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A.M. KUTSYK, V.V. OBUKHOVSKY

Taras Shevchenko National University of Kyiv, Faculty of Physics
*(64, Volodymyrs'ka Str., Kyiv 01033, Ukraine; e-mail: a.m.kutsyk@gmail.com,*
*vobukhovsky@yandex.ru)*

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# NONLINEAR DIFFUSION IN THE LIQUID SOLUTION OF DIETHYL ETHER WITH CHLOROFORM

*Nonlinear diffusion in the binary liquid solution of diethyl ether with chloroform accompanied by a complex formation reaction has been considered. It is shown that the account for the possibility of the* $[A_1B_1]$ *complex formation can explain the nonlinear concentration dependence of the mutual diffusion coefficient. The calculation results are compared with the results of other approaches. A nonlinear modification of Fick's law was demonstrated to provide the best description of experimental results, i.e. it gives the smallest average relative deviation.*

*Keywords*: nonlinear diffusion, mutual diffusion coefficient, complex formation, diethyl ether, chloroform.

## 1. Introduction

Diffusive mass transfer can be met in plenty of chemical and technological processes, where it plays an important role [1, 2]. Therefore, the correct determination of diffusion laws is not only important from the theoretical viewpoint, but it also has a practical value.

Transfer phenomena in solutions are closely associated with the liquid structure and its modifications owing to the dissolution. Difficulties associated with taking the interaction between molecules into account still do not allow the theory of solutions to be developed to a level reached in the gas and solid-state theories [3]. It was the absence of a comprehensive theory of liquids that resulted in the existing variety of approaches to the description of the mutual diffusion in liquid molecular solutions [4–18].

The presence of rather strong directed intermolecular interactions between the components of a solution can give rise to the formation of associates and complexes [19]. An idea concerning the influence of chemical transformations on the properties of a solution was put forward for the first time by D.I. Mendeleev and formed a basis of his doctrine concerning the solutions [20]. This idea enriched with new concepts, new methods of the intermolecular interaction theory, and new capabilities of experimental studies of solutions is widely used and developed today [21].

The associate (complex) can be defined as a group of molecules in a liquid system with certain internal (spatial, orientational) structure resulted from the formation of intermolecular bonds, the lifetime of which exceeds the period of intermolecular vibrations at least by an order of magnitude. Groups formed by molecules of the same kind will be called associates, and groups formed by molecules of various kinds will be called complexes [1] [19, 22].

The influence of the association and the formation of complexes on the mutual diffusion process in liquid solutions can be taken into account in the framework of a nonlinear modification of Fick's law [24, 25]. This

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[1] This terminology is rather convenient, but not standard. Another terminology can also be found in the literature [23].

work was aimed at the application of the given approach to describe the concentration dependence of the mutual diffusion coefficient in the liquid solution of diethyl ether with chloroform and at the quantitative comparison of the results obtained with the available theories, in particular, those in [5, 7, 9, 11, 13, 17].

## 2. Main Approaches to Mutual Diffusion Description

The classical Fick's law couples a flux of particles with the gradient of their concentration:

$$\mathbf{j}_1 = -D_{12}\nabla c_1, \tag{1}$$

where $D_{12}$ is the Fick mutual diffusion coefficient. Numerous experimental researches testify to a strong dependence of the latter on the concentration. Therefore, a lot of attempts were made to explain this dependence [4–18].

From the viewpoint of nonequilibrium thermodynamics, the gradient of the chemical potential is a driving force of the mass transfer processes. At a constant temperature and pressure, the particle flux can be written as follows [26]:

$$\mathbf{j}_1 = -\frac{D_0 c_1}{RT}\nabla\mu_1. \tag{2}$$

The chemical potential of a solution component can be presented in the form

$$\mu_1 = \mu_1^0 + RT\ln a_1, \tag{3}$$

where $a_1$ is the activity of component 1 (for an ideal solution, the activity $a_1$ of the component is equivalent to its molar fraction $x_1$). Substituting expression (3) into Eq. (2) allows the flux to be rewritten as follows:

$$\mathbf{j}_1 = -D_0\left(\frac{\partial\ln a_1}{\partial\ln x_1}\right)\nabla c_1. \tag{4}$$

A comparison with Fick's law gives the following expression for the mutual diffision coefficient:

$$D_{12} = D_0\left(\frac{\partial\ln a_1}{\partial\ln x_1}\right). \tag{5}$$

Schreiner was the first who obtained this expression for the mutual diffusion coefficient in 1922 [27].

The parameter $D_0$ in Eq. (5) can be regarded as an effective mobility of the particle, and the multiplier $\left(\frac{\partial\ln a_1}{\partial\ln x_1}\right)$ as a thermodynamic factor that takes into account the action of a "force" on a diffusing molecule owing to the presence of the chemical potential gradient. Equation (4) is derived by supposing that a particle moves in the continuous motionless medium. Taking into account that the solvent molecules also participate in the diffusive transfer brings us to the well-known Darken expression [5]

$$D_{12} = (D_1^* x_2 + D_2^* x_1)\left(\frac{\partial\ln a_1}{\partial\ln x_1}\right), \tag{6}$$

where $D_1^*$ and $D_2^*$ are the diffusion coefficients of labeled particles.(the tracer diffusion coefficients) [2]. The tracer diffusion coefficient, as well as the coefficient of mutual diffusion, can be a function of the solution content (concentration) [28]. The application of tracer self-diffusion coefficients is possible only if they can be associated with the motion of a separate particle, which is correct only if the particles do not interact with one another. The interaction between particles results in that the motion of particles becomes correlated, so that it is necessary to take into account such effects as the formation of complexes.

The Darken equation (6) effectively describes the coefficients of mutual diffusion only in metal alloys and in solutions close to ideal omes. Despite that, this equation became a basis for many interpolation schemes. In particular, the mutual diffusion coefficients rather than the tracer ones are used for infinitely diluted solutions, together with an additional averaging over the values of viscosity [1].

Using the model of local composition for binary solutions, Li *et al.* [13] modified Darken's expression for the mutual diffusion coefficient as follows:

$$D = \left(\frac{\phi_{22}\bar{V}}{\bar{V}_2}D_1^* + \frac{\phi_{11}\bar{V}}{\bar{V}_1}D_2^*\right)\left(\frac{\partial\ln a_1}{\partial\ln x_1}\right), \tag{7}$$

Here, $\phi_{ii}$ are the so-called local volume fractions; and $\bar{V}_1$, $\bar{V}_2$, and $\bar{V}$ are the molar volumes of components 1

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[2] The concept of tracer diffusion coefficient is more general than that of self-diffusion. It concerns the diffusion of labeled component in a homogeneous (not only one-component) mixture [1, 28]. In the case of binary mixture, the limiting value of tracer diffusion coefficient coincides with the the self-diffusion coefficient: $D_1^*(x_1 \to 1) = D_1^0$ at $x_1 \to 1$; and with the coefficient of mutual diffusion in the infinitely diluted solution: $D_1^*(x_1 \to 0) = D_{12}^0$ at $x_1 \to 0$.

and 2 and the solution, respectively. The expediency of changing to the local volume fractions follows from the local composition concept of Wilson [29], because the local composition considerably differs from the macroscopic one (this is a manifestation of various interactions, including the association). According to Wilson, the local volume fractions are defined as follows:

$$\phi_{11} = \frac{x_1}{x_1 + x_2\Lambda_{12}}, \quad \phi_{11} = \frac{x_2}{x_2 + x_1\Lambda_{21}}. \tag{8}$$

Here, $\Lambda_{ij}$ are the Wilson parameters, which can be determined from experiments. In order to predict the behavior of the mutual diffusion coefficient (7), the tracer ones $D_i^*$ also have to be known. However, in work [13], it was assumed that the molecules of both kinds diffuse not individually, but as a part of clusters, the dimensions of which depend on the solution concentration, and the following expression for the tracer diffusion coefficients was obtained:

$$D_i^* = \frac{D_i^0 \eta_i}{\eta}\left(\frac{n_i^0}{1 + (n_i^0 - 1)x_i}\right)^{1/2}, \quad i = 1, 2. \tag{9}$$

Here, $D_i^0$ is the self-diffusion coefficient of the $i$-th component; $\eta_i$ and $\eta$ are the viscosity coefficients of the $i$-th component and the solution, respectively; and $n_i^0$ are the sizes of clusters of diffusing particles in the case of self-diffusion, which equal

$$n_1^0 = \left(\frac{\eta_2 D_{21}^0}{\eta_1 D_1^0}\right)^{1/2}, \quad n_2^0 = \left(\frac{\eta_1 D_{12}^0}{\eta_2 D_2^0}\right)^{1/2}, \tag{10}$$

where $D_{12}^0 = D_{12}(x_1 \to 0)$ and $D_{21}^0 = D_{12}(x_1 \to 1)$ are the mutual diffusion coefficients in the infinitely diluted solutions.

In works by Moggridge and D'Agostino [17, 30, 31], the expression for the Darken mutual diffusion coefficient was generalized, by using the ideas of the critical phenomenon theory. In a vicinity of the critical point, the temperature dependence of the diffusion coefficient is given by the expression

$$D_{12} = D_0\left(\frac{T - T_c}{T_c}\right)^{\alpha}, \tag{11}$$

where $T_c$ is the critical temperature, $D_0$ a temperature-independent constant, and $\alpha = 0.62 \div 0.685$ is a parameter of the theory with a value slightly depending on the approach. In the framework of works [17, 30, 31], the thermodynamic factor has a simple temperature dependence

$$\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right) = \left(\frac{T - T_c}{T}\right). \tag{12}$$

This equation is correct, if the excess Gibbs energy is almost independent of the temperature (rather often, the assumption that the temperature interval is narrow turns out enough for this purpose, because the entropic term dominates, as a rule).

Supposing that expressions (11) and (12) are valid and comparing them with Eq. (5), Darken's expression (6) can be modified, so that the mutual diffusion coefficient looks like [30]:

$$D_{12} = (x_1 D_2^* + x_2 D_1^*)\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)^{\alpha}. \tag{13}$$

The transformation of Eq. (6) into Eq. (13) is not strictly proved, but Eq. (13) made it possible to describe the concentration dependence of mutual diffusion coefficients in some systems with a reasonable accuracy [17]. However, it turned out inapplicable for strongly associated systems, in particular, for alcohol solutions in nonpolar solvents, as well as acetone–chloroform solutions. For those systems, the association effects [32, 33] have to be taken into consideration.

There are a number of approaches for the description of the mutual diffusion coefficient, whiich are based on the Eyring kinetic theory [4, 7, 9, 11, 12, 16, 18]. According to those theories, it is supposed that the diffusion process can be described similarly to the monomolecular reaction, by including the transient formation of such a configuration of a particle and its environment that can be considered as an activated state. During its motion, the solute molecule should overcome a potential barrier between two equilibrium states corresponding to two neighbor molecule positions. The mutual diffusion coefficient in ideal solutions is written as follows:

$$D = \lambda^2 k, \tag{14}$$

where $\lambda$ is the distance between two neighbor positions, and $k$ is the hopping frequency. For nonideal solutions, expression (14) has to be multiplied by the thermodynamic factor [34],

$$D_{12} = \lambda^2 k_{\text{eff}} = \lambda^2 k\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right). \tag{15}$$

Equations (14) and (15) were derived supposing the solvent to be at rest. The account of solute molecule jumps gives rise to the following expression, which was theoretically substantiated by Cullinan [35]:

$$D_{12} = (D_{12}^o)^{x_2}(D_{21}^o)^{x_1}\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right). \tag{16}$$

Equation (14) was obtained for the first time empirically by Vignes, while studying the concentration behavior of the mutual diffusion coefficient for a set of mixtures [7]. As a rule, the Vignes equation gives good results for ideal (or close to ideal) solutions. For strongly nonideal solutions, this equation gives values that considerably differ from experimental ones. However, along with the Darken equation, the Vignes one is widely applied as a basis for empirical modifications.

The main shortcoming of expressions, in which the thermodynamic factor is used, is the absence of procedures to calculate the latter or, to be more specific, the absence of a general thermodynamic model for the determination of the excess Gibbs energy, which the thermodynamic factor is connected with [29]. Therefore, even if using either of the Darken and Vignes expressions, the application of various thermodynamic models gives rise to different results [11, 16, 18].

In the general case, the equilibrium distances passed by particles (of both the solute and the solvent) within the jump time are not equal, $\lambda_1 \neq \lambda_2$. A generalization to this case was made by He [9], who obtained the following expression:

$$D_{12} = \left(D_{12}^0\right)^{x_2}\left(D_{21}^0\right)^{x_1}(x_2\xi_1^{x_1} + x_1\xi_2^{x_2}), \tag{17}$$

where $\xi_1$ and $\xi_2$ are empirical constants. The analysis of more than thirty binary mixtures showed that the He equation gives better results than the Vignes one. However, the scope of its application is rather limited: it is inapplicable for strongly associated systems, such as solutions of water, alcohols, and aniline, with binary alcohol solutions being an exception.

The Eyring theory was further developed by Hsu and Chen in a model called UNIDIF [11]. The expression obtained for the mutual diffusion coefficient turned out identical to Eq. (14), but the distance between neighbor equilibrium positions, $\lambda_{12}$, should be taken as a geometrical mean with respect to the concentration:

$$\lambda_{12} = \lambda_1^{x_2}\lambda_2^{x_1}. \tag{18}$$

In turn, the hopping frequency $k_{12}$ should be determined as

$$\ln k_{12} = x_1\left(\frac{\partial \ln k_{am}}{\partial x_2} + x_2\frac{\partial \ln k_{am}}{\partial x_1}\right). \tag{19}$$

The hopping frequency of molecules between equilibrium positions, $k_{am}$, is determined in accordance with the lattice model of the solution,

$$k_{am} = \prod_{i=1}^{n}\left(\frac{k_{\mathrm{B}}T}{2\pi M_i}\right)^{\frac{x_i}{2}}\exp\left(\frac{N_C}{2k_{\mathrm{B}}T}\sum_{i=1}^{n}x_i q_i\sum_{j=1}^{n}U_{ji}\theta_{ji}\right), \tag{20}$$

where $N_C$ is the coordination number, $q_i$ the surface area of the $i$-th component, $U_{ji}$ the potential energy of interaction between the $j$-th and $i$-th components, and $\theta_{ji}$ the parameter of local composition related to the average fractions of the surface areas of the $i$-th and $j$-th components. The parameters in Eq. (20) are the same as in the UNIQUAC model (see Appendix); therefore, the model for diffusion was called UNIDIF by analogy. The mutual diffusion coefficient acquires the following form:

$$\begin{aligned} D_{12} = {} & (D_{12}^o)^{x_2}(D_{21}^o)^{x_1}\exp\Bigg(2\left\{x_1\ln\frac{x_1}{\phi_1} + x_2\ln\frac{x_2}{\phi_2}\right\} + \\ & + 2x_1x_2\left\{\frac{\phi_1}{x_1}\left(1-\frac{\lambda_1}{\lambda_2}\right) + \frac{\phi_2}{x_2}\left(1-\frac{\lambda_2}{\lambda_1}\right)\right\} + \\ & + \Big\{x_2q_1[(1-\theta_{21}^2)\ln\tau_{21} + (1-\theta_{22}^2)\tau_{12}\ln\tau_{12}] + \\ & + x_1q_2[(1-\theta_{12}^2)\ln\tau_{12} + (1-\theta_{11}^2)\tau_{21}\ln\tau_{21}]\Big\}\Bigg), \end{aligned} \tag{21}$$

Here, $\phi_1$ and $\phi_2$ are the volume fractions of components 1 and 2, respectively; the parameters $\lambda_1$ and $\lambda_2$ are assumed to be proportional to the cubic root of the molar volume or to the volume parameter in the UNIQUAC model; and

$$\tau_{12} = \exp\left(-\frac{N_C(U_{12}-U_{22})}{2k_{\mathrm{B}}T}\right),$$

$$\tau_{21} = \exp\left(-\frac{N_C(U_{21}-U_{11})}{2k_{\mathrm{B}}T}\right)$$

are interaction parameters, which are to be fitted in the UNIDIF model.

An alternative approach to the description of the mutual diffusion coefficient was proposed by A. Shapiro [14]. His theory was called the fluctuation diffusion theory. It is based on the thermodynamics of irreversible processes, namely, on the Onsager linear phenomenological theory. According to the latter, the thermodynamic fluxes that arise in the system are linear combinations of thermodynamic forces. The diffusive flux for an $n$-component mixture of noninteracting components is taken in the ordinary form

$$\mathbf{j}_i = \sum_{j=1}^{n-1} L_{D,ij}\mathbf{X}_D^j. \tag{22}$$

The standard diffusion theory, which is based on the thermodynamics of nonequilibrium processes, does not have large advantages at the study of the ordinary diffusion, but it forms a basis for the consideration of phenomena emerging at superposing several gradients of various origins.

The Shapiro fluctuation theory connects the matrix of phenomenological coefficients $\mathbf{L}_D$ with the so-called transition matrix $\mathbf{L}_{Tr}$ in the following way:

$$\mathbf{L}_D = \mathbf{G}\overline{\mathbf{L}}_{Tr}\mathbf{G}^T, \quad \overline{\mathbf{L}}_{Tr} = \frac{1}{2}\left(\mathbf{L}_{Tr} + \mathbf{L}_{Tr}^T\right). \tag{23}$$

The matrix $\mathbf{G}$ depends on the choice of thermodynamic fluxes and forces.

In turn, the transition matrix $\mathbf{L}_{Tr}$ is a product of three components: the resistance matrix $\mathbf{L}_R$ and the matrices describing the kinetic, $\mathbf{L}_K$, and thermodynamic, $\mathbf{L}_T$, contributions to the diffusive mass transfer,

$$\mathbf{L}_{Tr} = \frac{1}{4}\mathbf{L}_K\mathbf{L}_T\mathbf{L}_R. \tag{24}$$

In the case of binary diffusion, the dimension of the kinetic matrix $\mathbf{L}_K$ is $2\times 2$. It takes contributions from the molecular motion into account and is defined as a diagonal matrix composed of the average molecular velocities $u_i$ of various components,

$$L_{K,ij} = \delta_{ij}u_j, \quad u_j = \sqrt{\frac{8RT}{\pi M_j}} \quad (i,j=1,2). \tag{25}$$

The thermodynamic matrix $\mathbf{L}_T$,

$$\mathbf{L}_T = \mathbf{F}^{-1} \tag{26}$$

has a dimension of $3 \times 2$. It is expressed in terms of the matrix $\mathbf{F}$ for the entropy derivatives with respect to the molar densities $c_i$ and the internal energy $U$:

$$\begin{aligned} &F_{ij} = \frac{\partial^2 S}{\partial c_i \partial c_j}, \\ &F_{i,n+1} = F_{n+1,i} = \frac{\partial^2 S}{\partial c_i \partial U}, \\ &F_{n+1,n+1} = \frac{\partial^2 S}{\partial U^2} \ (i,j=1,2). \end{aligned} \tag{27}$$

The resistance matrix $\mathbf{L}_R$, the dimension of which equals $2 \times 3$, involves the resistance to the molecular motion from other molecules. It is expressed in terms of the so-called penetration lengths [14],

$$\begin{aligned} &L_{R,ij} = \delta_{ij}Z_i(\mathbf{N},U) - N_i\frac{\partial Z_i(\mathbf{N},U)}{\partial N_i}, \\ &L_{R,i,n+1} = -N_i\frac{\partial Z_i(\mathbf{N},U)}{\partial U} \quad (i=1,...,2). \end{aligned} \tag{28}$$

According to Shapiro, the penetration length is the average distance of particle displacements, after which the particle “forgets” its initial velocity. The penetration lengths can be obtained with the help of simulation molecular dynamics methods [36] or using interpolation formulas [15,37]. Since the dependences of diffusion coefficients on the penetration lengths are nontrivial, the interpolation formulas should be simple dependences with a few fittng parameters. In particular, the following interpolation formulas were used in works [15, 37]:

$$\begin{aligned} &Z_i = \sqrt{\frac{M_i}{M_{\text{mix}}}}A_i\exp(-B_1c_1 - B_2c_2), \\ &Z_i = \sqrt{\frac{M_i}{M_{\text{mix}}}}A_i(1 - B_1c_1 - B_2c_2 - \\ &- B_{12}c_1c_2/(c_1+c_2)), \end{aligned} \tag{29}$$

where $M_i$ and $M_{\text{mix}}$ are the molar masses of the $j$-th component and the solution, respectively.

According to Shapiro [15], the binary mixture is characterized by a single parameter $L_D$, and the mutual diffusion coefficient is written in the form

$$D_{12} = L_D\frac{M_{\text{mix}}}{M_1M_2T}\left(\frac{1}{x_1M_2}\frac{\partial\ln\mu_2}{\partial c_2} + \frac{1}{x_2M_1}\frac{\partial\ln\mu_1}{\partial c_1}\right). \tag{30}$$

The main advantage of the fluctuation diffusion theory is its ability to consider multicomponent systems. However, the determination of the thermodynamic matrix $\mathbf{L}_T$ is a rather laborious procedure. In addition, a certain thermodynamic model for the equation of state is required, because the derivatives of the entropy of a system have to be calculated. At the same time, the major difficulty is the determination of the resistance matrix (more precisely, the penetration lengths, which it depends on). The description accuracy of the concentration dependence of the mutual diffusion coefficient depends on the form of the interpolation formula for the penetration length and the number of fitting parameters. The increase of their number from three to four allowed the concentration dependences of the diffusion coefficient to be described with quite a good accuracy for many solutions with small molecular masses. The exceptions include strongly associated aqueous and alcohol solutions [15].

## 3. Account of Complex Formation Processes

Despite that the complexes which are formed, when one substance is dissolved in the other one, are chemically unstable, they substantially affect the diffusion process. When such interaction processes are taken into account, the solution is considered as multicomponent and consisting of unbound (pure) components, as well as associates and complexes.

The rates of complex formation reactions are so high that, for a system to come locally to the equilibrium state, the time required for that is much shorter than the characteristic time of the mass transfer (diffusion). Therefore, in multicomponent solutions, the ordinary diffusion fluxes of pure components can be considered together with additional fluxes associated with the mutual diffusion of complexes and associates. In the literature, as a rule, additional fluxes are introduced, which are governed by first Fick's law [38–44]. However, if the particles interact with one another, such fluxes are nonlinear, because the transport of particles of one sort is automatically accompanied by the transfer of the particles of the other sort. In the specific case of interaction of the "excluded volume" type, the nonlinear equations of mass transfer were derived in the framework of the lattice gas model [45–49].

The same expression for the nonlinear flux was used in works [24, 25] to describe the nonlinear diffusion kinetics taking the formation of complexes into account. Considering the mass transfer processes under conditions of a local chemical equilibrium for every solution component, it is possible to introduce the flux by the formula [25]:

$$\mathbf{j}_i = \sum_j d_{ij}\,[\phi_i \nabla \phi_j - \phi_j \nabla \phi_i], \tag{31}$$

where

$$\sum_i \phi_i = 1, \tag{32}$$

and the following notations were introduced: $\phi_i \equiv \phi_i(\mathbf{r}, t)$ is the volume fraction of the $i$-th substance in a physically infinitesimal volume centered at the point $\mathbf{r}$ at the time moment $t$; and $d_{ij} = d_{ji}$ are the mutual diffusion coefficients [3]. The expediency of using the partial volume fractions $\phi_i \equiv \phi_i(\mathbf{r}, t)$ follows from the fact that the relative motion of various components occurs provided that the total volume of the mixture is constant.

In the framework of this approach, arbitrary multicomponent mixtures can be examined. However, for the sake of simplification, let us consider a binary mixture of substances A and B, which can form the equimolecular complex AB, i.e. the effective mixture will be ternary. The volume fraction of the complex in the solution, $\phi_3$, is related to the volume fractions of unbound components as follows:

$$\phi_3 = K\phi_1\phi_2, \tag{33}$$

where $K$ is the equilibrium constant.

In the course of diffusion, the molecules of substance A are transported both separately and as a component of complex AB. The effective flux registered in experiment is equal to

$$\mathbf{j}_1^{\mathrm{tot}} = \mathbf{j}_1 + \bar{\alpha}_{13}\mathbf{j}_3, \tag{34}$$

where $\bar{\alpha}_{13}$ is the volume fraction of substance A in the complex. The total volume fraction of the $i$-th substance (both unbound and in the complex) can be determined as follows:

$$\phi_i^{\mathrm{tot}} = \phi_i + \bar{\alpha}_{i3}\phi_3, \quad i = 1, 2. \tag{35}$$

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[3] In our opinion, it is the coefficients $d_{ij}$ that should be referred to as the mutual diffusion ones, because they are constants, unlike the coefficients $D_{12}$ in formulas (5)–(7), (13), (15)–(17), and (26).

After substituting the partial fluxes into the total one, we obtain the expression

$$\mathbf{j}_1^{\mathrm{tot}} = \sum_{i\neq j, i<j}^{3} d_{ij}(\bar{\alpha}_{1i} - \bar{\alpha}_{1j})\,[\phi_i \nabla\phi_j - \phi_j \nabla\phi_i]. \qquad (36)$$

Here, $\bar{\alpha}_{1i}$ is the volume fraction of substance A in the other substance, i.e. $\bar{\alpha}_{11} = 1$, $\bar{\alpha}_{12} = 0$, and $\bar{\alpha}_{13} = \bar{V}_1/(\bar{V}_1 + \bar{V}_2)$.

Flux (34) can be rewritten analogously to first Fick's law in the form

$$\mathbf{j}_1^{\mathrm{tot}} = \sum_{i\neq j, i<j}^{3} d_{ij}(\bar{\alpha}_{1i} - \bar{\alpha}_{1j})\left[\phi_i \frac{\partial\phi_j}{\partial\phi_1^{\mathrm{tot}}} - \right.$$
$$\left. - \phi_j \frac{\partial\phi_i}{\partial\phi_1^{\mathrm{tot}}}\right] \nabla\phi_1^{\mathrm{tot}} = -D_{12}\left(\phi_1^{\mathrm{tot}}\right)\nabla\phi_1^{\mathrm{tot}}. \qquad (37)$$

Finally, the mutual diffusion coefficient can be written as follows:

$$D_{12}\left(\phi_1^{\mathrm{tot}}\right) = \sum_{i\neq j, i<j}^{3} d_{ij}(\bar{\alpha}_{1j} - \bar{\alpha}_{1i})\left[\phi_i \frac{\partial\phi_j}{\partial\phi_1^{\mathrm{tot}}} - \phi_j \frac{\partial\phi_i}{\partial\phi_1^{\mathrm{tot}}}\right] =$$
$$= d_{12}w_{12} + d_{13}(1 - \bar{\alpha}_{13})w_{13} + d_{23}(\bar{\alpha}_{23} - \bar{\alpha}_{13})w_{23}. \qquad (38)$$

## 4. Results and their Discussion

Let us consider a molecular mixture diethyl ether–chloroform. Experimental researches of the corresponding diffusion coefficients were made in works [38, 50].

The hydrogen bond C–H$\cdots$O between the diethyl ether and chloroform molecules results in the appearance of an equimolecular complex [$A_1B_1$]. Its existence is confirmed by the research of excess thermodynamic functions [21, 51] and by spectroscopic methods: the nuclear magnetic resonance spectroscopy [52] and the Rayleigh light scattering [53].

In the framework of our model, the liquid mixture of diethyl ether with chloroform is considered as a ternary one (the components A, B, and C are considered). The experimental curve of the concentration dependence of the mutual diffusion coefficient at $T = 25°\mathrm{C}$ was taken from work [50]. Using the methods of nonlinear regression analysis and formula (38), the following optimal values for the parameters entering the diffusion coefficient $D_{12}\left(\phi_1^{\mathrm{tot}}\right)$ were determined: $d_{12} = 4.57 \times 10^{-9}$ m$^2$/s, $d_{13} = 4.42 \times 10^{-9}$ m$^2$/s, $d_{23} = 0.48 \times 10^{-9}$ m$^2$/s, $K = 2.64$, and $\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(D_i^{\exp} - D_i^{\mathrm{calc}}\right)^2} = 0.024 \times 10^{-9}$ m$^2$/s. Those values were used to plot the concentration dependence of the diffusion coefficient, which was compared with the experimental data (Fig. 1). One can see that taking the complex formation into account allowed the experimental data to be described very accurately. The optimal value of the equilibrium constant for the complex formation process, $K$, was used to plot the concentration profiles of solution components (Fig. 2).

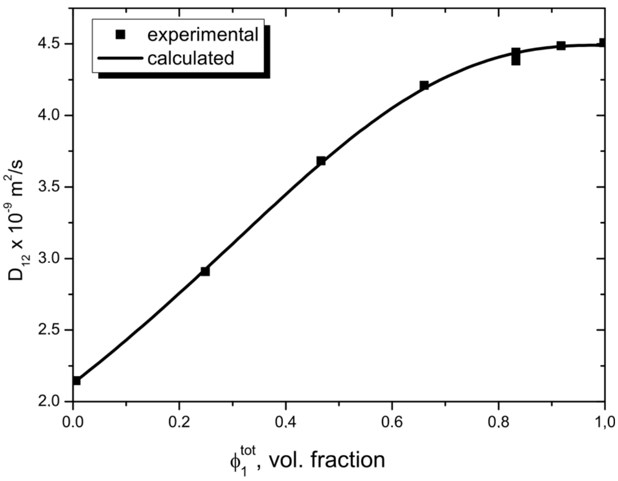

***Fig. 1.*** Comparison of the calculated curve with experimental data

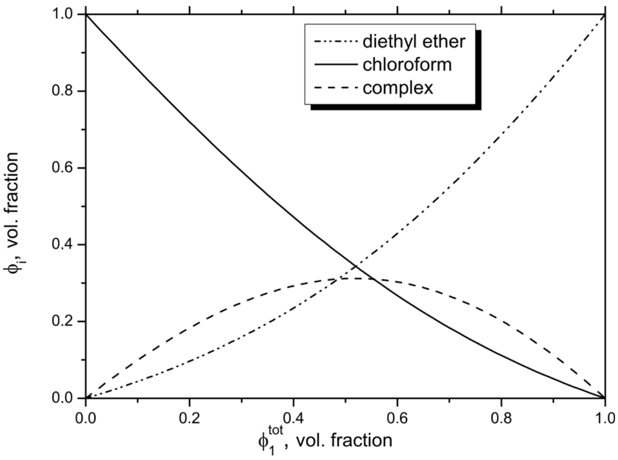

***Fig. 2.*** Concentration profiles of solution components

The concentration dependence of the mutual diffusion coefficient in the solution diethyl ether–chloroform was analyzed in a number of works [9, 11, 13, 15, 17]. A description quality criterion was the average relative deviation (ARD) of the calculated quantities from the corresponding experimental data, which is defined by the following formula:

$$\mathrm{ARD} = \frac{1}{N}\sum_{i=1}^{N}\frac{|D_i^{\mathrm{calc}} - D_i^{\mathrm{exp}}|}{D_i^{\mathrm{exp}}} \times 100\%. \qquad (39)$$

Table contains the ARD values obtained in the available approaches and the result of our calculations. The error values were taken from the original works.

In the majority of approaches (see formulas (6), (7), (16), (17), and (21)), in order to determine the mutual diffusion coefficient, one has additionally to know the limiting values of this parameter in the infinitely diluted solution. These values are determined with the help of empirical formulas or by extrapolating experimental data to the region of limiting concentrations. In addition, the Li model (7) also requires the values of self-diffusion coefficients, and Moggridge one (13) the concentration dependences of the tracer mutual diffusion coefficients for both components. Therefore, in those cases, a large role in the description of the mutual diffusion coefficient is played by the determination accuracy of corresponding quantities.

As one can see from Table, if the number of fitting parameters does not exceeds four, the error falls within the limits of 0.8–13.5% in various approaches. Even in the framework of the same approach, the application of various thermodynamic models for the solution results in different errors, which is clearly seen for the Darken and Vignes formulas. The thermodynamic models used for the determination of the thermodynamic factor also contain fitting parameters (see Appendix). Those parameters can be determined from other experiments, as was done in the works by Moggridge [17] and Li [13], where the Redlich–Kister and Wilson, respectively, models were used. In work by Hsu and Chen [11], the parameters of NRTL, Eq. (A5), and UNIQUAC, Eq. (A7), thermodynamic models were determined from the diffusion data; and the expression in the UNIDIF model had two fitting parameters.

| No. | Approach | ARD, % | Source |
|---|---|---|---|
| 1 | Xe | 2.3 | [9] |
| 2 | Li *et al.* | 3.3 | [13] |
| 3 | Darken + Wilson | 13.5 | [13] |
| 4 | Darken + NRTL | 1 | [11] |
| 5 | Darken + UNIQUAC | 3.4 | [11] |
| 6 | Vignes + NRTL | 1.2 | [11] |
| 7 | Vignes + UNIQUAC | 4.5 | [11] |
| 8 | UNIDIF | 0.8 | [11] |
| 9 | Shapiro and Medvedev | 0.9–8 | [15] |
| 10 | Moggridge [a] | 1.5 | [17] |
| 11 | Kutsyk, Obukhovsky | 0.45 | |

[a] This quantity was recalculated, because Moggridge's work contains only the root-mean-square deviation value $\sigma = 0.056 \times 10^{-9}$ m$^2$/s.

The Shapiro fluctuation theory gives a very wide spread of errors, depending on the choice of the equation of state for the liquid solution. Again, owing to the absence of an analytical expression for the penetration length $Z$, interpolation formulas with different numbers (three or four) of fitting parameters (29) were used.

Table demonstrates that our calculations give the smallest relative deviation, which testifies to the adequacy of the model used to describe the diffusion in the solution of diethyl ether with chloroform.

## 5. Conclusions

The account for a possibility of the equimolecular complex formation in the liquid solution of diethyl ether with chloroform allowed the concentration dependence of the mutual diffusion coefficient to be explained. A nonlinear modification of Fick's law on the basis of the applied structural model of the solution made it possible to describe experimental data not only at the qualitative level, but also at the quantitative one. A comparison of our calculation results with the results of other approaches shows that the nonlinear diffusion theory together with the application of a model approach to determine the liquid structure can be used to describe the concentration dependence of the diffusion coefficient rather exactly.

## APPENDIX A

### Determination of the thermodynamic factor in various models

The thermodynamic factor $\Gamma = \left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)$, which is used in expressions for the mutual diffusion coefficient, is related to the excess Gibbs energy as follows:

$$\Gamma = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^E}{\partial x_1^2} + \frac{\partial^2 G^E}{\partial x_2} - 2\frac{\partial^2 G^E}{\partial x_1 \partial x_2}\right). \qquad (A1)$$

When differentiating in this formula, the molar fractions $x_1$ and $x_2$ should be considered as independent variables.

There are a number of models for the excess Gibbs energy [29]. Here, we mention only those that were used in the theories described above for the determination of the mutual diffusion coefficient. Some expressions for the thermodynamic factors are also quoted in work [54].

### *1. Wilson's model (1964)*

$$\frac{G^E}{RT} = -\sum_{i=1}^{k} x_i \ln \sum_{j=1}^{k} x_j \Lambda_{ij}, \tag{A2}$$

where $\Lambda_{ij} = \frac{\bar{V}_j}{\bar{V}_i} \exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right)$ is the Wilson parameter, and $\lambda_{ij}$ is the parameter of the interaction between components $i$ and $j$. The equation for the binary mixture contains two parameters, $\Lambda_{12}$ and $\Lambda_{21}$. At calculations, those parameters are fitting ones, being determined from any experimental data for $G^E$. The thermodynamic factor in this model looks like

$$\Gamma = 1 - \frac{x_1}{x_1 + \Lambda_{12} x_2} + \frac{x_1 \Lambda_{21}}{x_2 + \Lambda_{21} x_1} - \\ - x_1 x_2 \left[\frac{\Lambda_{12}(1-\Lambda_{12})}{(x_1 + \Lambda_{12} x_2)^2} + \frac{\Lambda_{21}(1-\Lambda_{21})}{(x_2 + x_1 \Lambda_{21})^2}\right]. \tag{A3}$$

### *2. NRTL model (Renon and Prausnitz, 1968)*

The Renon–Prausnitz equation, which is called the NRTL (Non-Random Two-Liquid) equation, besides two energy parameters, the sense of which is similar to that of the Wilson parameters, contains a third parameter for a binary system. This parameter characterizes the ordering degree of the molecular distribution in the solution. The NRTL equation looks like

$$\frac{G^E}{RT} = \sum_{i=1}^{k} x_i \left(\frac{\sum_{j=1}^{k} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{k} G_{li} x_l}\right), \tag{A4}$$

where $G_{ji} = \exp(-a_{ji}\tau_{ji})$, $\tau_{ji} = \frac{g_{ji}-g_{ii}}{RT}$, $a_{ji} = a_{ij}$, and $a_{ii} = \tau_{ii} = 0$. In the NRTL model, no restrictions are imposed on the fitting parameters $\tau_{ji}$, whereas the parameter $a_{ji}$ may vary within an interval of 0.2–0.5. The thermodynamic factor in the NRTL model looks like

$$\Gamma = 1 + x_1 x_2 \left(\frac{\tau_{21}\exp(-2a\tau_{21})}{(x_1 + x_2\exp(-a\tau_{21}))^3} + \\ + \frac{\tau_{12}\exp(-2a\tau_{12})}{(x_2 + x_1\exp(-a\tau_{12}))^3}\right). \tag{A5}$$

### *3. UNIQUAC model (Abrams and Prausnitz, 1975)*

The UNIQUAC (UNIversal QUAsi-Chemical equation) model by Abrams and Prausnitz combines the local composition concept with the lattice solution theory. The quantity $G^E$ for the binary solution has the form

$$\frac{G^E}{RT} = x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} - \\ - \frac{N_C}{2}\left(x_1 q_1 \ln\frac{\phi_1}{\theta_1} + x_2 q_2 \ln\frac{\phi_2}{\theta_2}\right) - \\ - x_1 q_1 \ln(\theta_1 + \theta_2\tau_{21}) - x_2 q_2 \ln(\theta_1\tau_{12} + \theta_2). \tag{A6}$$

In the case of binary solution, we have six parameters: $\tau_{12}$ and $\tau_{21}$ are fitting ones, $r_1$ and $r_2$ are the so-called van der Waals volumes of molecules, and $q_1$, $q_2$ the van der Waals surfaces of molecules. The coordination number $N_C = 10$. The parameter $\theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j} = \frac{x_i q_i}{q}$ is the surface fraction of the $i$-th component, and $\phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j} = \frac{x_i r_i}{r}$ is its volume fraction. The expression for the thermodynamic factor in the UNIQUAC model is rather cumbersome:

$$\Gamma = 1 + x_1\left(\frac{(r_1 - r_2)^2 x_2}{r^2} + \frac{N_C q}{2}\left(\frac{r_1}{r} - \frac{q_1}{q}\right) \times \\ \times \left[\frac{r_2 - r_1}{r} - \frac{q_1 - q_2}{q}\right] + \frac{q_1^2}{q}\left[1 - \frac{2}{\theta_1 + \theta_2\tau_{12}} + \\ + \frac{\theta_1}{(\theta_1 + \theta_2\tau_{12})^2} + \frac{\theta_2\tau_{12}^2}{(\theta_2 + \theta_1\tau_{21})^2}\right] - \\ - \frac{q_1 q_2}{q}\left[1 - \frac{\theta_2\tau_{12}\tau_{21}}{(\theta_1 + \theta_2\tau_{12})^2} - \frac{\theta_1\tau_{12}\tau_{21}}{(\theta_2 + \theta_1\tau_{21})^2}\right]\right). \tag{A7}$$

### *4. Redlich–Kister expansion*

Although the local-composition models have fixed numbers of parameters, they are hardly applicable for strongly nonideal systems. On the other hand, the expression for the excess Gibbs energy can be selected in a form that provides the best fitting. In particular, the Redlich–Kister expansion looks like

$$G^E = x_1 x_2\big(A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \\ + D(x_1 - x_2)^3\big), \tag{A8}$$

Here, $A$, $B$, $C$, and $D$ are fitting parameters. Then the thermodynamic factor can be written as follows:

$$\Gamma = 1 - \frac{x_2}{RT}[2Ax_1 + B(12x_1^2 - 6x_1) + C(48x_1^3 - 48x_1 + \\ + 10x_1) + D(160x_4 - 240x_1^3 + 108x_1^2 - 14x_1)]. \tag{A9}$$

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*А.М. Куцик, В.В. Обуховський*

## НЕЛІНІЙНА ДИФУЗІЯ У РІДКОМУ РОЗЧИНІ ДІЕТИЛОВОГО ЕФІРУ З ХЛОРОФОРМОМ

Резюме

Розглянуто нелінійну дифузію у бінарному рідкому розчині діетилового ефіру з хлороформом за умови протікання реакцій комплексоутворення. Показано, що врахування можливості утворення комплексу [$A_1B_1$] дозволяє пояснити нелінійну концентраційну залежність коефіцієнта взаємної дифузії. Результати розрахунків було порівняно із результатами інших підходів. Було показано, що нелінійна модифікація закону Фіка найкраще описує експериментальні результат, тобто дає найменшу величину середнього відносного відхилення.