems.

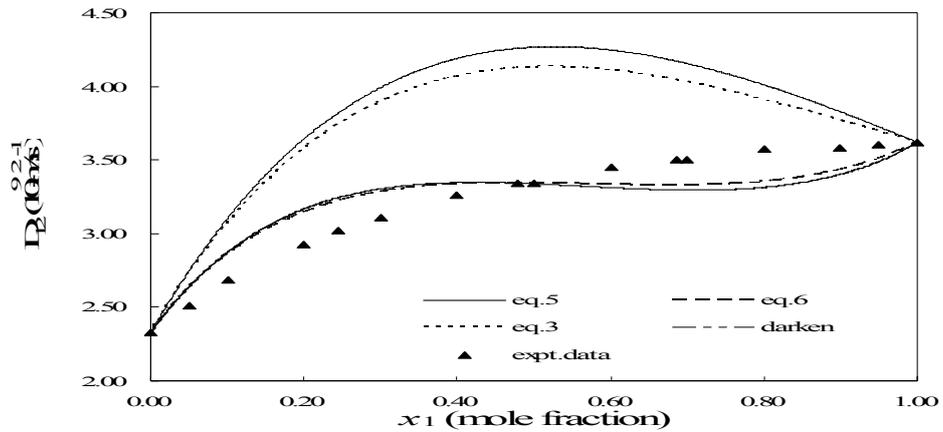


Figure 1. Experimental data and theory correlations for acetone (1)-chloroform (2) diffusivities at 298.15K

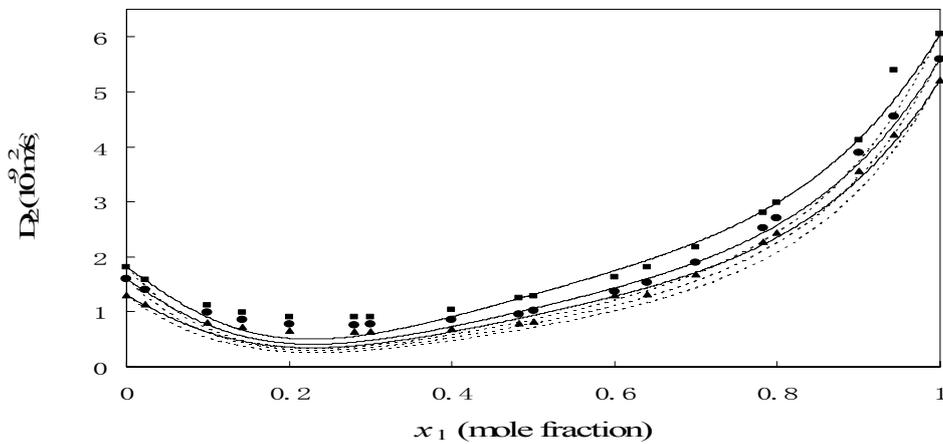


Figure 2. Diffusivities of acetone (1)-water (2) binary system at various temperatures.
 Solid line: eq. (6); dotted line: Darken model;
 Solid triangle, circle and square: experimental data from [14] at 298.15, 308.15 and 318.15K

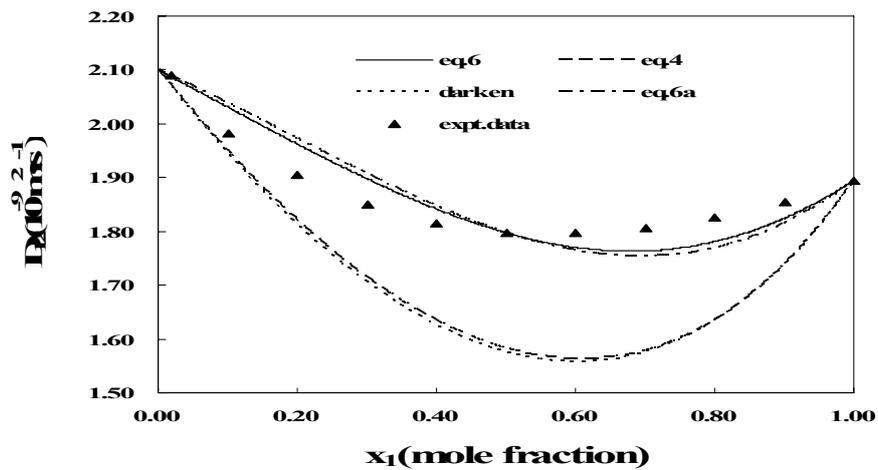


Figure 3. Experimental data and theory correlations for cyclohexane(1)-benzene(2) diffusivities at 298.15K

TERNARY LIQUID MIXTURES

Bulk diffusion is considered in a ternary non-ideal liquid mixture made up of the components acetone (1)-benzene (2)-carbon tetrachloride (3) at a temperature of 25°C. M-S diffusivities are calculated by eq. (6b) or eq. (4b); the matrix of Fick diffusivities can then be estimated by eq. (8) and compared with experimental data from[25]. The result data is listed in table 4, and these with big fractional error are labeled with italics bold figures.

Table 4. Ternary Diffusion Coefficients of acetone (1)-benzene (2)-carbon tetrachloride (3)

x_1	x_2	experiment data	predictions of eq. (3b)	predictions of eq. (6)
0.2989	0.349	D_{11} 1.887	1.816	1.914
		D_{12} -0.213	-0.447	-0.369
		D_{21} -0.037	-0.185	-0.229
		D_{22} 2.255	2.166	2.020
0.1496	0.1499	D_{11} 1.598	1.468	1.496
		D_{12} -0.058	-0.298	-0.287
		D_{21} -0.083	-0.182	-0.179
		D_{22} 1.812	1.673	1.654
0.1497	0.6984	D_{11} 1.961	2.101	2.148
		D_{12} 0.013	-0.154	-0.118
		D_{21} -0.149	-0.252	-0.511
		D_{22} 1.929	2.046	1.701
0.6999	0.1497	D_{11} 2.33	2.56	2.730
		D_{12} -0.432	-0.695	-0.291
		D_{21} 0.132	-0.115	-0.139
		D_{22} 2.971	3.070	2.745
0.0964	0.01	D_{22} 1.555	1.510	1.502
0.2416	0.0102	D_{22} 1.513	1.691	1.663
0.4921	0.0105	D_{22} 2.401	2.119	2.027
0.7419	0.0104	D_{22} 2.719	2.830	2.581
0.7439	0.0103	D_{22} 2.967	2.825	2.586
0.8951	0.01	D_{22} 3.351	3.526	3.096
0.0952	0.0101	D_{12} -0.195	-0.229	-0.219
0.2436	0.0103	D_{12} -0.40	-0.491	-0.453
0.4947	0.01	D_{12} -0.695	-0.722	-0.544
0.7461	0.0102	D_{12} -0.933	-0.751	-0.263
0.8956	0.0101	D_{12} -1.083	-0.692	-0.050
0.01	0.0951	D_{11} 1.813	1.732	1.733
0.01	0.0974	D_{11} 1.678	1.734	1.735
0.0101	0.2452	D_{11} 1.903	1.849	1.849
0.0096	0.2452	D_{11} 2.001	1.850	1.851
0.0094	0.4954	D_{11} 2.357	2.076	2.077
0.01	0.7452	D_{11} 2.582	2.355	2.357
0.0095	0.7452	D_{11} 2.525	2.356	2.358
0.0094	0.895	D_{11} 2.669	2.561	2.564
0.0093	0.895	D_{11} 2.51	2.561	2.564
0.0103	0.0941	D_{21} 0.097	-0.191	-0.191

To be continue

continued

x_1	x_2	experiment data	predictions of eq. (3b)	predictions of eq. (6)
0.01	0.493	D_{21} -0.62	-0.587	-0.616
0.0102	0.74	D_{21} -1.083	-0.683	-0.848
0.0933	0.8967	D_{11} 3.105	2.311	2.296
		D_{12} 0.55	-0.026	-0.025
		D_{21} -0.78	-0.311	-0.788
		D_{22} 1.86	2.024	1.524
0.2415	0.7484	D_{11} 3.069	2.199	2.161
		D_{12} 0.603	-0.112	-0.105
		D_{21} -0.638	-0.051	-0.498
		D_{22} 1.799	2.262	1.763
0.4924	0.4972	D_{11} 2.857	2.516	2.454
		D_{12} 0.045	-0.325	-0.251
		D_{21} -0.289	-0.051	-0.428
		D_{22} 2.471	2.792	2.268
0.7432	0.2466	D_{11} 3.251	2.986	2.926
		D_{12} -0.011	-0.528	-0.064
		D_{21} -0.301	-0.091	-0.336
		D_{22} 2.896	3.422	2.841
0.8954	0.0948	D_{11} 3.475	3.301	3.279
		D_{12} -0.158	-0.609	-0.133
		D_{21} 0.108	-0.065	-0.164
		D_{22} 3.737	3.844	3.230

By the data above, it can be concluded that predictive results by eq. (6b) or eq. (4b) both agree with the experimental data of the three-component liquid system, and eq. (6b) avoids much the dots with big fractional error. Therefore, the phenomenological models above can all be extended to multicomponent liquids, to calculate the M-S diffusivities in multicomponent liquid systems based on *binary* data alone.

CONCLUSIONS

By considering the local composition in liquid mixtures, explicit models for the prediction of M-S diffusivities are developed, an additional coefficient Ξ is specially brought forward as token of fractional diffusivity related with the interactions of same molecules, and local composition formulations of Wilson and NRTL are used in the derivation.

With additional coefficient Ξ , models by eq. (6) (6a) are superior to eq. (4) and Darken equation, especially for mixtures with polar or associating component. Altogether 17 ordinary and associating binary systems are tested. The total average relative deviation of eq. (6a) with respect to experimental data is 4.43%. This is excellent comparing with 13.18% by the classical Darken model. And for ternary system, the prediction of eq. (6b) avoids much the dots with big fractional error. The reason of the satisfactory may lie in the fact that the introduction of coefficient Ξ matches with the true picture of diffusion in liquid.

The structure of liquid mixture should be determined basically by thermodynamic factor, and has hardly influence on *the resistance factor*. For all 17 binary systems, the total average relative deviation of eq. (4) and (6) with local composition consideration is 6.73%. This is some better than 9.53% by the eq.

(6a) and classical Darken model without the consideration of local liquid structure.

LIST OF SYMBOLS

- B square matrix of inverted Maxwell-Stefan diffusivities
 D Fick diffusivity, m^2s^{-1}
 \mathfrak{D} Maxwell-Stefan diffusivity, m^2s^{-1}
 g NRTL parameter (g_{ij} for energies of interaction between an ij pair of molecules)
 N_p number of experimental data
 R gas constant ($1.98721\text{cal}\cdot\text{mol}^{-1}\text{K}^{-1}$)
 T absolute temperature (K)
 v_i diffusional velocity of component i
 V molar volume of component i ($\text{ml}\cdot\text{mol}^{-1}$)
 x_i mole fraction of component i
 x_{ij} mole fraction of molecule i in the immediate neighborhood of molecule j
 z direction coordinate (m)

Greek letters

- α_{12} the non-randomness constant for binary 1-2 interactions
 α_1 activity of component 1
 γ_1 activity of component 1
 μ chemical potential
 λ Wilson's parameter
 ϕ_{ij} local volume fraction of molecule i in the immediate neighborhood of molecule j
 ϕ local volume fraction
 Γ thermodynamic correction factors
 Λ parameter of Wilson or NRTL
 Ξ diffusion coefficient in token of interactions of same molecules, m^2s^{-1}

Subscripts

- 1,2 component 1 and 2 in binary systems
 i,j component i and j

Superscripts

- * diffusivities in infinite dilution
S self-diffusivities

REFERENCES

- [1] Krishna R., Wesselingh JA., "The Maxwell-Stefan approach to mass transfer," *Chemical Engineering Science*, 52,861-911 (1997)
- [2] Medvedev OO., "Diffusion Coefficients in Multicomponent Mixtures," Ph.D. thesis, Technical University of Denmark, Copenhagen, Denmark (2004)
- [3] Renon H, Prausnitz JM., "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE Journal*, 14,135-144 (1968)
- [4] Francesco Fornasiero, John M. Prausnitz, Clayton J. Radke. "Multicomponent Diffusion in Highly Asymmetric Systems. An Extended Maxwell-Stefan Model for Starkly Different- Sized, Segment-Accessible Chain Molecules," *Macromolecules*, 38, 1364-1370 (2005)
- [5] Piet J. A. M. Kerkhof and Marcel A. M. Geboers. "Toward a Unified Theory of Isotropic Molecular Transport Phenomena," *AIChE Journal*, 51, 79-121 (2005)
- [6] Krishna R, J M van Baten. "The Darken Relation for Multicomponent Diffusion in Liquid Mixtures of Linear Alkanes: An Investigation Using Molecular Dynamics (MD) Simulations," *Ind. Eng. Chem. Res.*, 44, 6939-6947(2005)
- [7] Shapiro AA, "Evaluation of diffusion coefficients in multicomponent mixtures by means of the fluctuation theory," *Physica A*, 320, 211-234 (2003)
- [8] Taylor R, Krishna R. "Multicomponent mass transfer," *Wiley, New York*, (1993)
- [9] Hendrik A. Kooijman, A Modification of the Stokes-Einstein Equation for Diffusivities in Dilute Binary Mixtures, *Ind. Eng. Chem. Res.*, 41, 3326-3328 (2002)
- [10] Dullien FAL. "Predictive equations for self-diffusion in liquids: a different approach," *AIChE Journal*, 18, 62-70 (1972)
- [11] Klein M., R. Fechete, D. E. Demco and B. Blümich. "Self-diffusion measurements by a constant-relaxation method in strongly inhomogeneous magnetic fields," *Journal of Magnetic Resonance*, 164, 310-320 (2003)
- [12] Gmeling J, Onken U. "Vapor-Liquid equilibrium data collection," *DECHMA Chemistry Series, Frankfurt*, 1977
- [13] Derlacki Z.J., Eastel A.J., Edge A.V.J., Woolf L.A., Roksandic Z., "Diffusion coefficients of methanol and water and the mutual diffusion coefficient in methanol-water solutions at 278 and 298 K," *J. Phys. Chem.*, 89, 5318 (1985)
- [14] Tyn M.T., Calus W.F., "Temperature and concentration dependence of mutual diffusion coefficients of some binary liquid systems," *J. Chem. Eng. Data*, 20, 310-316 (1975)
- [15] Anderson, D.K., Hall J.R., Babb A.L., "Mutual Diffusion in Non-ideal Binary Liquid Mixtures," *J. Phys. Chem.*, 62, 404-409 (1958)
- [16] Bidlack, D.L. Anderson D.K., "Mutual Diffusion in Non-ideal, Non-associating Liquid Systems," *J. Phys. Chem.*, 68, 3790-3794 (1964)
- [17] Caldwell, C.S., Babb A.L., "Diffusion in Ideal Binary Liquid Mixtures," *J. Phys. Chem.*, 60, 51-56 (1956)
- [18] Kelly, C.M., Wirth G.B., Anderson D.K., "Tracer and mutual diffusivities in the system chloroform-carbon tetrachloride at 25.deg," *J. Phys. Chem.*, 75, 3293-3296 (1971)

- [19] Irani, R.R., Adamson A.W., "Transport processes in liquid systems. III .Thermodynamic complications in the testing of existing diffusional theories," *J. Phys. Chem.*, 64, 199-204 (1960)
- [20] Sikiru A. Sanni, Peter Hutchison, "Diffusivities and densities for binary liquid mixtures," *J. Chem. Eng. Data*, 18, 317-322 (1973)
- [21] Harris, K.R., Pua C.K.N., Dunlop P.J., "Mutual and tracer diffusion coefficients and frictional coefficients for the systems benzene-chlorobenzene, benzene-n-hexane, and benzene-n-heptane at 25.deg," *J. Phys. Chem.*, 74, 3518-3529 (1970)
- [22] Tasic, A.Z., Djordjevic BD, Serbanovic SP, Grozdanic DK, "Diffusion coefficients for the liquid system acetone-cyclohexane at 298.15 K," *J. Chem. Eng. Data*, 26, 118-120 (1981)
- [23] Fernández G. A., Vrabec J., Hasse H., "Self-Diffusion and Binary Maxwell–Stefan Diffusion Coefficients of Quadrupolar Real Fluids from Molecular Simulation," *International Journal of Thermophysics*, 26, 1389-1407 (2005)
- [24] Li J., Liu H., Hu Y.. "Mutual-diffusion-coefficient model based on local composition," *Fluid Phase Equilibria.*, 187-188,193-208 (2001)
- [25] Cullinan H. T., Toor H. L., "Diffusion in the Three-Component Liquid System Acetone- Benzene carbon Tetrachloride," *J. Phys. Chem.*, 69, 3941-3949 (1965)