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Nonlinear diffusion in multicomponent liquid solutions

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Mutual diffusion in multicomponent liquids is studied. It is taken into consideration that the influence of complex formation on the diffusion process may be substantial. The theory is applied to analyze mass transfer in an acetone-chloroform solution. The molecular complex concentration was obtained from the analysis of Fourier transform infrared spectra of this solution. Taking into account molecular complex formation allows one to explain the experimental dependence of diffusion coefficients on the composition (components concentration). The accuracy of experimental and theoretical data descriptions in the frame of our model is compared to the accuracy for some other approaches.

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I. INTRODUCTION

Standard Fick laws [1] are usually used to describe experimental results of mutual diffusion, i.e., transport of solute from regions with high concentrations to low concentrations in nonuniform solutions. In this way, the velocity of matter transfer is determined with D_F, the mutual diffusion (interdiffusion) coefficient. Numerous experimental data indicate that in many solutions this coefficient D_F is not constant but sufficiently depends on the solute concentration (see, for example, Refs. [2–4]).

Many methods have been developed for the theoretical description of diffusion effects in liquid solutions by now (see, for example, Refs. [2–18] and references therein). The Darken equation [7] and its modifications [5,8,10] are widely used. Also the Vignes equation [13] is the basis of many empirical equations [5,14–16]. Fluctuation theories of diffusion arouse interest due to attention paid to the random spatial distribution of molecules [17,18]. The interconnection between mutual diffusion and viscosity of solutions allows us to predict some physical characteristics [12].

In some papers diffusion is considered a random walk of particles through free positions (vacancies) (see, e.g., Refs. [3,19]). But the concept of "vacancy" is very difficult to introduce in the multicomponent liquid mixture, in which molecules have significantly different sizes. Besides that, many liquids have low compressibility. This can be interpreted as an absence (or a very small quantity) of free volume.

Another direction of diffusion theories' development is connected with the application of probability theory for random walks of atoms in the nodes of a crystal lattice [20]. Note that in the framework of a two-component lattice gas model new nonlinear diffusion effects can be found: the drag effect, the formation of the drifting spatial structure, the effect of "negative" mass transport, etc. [20–26].

But the results of the latter papers are not adapted for the description of diffusion in liquid solutions. The reason is that mutual diffusion cannot be separated from the process of dissolving, and mixing of initial components is accompanied by the energetic process (change of enthalpy, heating and cooling). New components can be formed as the result of dissolution, and they are called "complexes" or "heteroassociates" [27]. In experiments [28–30] the average quantity of such structural formations was large enough (for example, it can exceed 50%), despite their instability.[1]

An essential step was made in Refs. [31–34],where the hypothesis of the influence of solution structure on the diffusion process was successfully realized. The impact of association or complex formation on interdiffusion and intradiffusion in multicomponent systems was investigated in the frame of traditional thermodynamic theories [35–39]. Peculiarities, which complicate their practical applications, include the necessity of taking into account (in some theories) the concentration dependence of auxiliary functions, e.g., thermodynamic factor, intradiffusion coefficients of solution components, etc.

The purpose of this work is the application of probability theory to the description of a mutual diffusion process in a liquid multicomponent solution with associates, or complex generation. As an example of our theoretical application, diffusion in an acetone-chloroform solution is analyzed.

II. NONLINEAR FLOW UNDER NORMALIZATION CONDITIONS

It is known that in an ideal binary mixture, where interactions between components are not taken into account, transport of particles A and B is governed by a linear diffusion law [2,3]. The simplest model, which implies nonlinear flow behavior (relative to concentration characteristics),[2] must include more than two types of particles ("particles" may include individual molecules, associates, and complexes).

Hereinafter a mixture of three components A, B, and C is considered. Diffusion takes place only along axis x. In the frame of our model construction, all the particles are located in planes x_i $(i = 0, \pm 1, \pm 2, \pm 3, \ldots)$. The distance ΔL between all adjacent planes is small. In any plane the total

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[1] The small lifetime of a molecular complex has to be compared with the small time of free motion of individual molecules.

[2] In our theory, diffusion flow relating to the corresponding thermodynamic force is considered in linear approximation.

amount of particles, N_0, is fixed (vacancies are not available). If a particle A is located in the plane x_i and a particle B is located in the plane x_{i+1} (near the molecule A), then the correlated process when A moves into the plane $i+1$ and B moves to the vacant place in plane i can occur. Therefore, this process $AB \rightarrow BA$ is called the "exchange of positions."

In fact, exchange of positions can be performed in a more difficult way (displacement of several neighboring particles in the closed loop). However, the flux density is determined only by the difference between initial and final molecular distributions and does not depend on the method of particle transfer. The exchange of positions of particles of one type is excluded from consideration because it does not result in experimentally registered changes.[3]

We denote p_{ab}, p_{bc}, and p_{ac} the probabilities of exchange of the positions (per unit time) for the processes $A \leftrightarrow B$, $B \leftrightarrow C$, and $C \leftrightarrow A$, respectively. The number of particles of type "s" in the plane x_i is denoted $N^S(x_i,t)$. The probability to find the particles with $s_1 \neq s_2$ in the neighboring positions with the coordinates (x_i,y_j,z_k), (x_{i+1},y_j,z_k) will be proportional to the product $(\frac{N^{S1}(x_i,t)}{N_0})(\frac{N^{S2}(x_{i+1},t)}{N_0})$. In any case, the normalization condition must be satisfied:

$$N^a(x_i,t) + N^b(x_i,t) + N^c(x_i,t) = N_0. \tag{1}$$

The particle flux is determined by the number of exchanges $A \leftrightarrow B$, $A \leftrightarrow C$ (per unit time) in the direction of the axis x and equal to

$$\begin{aligned} J_x^a(x,t) = \frac{1}{N_0^2}\,&\{p_{ab}[N^a(x_i,t)N^b(x_{i+1},t) \\ &- N^b(x_i,t),N^a(x_{i+1},t)] + p_{ac}[N^a(x_i,t)N^c(x_{i+1},t) \\ &- N^c(x_i,t)N^a(x_{i+1},t)]\}. \end{aligned} \tag{2}$$

If smooth spatial variations for functions $N^S(x)$ take place, it can be spread into a Taylor series:

$$N^S(x_{i+1}) \cong N^S(x_i) + \left.\frac{\partial N^S}{\partial x}\right|_{x_i} \Delta L \tag{3}$$

($\Delta L = x_{i+1} - x_i$). Substituting Eq. (3) in Eq. (2), we obtain for the three-component case

$$\begin{aligned} J_x^a(x_i,t) = &\left(\frac{p_{ab}\Delta L}{N_0^2}\right)\left[N^a\frac{\partial N^b}{\partial x} - N^b\frac{\partial N^a}{\partial x}\right]\Bigg|_{x_i} \\ &+ \left(\frac{p_{ac}\Delta l}{N_0^2}\right)\left[N^a\frac{\partial N^c}{\partial x} - N^c\frac{\partial N^a}{\partial x}\right]\Bigg|_{x_i}. \end{aligned} \tag{4}$$

It is easy to generalize Eq. (4) for continuous distribution of equal size particles, and then we obtain

$$\begin{aligned} \boldsymbol{J}^a(\boldsymbol{r},t) = \sum_q Q(a,q)[&N^a(\boldsymbol{r},t)\nabla N^q(\boldsymbol{r},t) \\ &- N^q(\boldsymbol{r},t)\nabla N^a(\boldsymbol{r},t)]. \end{aligned} \tag{5}$$

Here we introduce the following notations: a and q are components of the system, $\boldsymbol{J}^a$ is the total flux of the particles a, and the value $Q(a,q)$ is determined by the speed of position interchange for the substances (a,q). The flow (5) is a quadratic function of the concentration. Therefore, diffusion has to be classified as a second order nonlinear effect.

To generalize results above, it is necessary to take into account the differences in sizes of the diffusing particles. According to the principles of the phenomenological theories [40], the diffusion flux of the matter should be considered as the averaged value over "physically infinitesimal volume." Following Ref. [40], we select a physically infinitesimal volume[4] $V_0(\boldsymbol{r})$ in the mixture (centered at the point $\boldsymbol{r}$) and define the volume fraction $\varphi_n(\boldsymbol{r})$ as the relative portion of this volume occupied by all molecules of the type n:

$$\varphi_n(\boldsymbol{r}) = \frac{V_n(\boldsymbol{r})}{V_0(\boldsymbol{r})}, \quad \left(\sum_n \varphi_n(\boldsymbol{r},t) = 1\right), \tag{6}$$

where $V_n(\boldsymbol{r})$ is the part of the volume $V_0(\boldsymbol{r})$ occupied by the substance n.

The flow (5) was defined earlier as the number of particles that transit through a unit area per unit time. We can replace this flow by the φ stream. It is the volume of substance n which is carried over a unit area per unit time. It is easy to check that in this way the nonlinear diffusion flows can be written as follows:

$$\boldsymbol{j}_i = \sum_j b_{ij}[\varphi_i \nabla \varphi_j - \varphi_j \nabla \varphi_i]. \tag{7}$$

Here the indices i and j denote the components of the liquid mixture, φ_i is the volume fraction of the ith component, $\boldsymbol{j}_i$ is volume flow of the ith substance, and b_{ij} is the symmetric matrix of position interchange coefficients ($b_{ij} = b_{ji}$), that can be interpreted as "nonlinear diffusion coefficients." Contrary to the mutual diffusion coefficient D_F the values of b_{ij} are constant and do not depend on component concentration. Here and below, the volume-fixed frame of reference is used.

The nonlinearity of flow similar to Eq. (7) appears in other tasks. For example, it can be considered a generalization of the mass transfer law for the model [41] that was created for multicomponent photopolymers. Also the quadratic nonlinearity similar to Eq. (7) was met in the investigations of impurity diffusion in cubic crystals [20–26] and in monolayers of reagents on the surface of a catalyst [42,43].

Generally, the diffusion of liquid components has to be described as a macroscopic phenomenon. So, all physical quantities, related to mass transfer, have to be averaged over physically infinitesimal volume. As a result, all other equations could be formulated in terms of "partial volumes" too. Besides Eq. (7), the following laws (generalization of standard formulas [41,44]) can be used in investigation of diffusion:

(a) the equations of continuity

$$\frac{\partial \varphi_i}{\partial t} + \operatorname{div} \boldsymbol{j}_i = S_i, \tag{8}$$

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[3] This theory is oriented at macroscopic diffusion experiments, for example, with optical registration of spatial distributions of concentrations.

[4] According to the definition of physically infinitesimal volume (PIV), its sizes are much smaller compared to the precision of space coordinate measuring (in diffusion experiment), but the PIV contains a large number ($N \gg 1$) of particles.

(b) and the conditions of conservation

$$\sum_i \boldsymbol{j}_i = 0, \quad \sum_i S_i = 0. \tag{9}$$

Here S_i is the function of sources, which depends on the processes of i-component formation (decomposition).

For the case of the negligibly small influence of the shrinkage and swelling phenomenon on the processes of diffusive transport, we take into account the law of volume conservation:[5]

$$\sum_i \varphi_i = 1. \tag{10}$$

Equations (7)–(10) are valid in the range $0 \leqslant \varphi_i \leqslant 1$, ($i = 1,2,\ldots$).

It is obvious that macroscopic diffusion flux of any component must be accompanied by reverse flow of other components in the case of volume conservation. Hence the problem of macroscopic diffusion can be considered an analog of two-body problems (taking into account two related or interconnected flows). In the general case, the many-body problem can be described by nonlinear equations [46]. And it is not surprising that simultaneous consideration of two correlated subsystems, "direct flow–reverse flow," leads to quadratic dependence in the equations of motion.

First of all, it can be checked that the nonlinear form of the flow in Eq. (7) in the particular case does not contradict the linear Fick law. Indeed, consider a mixture of two noninteractive molecular liquids with the flow

$$\boldsymbol{j}_1 = b_{12}[\varphi_1 \boldsymbol{\nabla}\varphi_2 - \varphi_2 \boldsymbol{\nabla}\varphi_1]. \tag{11}$$

The condition of volume conservation $\varphi_1 + \varphi_2 = 1$ leads to

$$\varphi_2 = 1 - \varphi_1, \ \ \boldsymbol{\nabla}\varphi_2 = -\boldsymbol{\nabla}\varphi_1. \tag{12}$$

Substituting Eq. (12) into Eq. (11), we find the expression for the volume flow:

$$\boldsymbol{j}_1 = -b_{12}\boldsymbol{\nabla}\varphi_1. \tag{13}$$

The diffusion coefficient in Eq. (13) is constant. The volume flow $\boldsymbol{j}_1$ and molar flow $\boldsymbol{J}_1$ are interconnected by the following relation:

$$\boldsymbol{j}_1 = \bar{V}_1 \boldsymbol{J}_1, \tag{14}$$

where $\bar{V}_1$ is the molar volume of substance 1. Volume flow (13) can be rewritten as

$$\boldsymbol{J}_1 = -D_F \boldsymbol{\nabla} c_1, \tag{15}$$

where the coefficient $D_F = b_{12}$ is constant. Thus, in the case of two noninteractive components the diffusion flow is a linear function of concentration.

III. DIFFUSION IN LIQUID SOLUTION

Consider diffusion in the molecular solutions that are formed by mixing two liquid substances A and B. The theoretical description of this system is considered in the frame of ideal associated solution model (IASM) [27,47]. This model treats nonideal mixtures of associated components as ideal mixtures of free molecules and molecular complexes [48–51]. Interaction between molecules of the original components can lead to formation (with some probability) of complexes of the A_nB_m type. Below we discuss the system with the following interactions:

$$\begin{aligned} nA + mB &\rightarrow A_nB_m \quad \text{(formation of complex)},\\ A_nB_m &\rightarrow nA + mB \quad \text{(dissociation of complex)}. \end{aligned} \tag{16}$$

(To simplify the calculations, the intermediate steps of reactions are not considered.)

Within the framework of our model, this kind of mixture consists of three components: A, B, and A_nB_m. Hereinafter these components are denoted as 1, 2, and 3. The reactions (16) determine the form of the functions S_i (sources). In this case

$$\left.\begin{aligned} S_1 &= \beta_1\varphi_3 - \alpha_1\varphi_1^n\varphi_2^m,\\ S_2 &= \beta_2\varphi_3 - \alpha_2\varphi_1^n\varphi_2^m,\\ S_3 &= -S_1 - S_2. \end{aligned}\right\} \tag{17}$$

The form of the functions (17) is similar to the description of generation and decay processes for nonstable products of chemical reactions [52]. Below, the reaction rates are assumed to be rapid compared to diffusion so that chemical equilibrium exists locally [31]. Then the approximation

$$S_i \cong 0 \tag{18}$$

can be used in Eqs. (17). In other words, diffusion occurs under conditions of a local chemical equilibrium. In this case, the volume fraction of a complex component can be found from Eqs. (17) and (18):

$$\varphi_3 \cong K_\varphi \varphi_1^n (1 - \varphi_1 - \varphi_3)^m \quad \left(K_\varphi = \frac{\alpha_1}{\beta_1} = \frac{\alpha_2}{\beta_2}\right). \tag{19}$$

Below we take into account the following peculiarity. The transport of molecules in the diffusion process occurs via two mechanisms: (i) individually and (ii) as a part of the complex A_nB_m. Therefore, the total flow of the matter "A" (measurable in experiments) is defined as a linear combination,

$$\boldsymbol{j}_1^{\text{tot}} = \boldsymbol{j}_1 + \bar{\alpha}_1 \boldsymbol{j}_3 \quad \left(\bar{\alpha}_1 = \frac{n\bar{V}_1}{n\bar{V}_1 + m\bar{V}_2}\right), \tag{20}$$

where α_1 is the volume fraction of substance A in the complex A_nB_m, and $\bar{V}_1$ and $\bar{V}_2$ are the molar volumes of components 1 and 2.

After substitution of Eq. (7) in Eq. (20) we have the following relationship:

$$\begin{aligned} \boldsymbol{j}_1^{\text{tot}} = {} & b_{12}[\varphi_1\boldsymbol{\nabla}\varphi_2 - \varphi_2\boldsymbol{\nabla}\varphi_1] + b_{13}\bar{\alpha}_2[\varphi_1\boldsymbol{\nabla}\varphi_3 - \varphi_3\boldsymbol{\nabla}\varphi_1]\\ & + b_{23}\bar{\alpha}_1[\varphi_3\boldsymbol{\nabla}\varphi_2 - \varphi_2\boldsymbol{\nabla}\varphi_3]. \end{aligned} \tag{21}$$

As we highlighted above, there are two states of substance 1 in the solution: free and bonded (in molecular complex composition). Therefore, its total partial volume is

$$\varphi_1^{\text{tot}} = \varphi_1 + \bar{\alpha}_1\varphi_3. \tag{22}$$

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[5] Shrinkage and swelling effects can be taken into account if an additional component (free space) is added. See, for example, Ref. [45].

Similarly, we can determine the total partial volume for the second component, φ_2^{tot}:

$$\varphi_2^{\mathrm{tot}} = \varphi_2 + \bar{\alpha}_2\varphi_3 \quad \left(\bar{\alpha}_2 = \frac{m\bar{V}_2}{n\bar{V}_1 + m\bar{V}_2}\right). \tag{23}$$

In this case the normalization condition is identically satisfied:

$$\varphi_1^{\mathrm{tot}} + \varphi_2^{\mathrm{tot}} = 1 \quad (\bar{\alpha}_1 + \bar{\alpha}_2 = 1). \tag{24}$$

It is easy to verify the following assertion: the value φ_1^{tot} completely determines all other functions of diffuse flows [i.e., $\varphi_i = \varphi_i(\varphi_1^{\mathrm{tot}})$, $i = 1,2,3$] if conditions defined by Eq. (18) are valid. Therefore, the total flux of substance 1 also can be represented as the function of φ_1^{tot} only:

$$\boldsymbol{j}_1^{\mathrm{tot}} = -D_1^{\mathrm{ef}}(\varphi_1^{\mathrm{tot}})\nabla\varphi_1^{\mathrm{tot}}. \tag{25}$$

It is obvious that Eq. (25) has the same form as the first Fick law of diffusion; however, it contains the generalized (effective) coefficient of diffusion, D_1^{ef}. In fact, the "coefficient" D_1^{ef} is not constant but is a function which depends on the "concentration" of interacting substances:

$$D_1^{\mathrm{ef}}(\varphi_1^{\mathrm{tot}}) = w_{12}(\varphi_1^{\mathrm{tot}})b_{12} + w_{13}(\varphi_1^{\mathrm{tot}})b_{13} + w_{23}(\varphi_1^{\mathrm{tot}})b_{23}. \tag{26}$$

Here w_{ij} determines the relative contribution of the interactions between different components $\{i,j\} = \{1,2,3\}$ into the effective (measured) diffusion coefficient. In the general case[6]

$$\begin{aligned} w_{12} &= \varphi_2\frac{\partial\varphi_1}{\partial\varphi_1^{\mathrm{tot}}} - \varphi_1\frac{\partial\varphi_2}{\partial\varphi_1^{\mathrm{tot}}}, \\ w_{13} &= \bar{\alpha}_2\left(\varphi_3\frac{\partial\varphi_1}{\partial\varphi_1^{\mathrm{tot}}} - \varphi_1\frac{\partial\varphi_3}{\partial\varphi_1^{\mathrm{tot}}}\right), \\ w_{23} &= \bar{\alpha}_1\left(\varphi_2\frac{\partial\varphi_3}{\partial\varphi_1^{\mathrm{tot}}} - \varphi_3\frac{\partial\varphi_2}{\partial\varphi_1^{\mathrm{tot}}}\right). \end{aligned} \tag{27}$$

It is not difficult to verify that

$$w_{12} + w_{13} + w_{23} = 1. \tag{28}$$

All functions w_{ij} in Eqs. (26) and (28) must be expressed through φ_1^{tot}.

The results obtained above [Eqs. (25)–(27)] describe diffusion in a "binary" liquid solution with complex A_nB_m generation in the process of mixing. The material parameters of this system are K_φ and b_{ij}. In Appendix A it is proved that in the simplest case of solutions with 1:1 a complex these parameters can be found from the experimentally measured values on the borders of an area of measuring (in the case of infinite dilution of component A or B) D_1^{ef} ($\varphi_1^{\mathrm{tot}} = 0$), D_1^{ef} ($\varphi_2^{\mathrm{tot}} = 0$), $\partial D_1^{\mathrm{ef}}/\partial\varphi_1^{\mathrm{tot}}$ ($\varphi_1^{\mathrm{tot}} = 0$), and $\partial D_1^{\mathrm{ef}}/\partial\varphi_1^{\mathrm{tot}}$ ($\varphi_2^{\mathrm{tot}} = 0$). Therefore, parameters K_φ and b_{ij} do not need to be considered mathematically adjustable.

Unfortunately, precise experimental measuring of diffusion coefficients under conditions $\varphi_1^{\mathrm{tot}} = 0$ or $\varphi_2^{\mathrm{tot}} = 0$ usually is not realized (in practice they are found by extrapolation of the nearest points[7]). This is the reason why another way could be more preferable. Indeed, the equilibrium constant K_φ can be determined from other experimental data (for example, by vibrational spectroscopy or NMR techniques [53,54]). As a rule, use of additional data leads to improvement of calculation.

IV. MOLECULAR COMPLEX FORMATION IN ACETONE-CHLOROFORM MIXTURE

The presence of the C-H$\cdots$O hydrogen bond in the acetone-chloroform mixture causes the formation of the molecular complex which consists of one acetone molecule and one chloroform molecule. Equimolecular (1:1) complex formation is indicated by inelastic neutron scattering [55], low-Raman, far- [56], mid- [57], and near-infrared, and ^{1}H NMR [53] spectroscopies. On the other hand, the oxygen atom in acetone contains two electron lone pairs, so in fact two types of complexes may exist. The indirect evidence of 1:2 complex existence is the slight asymmetry of excess thermodynamic functions (excess Gibbs energy, enthalpy, and entropy) [58,59]. Due to the small number of 1:2 complexes fixed experimentally [54,60], hereinafter we consider only equimolecular 1:1 complex formation.

Before using Eqs.(26) and (27), we need to obtain the equilibrium constant K_φ of complex formation which allows determination of the volume fractions φ_3. It can be obtained from an infrared (IR) absorption spectroscopy, because it is well known that IR spectra are very sensitive to any structural changes which occur in the investigated system [61].

Fourier transform infrared (FTIR) absorption spectra, between 3750 and 6200 cm^{-1} (Fig. 1), were used to study intermolecular interactions between components of the acetone-chloroform liquid solution. FTIR spectra were measured using a Thermo Scientific Nicolet iS50 FTIR spectrometer with maximum spectral resolution of 0.125 cm^{-1}. Heating of the sample almost did not occur during the measurements due to the small value of the absorption coefficient at the excitation frequency. The temperature of liquid samples was $25 \pm 0.2\,^\circ$C. Chloroform and acetone with purity 99.9% were used in this research. The concentration of components was changed from 0% to 100% (in vol %) with a step of 10%. Spectra recordings were repeated 32 times for each sample. Thereafter the average spectrum was calculated for every concentration and used in further analysis.

Considering the liquid solution as multicomponent, which contains unbonded ("pure") and bonded (molecular complex) species, the IR data matrix may be written as

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{R}. \tag{29}$$

Here $\mathbf{D}$ is the measured IR absorption spectra matrix of solution, its rows containing spectra measured at different concentrations; $\mathbf{C}$ is the matrix of concentrations, its columns containing concentration profiles of solution components; $\mathbf{S}$ is the matrix, which contains spectral profiles of each solution component; and $\mathbf{R}$ is the residuals matrix.

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[6] For an arbitrary type of third component, particularly for any n, m.

[7] In many diffusion experiments the minimal step of concentrations is near 5–10 %.

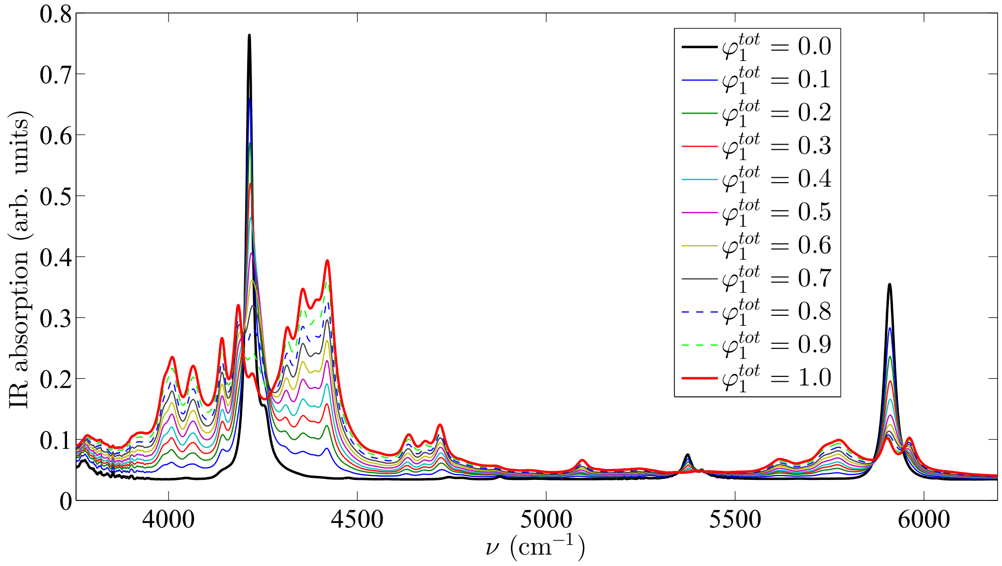

FIG. 1. FTIR absorption spectra of acetone-chloroform solutions between 3750 and 6200 cm^{-1}; φ_1^{tot} is the initial volume fraction of acetone (before mixing).

The goal of multivariate curve resolution (MCR) techniques is the determination of the matrices **C** and **S** using the experimental data matrix **D** [62,63]. The basic principle of MCR is to seek a bilinear model that gives the best fit to the matrix **D**.

Use of the liquid solution structural model may simplify greatly the decomposition of spectra matrix **D** [63]. The concentration matrix **C** (in our case it contains volume fractions) may be found by using a mass balance equation at fixed value of K_φ. The solution of Eq. (29) at fixed **D** may be estimated in sense of least squares:

$$\mathbf{S} = (\mathbf{C}^T\mathbf{C})^{-1}\mathbf{C}^T\mathbf{D} = \mathbf{C}^{+}\mathbf{D}. \qquad (30)$$

Here $\mathbf{C}^{+} = (\mathbf{C}^T\mathbf{C})^{-1}\mathbf{C}^T$ is Moure-Penrose pseudoinverse matrix. By using Eqs. (29) and (30), the residuals matrix **R** may be written as

$$\mathbf{R} = \mathbf{D} - \mathbf{C}\mathbf{C}^{+}\mathbf{D}. \qquad (31)$$

Matrix **C** depends on the equilibrium constant K_φ only; thus, matrix norm of **R** must be minimized for the estimation of the equilibrium constant optimal value:

$$\|\mathbf{R}\| = \|\mathbf{D} - \mathbf{C}(K_\varphi)\mathbf{C}^{+}(K_\varphi)\mathbf{D}\| \rightarrow \mathbf{min}, \quad K_\varphi > 0. \qquad (32)$$

The three-component model of the solution, which was proposed for the description of mutual diffusion, was used for decomposition of spectra matrix **D**. Using measured IR absorbance data, solution of Eq. (32) gives the following optimal value of the equilibrium constant:

$$K_\varphi^{\text{opt}} = 2.5 \pm 0.2. \qquad (33)$$

With this value of equilibrium constant K_φ^{opt} we can numerically solve Eq. (19) and calculate volume fractions of mixture components φ_3, φ_2, and φ_1 as a function of initial volume φ_1^{tot}. The results are shown in Fig. 2.

The complex fraction φ_3 arises as the result of interaction between molecules in the dissolution process and can occupy in our case up to 30% of the total volume.

V. ANALYSIS OF DIFFUSION IN ACETONE-CHLOROFORM MIXTURE

We applied the modified system of diffusion equations (7)–(10) to analyze the mass transfer processes in a liquid mixture of acetone (C_3H_6O, component 1) with chloroform ($CHCl_3$, component 2). These substances are completely mutually soluble. The molar volumes of molecules

$$\bar{V}_1 = 74.00\,\text{ml/mol}, \quad \bar{V}_2 = 80.64\,\text{ml/mol}, \qquad (34)$$

for acetone and chloroform, respectively (which are needed for the calculation of $\bar{\alpha}_1$ and $\bar{\alpha}_2$), were found from Ref. [27].

Experimental data on diffusion in an acetone-chloroform mixture were obtained in Refs. [64,65] at 25 °C. These data have been restated to build the curve of the diffusion coefficient D_{12}^{expt} as a function of the acetone partial volume φ_1^{tot} (Fig. 3).

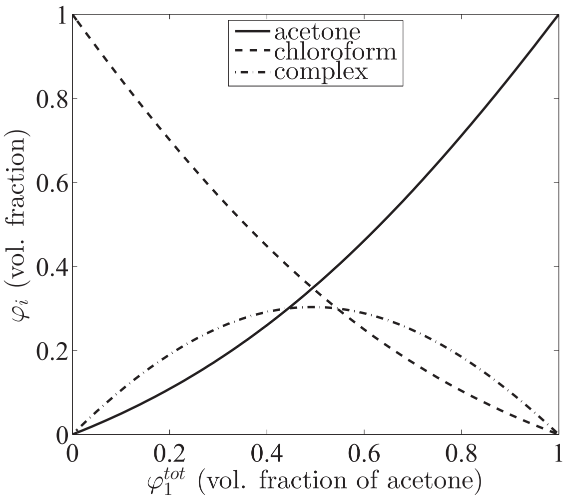

FIG. 2. Calculated volume fractions of mixture components. φ_1^{tot} is the initial volume fraction of acetone (before mixing).

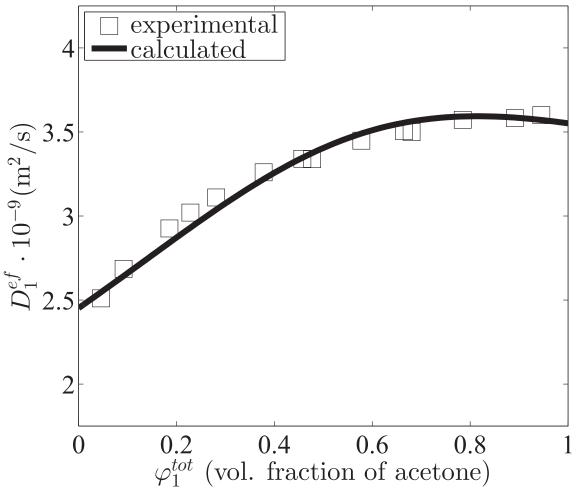

FIG. 3. Concentration dependence of the effective diffusion coefficient for the acetone-chloroform solution: points, experimental data [64]; solid curve, theoretical calculations; φ_1^{tot}, initial volume fraction of acetone (before mixing).

It is known that the concentration dependence of the excess enthalpy of mixing has a parabolic form with a minimum when the component concentration ratio is 1:1 [58,66]. It is an indirect evidence of equimolecular complex formation ($C = A + B$). This conclusion is confirmed by many other experimental results (see, for example, Refs. [53,55–57]). In our case, such a complex formation process corresponds to the following set of coefficients: $n = 1, m = 1$.

The concentration of components 1 and 2 after mixing can be written as

$$\varphi_1 = \varphi_1^{\mathrm{tot}} - \bar{\alpha}_1\varphi_3, \quad \varphi_2 = \varphi_2^{\mathrm{tot}} - \bar{\alpha}_2\varphi_3. \tag{35}$$

In this case the equation for the volume fraction of the component $C \equiv [A_1B_1]$ can be obtained from Eq. (19):

$$\varphi_3 = K_\varphi\big(\varphi_1^{\mathrm{tot}} - \bar{\alpha}_1\varphi_3\big)\big(\varphi_2^{\mathrm{tot}} - \bar{\alpha}_2\varphi_3\big), \tag{36}$$

which is a quadratic form of φ_3. The solution of Eq. (36) can be found as

$$\varphi_3(\varphi_1^{\mathrm{tot}},\ \varphi_2^{\mathrm{tot}}) = \frac{\big\{\big[1 + K_\varphi\big(\bar{\alpha}_1\varphi_2^{\mathrm{tot}} + \bar{\alpha}_2\varphi_1^{\mathrm{tot}}\big)\big] - \sqrt{\big[1 + K_\varphi\big(\bar{\alpha}_1\varphi_2^{\mathrm{tot}} + \bar{\alpha}_2\varphi_1^{\mathrm{tot}}\big)\big]^2 - 4\bar{\alpha}_1\bar{\alpha}_2K_\phi^2\varphi_1^{\mathrm{tot}}\varphi_2^{\mathrm{tot}}}\big\}}{2\bar{\alpha}_1\bar{\alpha}_2K_\varphi}. \tag{37}$$

We can rewrite Eqs. (27) for the case of 1:1 complex formation in the form

$$\begin{aligned} w_{12} &= \Psi(1 + \varphi_3),\\ w_{13} &= \Psi K_\varphi\bar{\alpha}_2\varphi_1(\varphi_1 + \varphi_3),\\ w_{23} &= \Psi K_\varphi\bar{\alpha}_1\varphi_2(\varphi_2 + \varphi_3), \end{aligned} \tag{38}$$

where $\Psi = [1 + K_\varphi(\bar{\alpha}_1\varphi_2 + \bar{\alpha}_2\varphi_1)]^{-1}$.

The explicit form for the concentration dependence of functions w_{nm} is obtained by use of Eqs. (35)–(37):

$$\begin{aligned} w_{12} &= \frac{1 + \varphi_3}{1 + K_\varphi\big(\bar{\alpha}_1\varphi_2^{\mathrm{tot}} + \bar{\alpha}_2\varphi_1^{\mathrm{tot}}\big) - 2\bar{\alpha}_1\bar{\alpha}_2K_\varphi\varphi_3},\\ w_{13} &= \frac{K_\varphi\bar{\alpha}_2(\varphi_1^{\mathrm{tot}} - \bar{\alpha}_1\varphi_3)(\varphi_1^{\mathrm{tot}} + \bar{\alpha}_2\varphi_3)}{1 + K_\varphi\big(\bar{\alpha}_1\varphi_2^{\mathrm{tot}} + \bar{\alpha}_2\varphi_1^{\mathrm{tot}}\big) - 2\bar{\alpha}_1\bar{\alpha}_2K_\varphi\varphi_3},\\ w_{23} &= \frac{K_\varphi\bar{\alpha}_1(\varphi_2^{\mathrm{tot}} - \bar{\alpha}_2\varphi_3)(\varphi_2^{\mathrm{tot}} + \bar{\alpha}_1\varphi_3)}{1 + K_\varphi\big(\bar{\alpha}_1\varphi_2^{\mathrm{tot}} + \bar{\alpha}_2\varphi_1^{\mathrm{tot}}\big) - 2\bar{\alpha}_1\bar{\alpha}_2K_\varphi\varphi_3}. \end{aligned} \tag{39}$$

Experimental data D_1^{expt} can be compared with the theoretical dependence of Eqs. (26) and (29). Fitting of b_{nm} can be realized by minimization of the difference $|D_1^{\mathrm{expt}}(\varphi_1^{\mathrm{tot}}) - D_1^{\mathrm{calc}}(\varphi_1^{\mathrm{tot}})|^2$ by the least-squares method. It leads to the following values of material parameters:

$$\begin{aligned} b_{12} &= 3.86 \times 10^{-9}\ \mathrm{m}^2/\mathrm{s},\\ b_{13} &= 3.32 \times 10^{-9}\ \mathrm{m}^2/\mathrm{s},\\ b_{23} &= 1.28 \times 10^{-9}\ \mathrm{m}^2/\mathrm{s}. \end{aligned} \tag{40}$$

A graphical comparison of the theoretical results with the experimental data is presented in Fig. 3. Good agreement of theory and experiment (average relative deviation 1.4 %) supports the assumption that the coefficients b_{ij} are really constants (material parameters) and do not depend on concentrations.

Despite the low share of complexes (does not exceed 30% of the volume), its influence on the diffusion is significant. This is manifested in the nonlinear dependence of the diffusion coefficient on the concentration of components.

VI. COMPARISON WITH OTHER APPROACHES

The mutual diffusion phenomenon has been investigated since Fick proposed his equation [1], but there is no unique theory for its description[8] [4,5]. The Darken equation[9] [7] is one of the earliest equations which takes into account the concentration dependence of the mutual diffusion coefficient. First, it was proposed for binary metal alloys, but now some modifications of it are used for description of diffusion in liquid solutions as well.

Concentration dependencies of tracer diffusion coefficients are needed for application of the Darken equation, but sometimes they cannot be measured directly. In such cases a modified Darken equation is formulated, in which mutual diffusion coefficients at infinite dilution are used instead of tracer diffusion coefficients [68]. The Vignes equation [13] is another widely used equation; it is based on Eyring's kinetic theory and theoretically substantiated by Cullinan [69]. Darken and Vignes equations are the basis for many empirical

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[8] For more details, see Appendix B.

[9] Sometimes it is called the Hartley-Crank equation (Hartley and Crank derived a similar equation independently in Ref. [67]).

TABLE I. Comparison of different approaches for acetone-chloroform solution.

Version	Number of specific parameters[a]	Number of nonspecific parameters[b]	CDAF[c]	ARD[d] (%)
Group 1 (measuring of auxiliary functions is needed)				
Moggridge + NRTL [10,11]	0	3	$2 \times N_p$	2.2
Zhu *et al.* + NRTL [11]	0	3	$2 \times N_p$	2.8
Li *et al.* [8]	4	5	$1 \times N_p$	3.3
Group 2 (theories with adjustable nonspecific parameters)				
UNIDIF [15]	2	6	0	1.5
Modified Darken + UNIQUAC [15]	2	7	0	1.9
Modified Darken + NRTL (version 2) [15]	2	3	0	2.1
Vignes + NRTL [15]	2	3	0	2.1
Vignes + UNIQUAC [15]	2	7	0	2.1
Medvedev and Shapiro [73]	0	8	0	1.4–7.4[e]
Group 3 (theories without adjustable nonspecific parameters)				
Yan *et al.* + Wilson [70]	4	2	0	2.3
Yan *et al.* + NRTL [70]	4	3	0	4.2
Zhou *et al.* + NRTL [14]	2	3	0	5.5
Bosse and Bart + Wilson [16]	2	2	0	6.0
Zhou *et al.* + Wilson [14]	4	2	0	6.2
Modified Darken + Wilson [70]	2	2	0	17.0
Modified Darken + NRTL (version 1) [14]	2	3	0	17.0
Vignes + Wilson [14]	2	2	0	18.4
Obukhovsky *et al.*	3	1	0	1.4

[a] Coefficients of self-diffusion D_1^0 and D_2^0 and/or mutual diffusion at infinite dilution D_{12}^0 and D_{21}^0 (material constants).
[b] Any other parameters (from nondiffusion experiments).
[c] Concentration-dependent auxiliary function (number of functions $\times N_p$, where N_p is the number of experimental points). Tracer diffusion coefficients D_i^* or viscosity of mixture, η, can be used as auxiliary functions. In this table, $N_p = 9$.
[d] Average relative deviation.
[e] ARD depends on the chosen thermodynamic model and the way of the determination of penetration length Z.

equations [5,8,10–12,14–16]. Nowadays, most popular modifications are based on the local composition concept [8,12,14,70]. All these equations contain a thermodynamic correction factor, but there is no unique theory for its determination [71].

Hsu and Chan proposed the UNIDIF model [15], which combines the lattice theory of liquids and absolute reaction rate theory. Shapiro proposed the fluctuation theory of diffusion [17] based on thermodynamics of irreversible processes. The main idea of this approach is the fact that the matrix of Onsager phenomenological coefficients is related to the product of three matrices: kinetic (which accounts for the rates of molecular motion), thermodynamic (which is connected with the second order derivatives of the entropy), and resistance (which accounts for the resistance to molecular motion by other molecules) matrices. Determination of the thermodynamic matrix requires knowledge of the equation of state. Also it is difficult to determine the resistance matrix from first principles [72]; thus, empirical formulas with variable numbers of adjustable parameters are used [18,73].

Calculation of the concentration dependence of the mutual diffusion coefficient $D_{12}(c_1)$ requires information (e.g., tracer diffusivities and activity coefficient) about the investigated mixture. Such information can be obtained (1) directly from diffusion coefficient data or (2) from other available experimental data (for example, the concentration dependence of the activity coefficient is often obtained from vapor-liquid equilibrium data [68]). In some theories the concentration dependence of accessory functions (tracer data and, viscosity) is needed [8,10,11]. Thus, all theoretical descriptions of the mutual diffusion coefficients mentioned above can be separated into three groups (see Table I and Appendix B) depending on the presence of auxiliary functions and specific and nonspecific parameters.

The acetone-chloroform solution is a popular system for diffusion theories. Below in Table I the results [8,10,11,14–16,70,73] are processed and classified.

In Table I the average relative deviation (ARD),

$$\mathrm{ARD} = \frac{1}{N_p}\sum_{i=1}^{N_p}\left|\frac{D_i^{\mathrm{expt}} - D_i^{\mathrm{calc}}}{D_i^{\mathrm{expt}}}\right|, \tag{41}$$

was used to define the difference between experimental and theoretical data. Values for ARD were taken from the respective cited papers. For the main formulas of different approaches see Appendix B.

Insertion of adjustable parameters into theoretical formulas leads to decreasing of ARD. Thus, minimization of ARD can be achieved by using three or four adjustable parameters (in the formula of penetration length Z) in the fluctuation theory of diffusion [73]. But there is no rigorous basis for the formula of penetration length Z, and its choice is quite arbitrary.

TABLE II. Some approaches to the description of the mutual diffusion coefficient.

Approach	Equation	Parameters of model		CDPC[a]
		Specific	Nonspecific	
	Group 1 (measuring of auxiliary functions are needed)			
Moggridge + NRTL [10,11]	$D_{12} = (x_1 D_2^* + x_2 D_1^*)\Gamma^{\tilde\alpha}, \tilde\alpha \approx 0.64; \Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$		$\tau_{12},\tau_{21}, \bar a$	$D_1^*(x_1), D_2^*(x_1)$
Zhu *et al.* + NRTL [11]	$D_{12} = (x_{11} D_2^* + x_{22} D_1^*)\Gamma^{\tilde\alpha}, \tilde\alpha \approx 0.64; \Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$		$\tau_{12},\tau_{21}, \bar a$	$D_1^*(x_1), D_2^*(x_1)$
Li *et al.* [8]	$D = \left(\frac{\phi_{22}\bar V}{\bar V_2} D_1^* + \frac{\phi_{11}\bar V}{\bar V_1} D_2^*\right)\Gamma; \Gamma = \Gamma(\Lambda_{12},\Lambda_{21}; x_1),$ $D_i^* = \frac{D_i^0\eta_i}{\eta}\left(\frac{n_i^0}{1+(n_i^0-1)x_i}\right)^{\tilde\beta}, i = 1,2$ $n_1^0 = \left(\frac{\eta_2 D_{21}^0}{\eta_1 D_1^0}\right)^{1/\tilde\beta}, n_2^0 = \left(\frac{\eta_1 D_{12}^0}{\eta_2 D_2^0}\right)^{1/\tilde\beta}$ $\tilde\beta = 1/2$	$D_{12}^0, D_{21}^0,$ D_1^0, D_2^0	$\Lambda_{12}, \Lambda_{21},$ $\eta_1, \eta_2\ \tilde\beta$	$\eta(x_1)$
	Group 2 (theories with adjustable nonspecific parameters)			
UNIDIF [15]	$\ln D_{12} = x_2 \ln D_{12}^0 + x_1 \ln D_{21}^0 + 2\left\{x_1 \ln \frac{x_1}{\phi_1} + x_2 \ln \frac{x_2}{\phi_2}\right\}$ $+2x_1x_2\left\{\frac{\phi_1}{x_1}\left(1 - \frac{\lambda_1}{\lambda_2}\right) + \frac{\varphi_2}{x_2}\left(1 - \frac{\lambda_2}{\lambda_1}\right)\right\}$ $+\left\{x_2 q_1[(1-\theta_{21}^2)\ln\tau_{21} + (1-\theta_{22}^2)\tau_{12}\ln\tau_{12}]\right.$ $\left.+x_1 q_2[(1-\theta_{12}^2)\ln\tau_{12} + (1-\theta_{11}^2)\tau_{21}\ln\tau_{21}]\right\}$ $\theta_{ji} = \frac{\theta_j\tau_{ji}}{\sum_l \theta_l\tau_{li}}, \theta_j = \frac{x_j q_j}{\sum_l x_l q_l}, \tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right),$ $\phi_i = \frac{x_i\lambda_i}{\sum_l x_l\lambda_l}, \lambda_i = (r_i)^{1/3}, i = 1,2$	$D_{12}^0, D_{21}^0,$	a_{12},a_{21} r_1,r_2 q_1,q_2	
Modified Darken + UNIQUAC [15,68]	$D_{12} = \left(D_{12}^0 x_2 + D_{21}^0 x_1\right)\Gamma; \Gamma = \Gamma(\tau_{12},\tau_{21},r_1,r_2,q_1,q_2,N_c; x_1)$	D_{12}^0, D_{21}^0	$\tau_{12}, \tau_{21}, q_1, q_2, N_c$ $r_1, r_2,$	
Modified Darken + NRTL(version 2) [15,68]	$D_{12} = \left(D_{12}^0 x_2 + D_{21}^0 x_1\right)\Gamma; \Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$	D_{12}^0, D_{21}^0	$\tau_{12}, \tau_{21}, \bar a$	
Vignes + NRTL [13,15]	$D_{12} = \left(D_{12}^0\right)^{x_2}\left(D_{21}^0\right)^{x_1}\Gamma; \Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$	D_{12}^0, D_{21}^0	$\tau_{12}, \tau_{21}, \bar a$	
Vignes + UNIQUAC [13,15]	$D_{12} = \left(D_{12}^0\right)^{x_2}\left(D_{21}^0\right)^{x_1}\Gamma; \Gamma = \Gamma(\tau_{12},\tau_{21},r_1,r_2,q_1,q_2,N_c; x_1)$	D_{12}^0, D_{21}^0	$\tau_{12}, \tau_{21},$ r_1, r_2, q_1,q_2, N_c	
Medvedev and Shapiro [73]	$D_{12} = L_D \frac{M_m}{M_1 M_2 T}\left(\frac{1}{x_1 M_2}\frac{\partial \ln\mu_2}{\partial c_2} + \frac{1}{x_2 M_1}\frac{\partial \ln\mu_1}{\partial c_1}\right),$ $L_D = G\overline{L}_{Tr}G^T, \quad \overline{L}_{Tr} = \frac{1}{2}\left(L_{Tr} + L_{Tr}^T\right),$ $L_{Tr} = \frac{1}{4}L_K L_T L_R. L_{K,ij} = \delta_{ij}\sqrt{\frac{8RT}{\pi M_j}},$ $L_{T,ij} = -f_{ij}, f = F^{-1}\ F_{ij} = \frac{\partial^2 S}{\partial c_i \partial c_j},$ $F_{i,3} = F_{3,i} = \frac{\partial^2 S}{\partial c_i \partial U}, F_{3,3} = \frac{\partial^2 S}{\partial U^2},$ $L_{R,ij} = \delta_{ij}Z - c_i\frac{\partial Z_i}{\partial c_i}, L_{R,i3} = -c_i\frac{\partial Z_i}{\partial U},$ $Z_i = \sqrt{\frac{M_i}{M_{mix}}}A\left(1 - B_1c_1 - B_2c_2 - \frac{B_{12}c_1c_2}{c_1+c_2}\right), (i,j = 1,2)$	A, B_1 B_2, B_{12}	$a_1, a_2,$ b_1, b_2	
	Group 3 (theories without adjustable nonspecific parameters)			
Yan *et al.* + Wilson [70]	$D_{12} = \left[x_2\left(\frac{\phi_{21}}{D_{12}^0} + \frac{\phi_{11}}{D_1^0}\right) + x_1\left(\frac{\phi_{12}}{D_{21}^0} + \frac{\phi_{22}}{D_2^0}\right)\right]^{-1}\Gamma;$ $\Gamma = \Gamma(\Lambda_{12},\Lambda_{21}; x_1)$	$D_{12}^0, D_{21}^0,$ D_1^0, D_2^0	$\Lambda_{12}, \Lambda_{21}$	
Yan *et al.* + NRTL [70]	$D_{12} = \left[x_2\left(\frac{\phi_{21}}{D_{12}^0} + \frac{\phi_{11}}{D_1^0}\right) + x_1\left(\frac{\phi_{12}}{D_{21}^0} + \frac{\phi_{22}}{D_2^0}\right)\right]^{-1}\Gamma;$ $\Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$	$D_{12}^0, D_{21}^0,$ D_1^0, D_2^0	$\tau_{12}, \tau_{21}, \bar a$	
Zhou *et al.* + NRTL [14]	$D_{12} = \left(D_{12}^0\right)^{\bar V\phi_{22}/\bar V_2}\left(D_{21}^0\right)^{\bar V\phi_{11}/\bar V_1}\Gamma; \Gamma = \Gamma(\tau_{12},\tau_{21},\bar a; x_1)$	D_{12}^0, D_{21}^0	$\tau_{12}, \tau_{21}, \bar a$	
Zhou *et al.* + Wilson [14]	$D_{12} = \left(D_{12}^0\right)^{\bar V_m\phi_{22}/\bar V_2}\left(D_{21}^0\right)^{\bar V_m\phi_{11}/\bar V_1}\Gamma; \Gamma = \Gamma(\Lambda_{12},\Lambda_{21}; x_1)$	D_{12}^0, D_{21}^0	$\Lambda_{12},\Lambda_{21}$	
Bosse and Bart + Wilson [16]	$D_{12} = \left(D_{12}^0\right)^{x_2}\left(D_{21}^0\right)^{x_1}e^{-\frac{G^E}{RT}}\Gamma; G^E = G^E(\Lambda_{12},\Lambda_{21}; x_1);$ $\Gamma = \Gamma(\Lambda_{12},\Lambda_{21}; x_1)$	D_{12}^0, D_{21}^0	$\Lambda_{12}, \Lambda_{21}$	
Modified Darken + Wilson [68,70]	$D_{12} = \left(D_{12}^0 x_2 + D_{21}^0 x_1\right)\Gamma; \Gamma = \Gamma(\Lambda_{12},\Lambda_{21}; x_1)$	D_{12}^0, D_{21}^0	$\Lambda_{12}, \Lambda_{21}$	

TABLE II. (*Continued.*)

Approach	Equation	Parameters of model		CDPC[a]
		Specific	Nonspecific	
Modified Darken[b] +NRTL (version 1)[c] [14,68]	$D_{12} = \left(D_{12}^0 x_2 + D_{21}^0 x_1\right)\Gamma;\ \Gamma = \Gamma(\tau_{12},\tau_{21},\bar{a};x_1)$	$D_{12}^0,\ D_{21}^0$	$\tau_{12},\ \tau_{21},\ \bar{a}$	
Vignes + Wilson [13,14]	$D_{12} = \left(D_{12}^0\right)^{x_2}\left(D_{21}^0\right)^{x_1}\Gamma;\ \Gamma = \Gamma(\Lambda_{12},\Lambda_{21};x_1)$	$D_{12}^0,\ D_{21}^0$	$\Lambda_{12},\ \Lambda_{21}$	

[a] Concentration-dependent physical characteristic. Such functions are determined experimentally without theoretical description in corresponding cited works.

[b] Original Darken equation is $D_{12} = (D_1^* x_2 + D_2^* x_1)\Gamma$. D_i^* is the tracer diffusivity of the ith component (it depends on the concentration of the solution), but it is often replaced by a value at infinite dilution (which leads to the modified Darken equation).

[c] The modified Darken + NRTL (version 1) model differs from the modified Darken + NRTL (version 2) model only by the way of extraction of interaction parameters a_{12}, a_{21} in the thermodynamic factor model. They may be regressed from mutual diffusion data (as in version 2) or obtained from other experimental data (as in version 1).

As follows from Table I, our theory produces good results. At the current stage of developing this model, the material parameters b_{12}, b_{13}, and b_{23} cannot be determined from independent data. But they can be obtained using diffusion characteristics at infinite dilution (see Appendix A). Thereby, there are no adjustable parameters in this model.

VII. CONCLUSIONS

The proposed approach can be applied to the description of mutual diffusion in nonideal liquid solutions. Based on the obtained results, we can conclude the following:

(a) Intermolecular interactions between mixture components can be taken into account as a formation of molecular complexes. Thus an initially binary (before mixing) solution has to be modeled as a multicomponent system (three or more components).

(b) For acetone-chloroform mixtures, the three-component model can be successfully used to explain the specifics of the coefficient of mutual diffusion.

(c) The concentrations of the complexes are needed to explain the nonlinearity of diffusion. These values can be obtained from other experiments (optical spectroscopy and NMR) or calculated from experimental mutual diffusion data.

(d) The proposed theory could be generalized for other multicomponent mixtures (two types of complexes or more).

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APPENDIX A

The case of the simplest complex (1:1) formation is considered below. It corresponds to $n = 1$, $m = 1$ in Eq. (19). Experimentally measured data for D_1^{expt} and their derivatives $\partial D_1^{\text{expt}}/\partial \varphi_1^{\text{tot}}$ at the limiting points[10] ($\varphi_1^{\text{tot}} = 0$, or $\varphi_2^{\text{tot}} = 0$) may be used for determination of the unknown parameters b_{12}, b_{13}, b_{23}, and K_φ. The following system of four equations can found from Eqs. (26) and (39):

$$B_1 \equiv D_{12}^{\text{expt}}\left(\varphi_1^{\text{tot}} = 0\right) = \frac{b_{12} + (K_\varphi \bar{\alpha}_1)\, b_{23}}{1 + (K_\varphi \bar{\alpha}_1)}, \tag{A1}$$

$$B_2 \equiv D_{12}^{\text{expt}}\left(\varphi_2^{\text{tot}} = 0\right) = \frac{b_{12} + (K_\varphi \bar{\alpha}_2)\, b_{13}}{1 + (K_\varphi \bar{\alpha}_2)}, \tag{A2}$$

$$B_3 \equiv \frac{dD_{12}^{\text{expt}}}{d\varphi_1^{\text{tot}}}\left(\varphi_1^{\text{tot}} = 0\right)$$

$$= +2\,(K_\varphi \bar{\alpha}_1)(1 + K_\varphi)\frac{(b_{12} - b_{23})}{(1 + (K_\varphi \bar{\alpha}_1))^3}, \tag{A3}$$

$$B_4 \equiv \frac{dD_{12}^{\text{expt}}}{d\varphi_1^{\text{tot}}}\left(\varphi_2^{\text{tot}} = 0\right)$$

$$= -2\,(K_\varphi \bar{\alpha}_2)(1 + K_\varphi)\frac{(b_{12} - b_{13})}{(1 + (K_\varphi \bar{\alpha}_2))^3}. \tag{A4}$$

The solution of Eqs. (A1) and (A2) allows the determination of all the necessary parameters: $b_{nm} = b_{nm}(B_1,B_2,B_3,B_4)$. Thus, in this case, the theory which uses a three-component model of the liquid solution does not have any adjustable parameters. The problem of calculation accuracy is still open, because a big step in concentration change (typical for experimental conditions) may produce big uncertainty of some coefficients (in particular, K_φ).

To improve the precision of the calculation, data from independent experiments[11] can be used, as it was demonstrated above for the case of acetone-chloroform solutions.

APPENDIX B

Table II represents some of the most widely used approaches for description of the concentration dependence of the mutual diffusion coefficient in binary liquid mixtures. Many of them require additional thermodynamic models for determination of excess Gibbs energy G^E and, thus, for determination of the thermodynamic factor Γ. These models are represented in Table III. Classification in Table II was made not only by the model of mutual diffusion used but also by

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[10] Note that the volume conservation law in Eqs. (10) and (24) should be kept.

[11] Constant K_φ can be obtained, for example, from NMR or optical experiments.

TABLE III. Some thermodynamic models of the solution.

Model	Excess Gibbs energy, G^E	Parameters
Wilson [74]	$\frac{G^E}{RT} = -\sum_{i=1}^{k} x_i \ln \sum_{j=1}^{k} x_j \Lambda_{ij},$	$\Lambda_{12}, \Lambda_{21}$
	$\Lambda_{ii} = \Lambda_{jj} = 1$	
NRTL [75]	$\frac{G^E}{RT} = \sum_{i=1}^{k} x_i \left(\frac{\sum_{j=1}^{k} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{k} G_{li} x_l} \right),$	$\tau_{12}, \tau_{21}, \bar{a}$
	$G_{ij} = \exp(-\bar{a}\tau_{ij})$	$\tau_{12}, \tau_{21}, \bar{a}$
UNIQUAC [76]	$\frac{G^E}{RT} = \sum_i \Big[x_i \ln \frac{\phi_i}{x_i}$ $- \frac{N_C}{2} x_i q_i \ln \frac{\phi_i}{\theta_i} - x_i q_i \ln \left(\sum_k \theta_j \tau_{ji} \right) \Big]$	$\tau_{12}, \tau_{21},$
	$\tau_{ii} = \tau_{jj} = 1, \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j} = \frac{x_i q_i}{q}$	$r_1, r_2, q_1,$
	$\phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j} = \frac{x_i r_i}{r}$	$q_2, N_C = 10$

the thermodynamic models used. Additionally, classification of the required parameters of the model was made. All parameters were divided in two parts: specific and nonspecific. Specific parameters of the model can be determined from diffusion experiments only. Nonspecific parameters may be determined from other available experiments. Some models need additional values of physical quantities which depend on solution concentration (e.g., viscosity of mixture); such types of quantities are aggregated in the CDPC column of Table II.

The thermodynamic factor Γ is connected with excess Gibbs energy in the following way:

$$\Gamma = 1 + \frac{x_1 x_2}{RT} \left(\frac{\partial^2 G^E}{\partial x_1^2} + \frac{\partial^2 G^E}{\partial x_2^2} - 2 \frac{\partial^2 G^E}{\partial x_1 \partial x_2} \right). \tag{B1}$$

Local composition models (Wilson, NRTL, UNIQUAC) are widely used for description of the thermodynamic factor in mutual diffusivity equations. These models do not have rigorous theoretical backgrounds and are semiempirical [71], but incorporation of more advanced thermodynamics models leads to significant complication of expressions for the description of mutual diffusion coefficients. Thermodynamic models, which are regarded in Table II, are represented in Table III. Parameters Λ_{12} and Λ_{21} (Wilson model) and τ_{12} and τ_{21} (NRTL and UNIQUAC models) represent interaction between the mixture components and are regressed from experimental data (for more details see Ref. [71]).

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