
**INTERDIFFUSION IN WATER SOLUTIONS
OF ETHYL ALCOHOL****V.V. OBUKHOVSKY, V.V. NIKONOVA**

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PACS 66.10.c, 66.30.My
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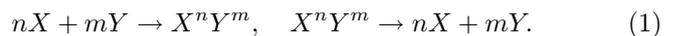
The interdiffusion in multicomponent liquids under influence of chemical reactions has been studied. A nonlinear modification of Fick's law of diffusion [8, 9] is used. The concentration dependence of the diffusion coefficient D_{eff} for solutions "ethyl alcohol + water" is analyzed. It has been shown that the creation of molecular complexes (alcohol hydrates) should be taken into account in order to explain the non-monotonic experimental dependence of D_{eff} on the alcohol concentration in solution (at 40 ÷ 60% of alcohol, the minimum of the coefficient of diffusion is realized).

As is well known, the thermodynamics of multicomponent mass transfer in liquids is described by nonlinear differential equations [1, 2]. Thus, the diffusion coefficients measured in the experiment are functions of mixture component concentrations¹. A specific feature of multicomponent solutions is the appearance of additional flows associated with the interdiffusion of different components besides the ordinary diffusion flows. If interactions between particles take place, such flows are nonlinear, as the transport of particles of some sort is accompanied by the transport of particles of other sorts. In the partial case of an interaction of the "excluded volume" type, a nonlinear mass transfer equation was derived (in the long-wave approximation) within the lattice gas model and in the phenomenological symmetry approach based on an effective Ginzburg-Landau Hamiltonian [3–7].

The same view of a nonlinear mixed flow was used in [8, 9] to describe the nonlinear diffusion kinetics in

multicomponent fluids. In this paper, we use a method developed in [8, 9] to describe the kinetic properties of solutions $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$. The results are compared with experiment [14].

It is known that the dissolution of one substance in another one is accompanied by the formation of molecular complexes arising due to the intermolecular interaction. In the frame of the posed problem, we now consider a mixture of two molecular substances X and Y in the liquid state. The interaction between molecules leads to the formation (with some probability) of complexes of the X^nY^m type (m and n are the numbers of structural units (e.g., molecules) of a certain type in the complex). In what follows, we will consider only the "formation-decay" reactions:



Within our model, this kind of a mixture consists of three components²: X , Y , and X^nY^m .

The process of mass transfer involves structural units (molecules) of pure substances and complexes (the result of chemical reactions). Note that the real solutions can contain molecular complexes of different compositions, and the consideration of a single complex X^nY^m is a certain simplification. Therefore, we will interpret the numbers n and m as the mean (effective) numbers for the corresponding structural units (molecules) in the complexes.

Chemical reactions (the formation of complexes or associations) result in a local imbalance (the concentrations of individual components are changed) and in the

¹ Further, we examine only the effects associated with the interdiffusion. The self-diffusion does not change the experimentally detected concentrations of components of solutions.

² Generally speaking, the components X and Y are not necessarily monomolecular. In most cases, alcohols have such structural forms of the liquid state as dimers, trimers, tetramers, etc.

appearance of nonlinear mixing flows. The mutual movement of various components occurs under the preservation of the total volume of a mixture [8, 9]. Due to this circumstance, we will work with partial volumes, rather than with concentrations. Within this approach, the diffusion is described by the equations of continuity [9, 10]

$$\partial M_i / \partial t + \text{div} \mathbf{j}_i = S_i, \quad (2)$$

$$\mathbf{j}_i = \sum_j d_{ij} [M_j \nabla M_i - M_i \nabla M_j]. \quad (3)$$

Here, $M_i \equiv M_i(\mathbf{r}, t)$ is the volume fraction of the substance “ i ” in a physically infinitely small volume, whose center is at a point \mathbf{r} in time t ; $\mathbf{j}_i \equiv \mathbf{j}_i(\mathbf{r}, t)$ are the flows characterized by the mutual attraction of particles; S_i are functions of the sources (sinks) which depend on the processes of creation (disappearance) of molecules of the substance i ; and d_{ij} are the coefficients of a symmetric tensor (“interdiffusion coefficients”) which can be considered as mass transfer characteristics, material parameters of a liquid solution.

The preservation conditions of the substance and the volume are determined by three integrals of motion (conservation laws):

$$\sum_i M_i = 1, \quad \sum_i \mathbf{j}_i = 0, \quad \sum_i S_i = 0. \quad (4)$$

In what follows, we neglect the shrinkage or swelling and consider the system temperature to be constant: $T_0 = \text{const}$. In view of (4), we have the relations

$$M_2 = 1 - M_1 - M_3, \quad \nabla M_2 = -\nabla M_1 - \nabla M_3 \quad (5)$$

that allow us to exclude M_2 from the relevant equations. Given (1), the source functions can be written as follows³:

$$\left. \begin{aligned} S_1 &= \beta_1 M_3 - \alpha_1 M_1^n M_2^m, \\ S_2 &= \beta_2 M_3 - \alpha_2 M_1^n M_2^m, \\ S_3 &= -(S_1 + S_2). \end{aligned} \right\} \quad (6)$$

In the process of diffusion, the molecules of substance X are transferred both individually and in complexes

$X^n Y^m$. In this case, the total (registered by devices) flows of substances “ X ” or “ Y ” (in the free or bound state) are defined as linear combinations

$$\mathbf{j}_1^{\text{total}} = \mathbf{j}_1 + \eta_1 \cdot \mathbf{j}_3, \quad \mathbf{j}_2^{\text{total}} = \mathbf{j}_2 + \eta_2 \cdot \mathbf{j}_3, \quad (7)$$

where $\eta_1 = n\Delta V_X / (n\Delta V_X + m\Delta V_Y)$ and $\eta_2 = m\Delta V_Y / (n\Delta V_X + m\Delta V_Y)$ are the ratios of molecular volumes of pure substances and complexes $X^n Y^m$. Hence, the relative volumes, which determine the total number of molecules of the substance (free and a part of any combinations), are as follows:

$$\begin{aligned} M_1^{\text{total}} &= M_1 + \eta_1 M_3, & \nabla M_2^{\text{total}} &= \nabla M_2 + \eta_2 \nabla M_3, \\ (\eta_1 + \eta_2) &= 1. \end{aligned} \quad (8)$$

Moreover,

$$M_1^{\text{total}} + M_2^{\text{total}} = 1. \quad (9)$$

Using (2), (8), and (9), it is easy to prove that the following continuity equation is satisfied (see Appendix B):

$$\frac{\partial M_n^{\text{total}}}{\partial t} + \text{div} \mathbf{j}_n^{\text{total}} = 0. \quad (10)$$

The last equation has a simple interpretation: at the mixing, the substances do not disappear, but simply change their states (the “free particles – bound particles” transition).

The lack of “sources” in relation (10) allows us to pass to the description of a general mass transfer characterized only the functions M_1^{total} and M_2^{total} . Since the formation rate of complexes⁴ is much higher than the characteristic speed of the diffusion ($d/\alpha \propto \varepsilon \ll 10^{-3}$ see, e.g., [13, 19, 20]), (10) can be averaged by the fast variable τ (scale τ_{int}) that characterizes the processes of intermolecular interaction (the complex formation and chemical processes). This procedure yields the equation that describes only the slow process of mass transfer (slow changing t' on the scale τ_{dif}). Clearly, $\tau_{\text{int}} \ll \tau_{\text{dif}}$.

The lack of sources in (10) means that M_1^{total} and M_2^{total} are the integrals of motion for fast processes (chemical reactions). In other words, M_1^{total} and M_2^{total} depend only on the “slow time” t' associated with the mass transfer. In this case, information about the fast (chemical) processes is implicitly included in $\mathbf{j}_n^{\text{total}}$ (7) through $M_n(t', \tau, \mathbf{r})$. The fact that M_1^{total} and M_2^{total} depend only on the “slow time”,

$$M_1(t', \tau, \mathbf{r}) + \eta_1 M_3(t', \tau, \mathbf{r}) \cong M_1^{\text{total}}(t', \mathbf{r}), \quad (11)$$

⁴ It is determined by the constants α and β .

³ The equations contain only partial volumes and the phenomenological constants of reactions α, β . Therefore, the structure of pure substances (monomolecules, dimers, trimers, etc.) is not relevant. In chemistry, n and m are called “orders of reaction” in reagents 1 and 2. It is noted that the orders of reactions almost never coincide with the stoichiometric coefficients (see [11, 12]). So n and m should not be necessarily integers, because they can be interpreted as the corresponding averages by group effects.

gives us the opportunity to average $\mathbf{j}_n^{\text{total}}$ over the “quick time” (see, e.g., [18]). Then we arrive at the system of mass-transfer equations with the “slow time” without additional sources or external fields:

$$\frac{\partial M_n^{\text{total}}}{\partial t'} + \text{div} \langle \mathbf{j}_n^{\text{total}} \rangle_\tau = 0. \quad (12)$$

We will assume that the chemical reactions are so fast that the system can locally come to an equilibrium during the time which much smaller than the characteristic mass-transfer (diffusion) time. Furthermore, we neglect the time correlations on a small time scale, which corresponds to the mean-field approximation. Thus, for $\langle \mathbf{j}_n^{\text{total}} \rangle_\tau$, we get

$$\begin{aligned} \langle \mathbf{j}_1^{\text{total}} \rangle_\tau &= [-d_{12} + q_0 \langle M_3 \rangle_\tau] \nabla \langle M_1 \rangle_\tau + \\ &+ [-\eta_1 d_{23} - q_0 M_1] \nabla \langle M_3 \rangle_\tau, \end{aligned} \quad (13)$$

where

$$q_0 = (d_{12} - d_{13}) + \eta_1 (d_{13} - d_{23}). \quad (14)$$

The averaging time τ is chosen with regard for the condition $\tau_{\text{int}} \ll \tau \ll \tau_{\text{diff}}$ (τ_{int} is the characteristic time of formation of intermolecular bonds (chemical reaction time) and τ_{diff} is the characteristic time of a diffusion displacement at a distance determined by the equipment resolution).

Considering that the liquid mixture is near the state of local equilibrium and averaging by the “quick time,” we obtain the following relation from (6) for the “slow time”:

$$\begin{aligned} \langle M_3(\mathbf{r}, t) \rangle_\tau &\approx \gamma [\langle M_1(\mathbf{r}, t) \rangle_\tau]^n [\langle M_2(\mathbf{r}, t) \rangle_\tau]^m = \\ &= \gamma [\langle M_1(\mathbf{r}, t) \rangle_\tau]^n \cdot [1 - \langle M_1(\mathbf{r}, t) \rangle_\tau - \langle M_3(\mathbf{r}, t) \rangle_\tau]^m, \end{aligned} \quad (15)$$

where $\gamma = \alpha/\beta$. This result together with (11) allow us to express $\langle M_n \rangle_\tau$ in terms of $M_1^{\text{total}}(\mathbf{r}, t)$ (or $M_2^{\text{total}}(\mathbf{r}, t)$). To reduce the recording, we introduce the notation $\langle M_n \rangle_\tau \equiv G_n(M_1^{\text{total}})$. As a result, the system of equations (10) becomes

$$\frac{\partial M_n^{\text{total}}}{\partial t'} + \text{div} [D_n^{\text{total}}(M_n^{\text{total}}) \nabla M_n^{\text{total}}] = 0, \quad (n = 1, 2), \quad (16)$$

where the function $D_n^{\text{total}}(M_n^{\text{total}})$ can be found in the explicit form within the given model of chemical reactions (sources S_n) and nonlinear flows (coefficients d_{nm}).

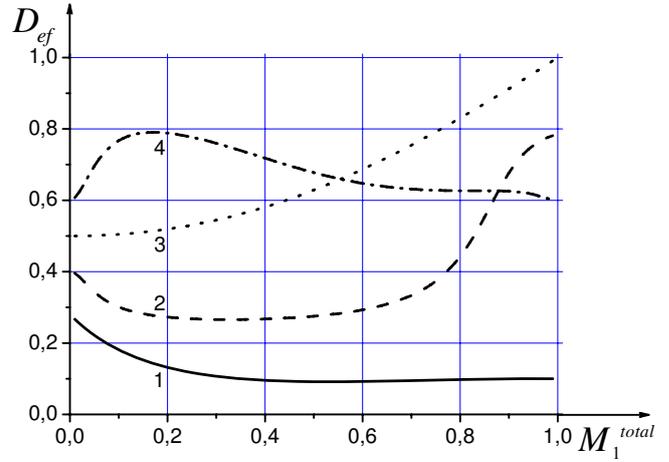


Fig. 1. Typical forms of the concentration dependence of the diffusion coefficient of binary mixtures in the model $\{X, X^n Y^m, Y\}$: 1 - $n = 1, m = 3, d_{12} = 0.1, d_{13} = 0.1, d_{23} = 1, \eta = 0.25, \gamma = 1$. 2 - $n = 3, m = 3, d_{12} = 0.4, d_{13} = 0.8, d_{23} = 0.2, \eta = 0.75, \gamma = 100$. 3 - $n = 1, m = 1, d_{12} = 0.5, d_{13} = 2.0, d_{23} = 0.5, \eta = 0.5, \gamma = 1$. 4 - $n = 3, m = 3, d_{12} = 0.6, d_{13} = 0.7, d_{23} = 1.1, \eta = 0.5, \gamma = 100$. (d_{nm} are components of the diffusion matrix)

For a triple system described by sources (6), we obtain the effective diffusion coefficient in the form suitable for further numerical calculations:

$$D_{\text{eff}}(M_1^{\text{total}}) = \frac{(d_{12} - q_{11} G_3) + \Phi_0 \cdot (\eta_1 d_{23} + q_{11} G_1)}{1 + \eta_1 \cdot \Phi_0}. \quad (17)$$

Here, we denote

$$\begin{aligned} \Phi_0 &\equiv \Phi_0(M_1^{\text{total}}) = \\ &= \left(n \frac{G_3}{G_1} - m \frac{G_3}{1 - G_1 - G_3} \right) \left(1 + m \frac{G_3}{1 - G_1 - G_3} \right)^{-1}. \end{aligned} \quad (18)$$

Once again, we note that the opportunity to pass to the consideration of a slow (diffusion) dynamics is related to the fact that the functions M_1^{total} and M_2^{total} are the integrals of motion for rapid (chemical) processes. In other words, these functions depend only on the “slow time”. Consequently, the prime at t will be dropped.

The specific features of the functional dependence $D_{\text{eff}}(M_1^{\text{total}})$ are determined by the parameters $\alpha_n, \beta_n, d_{nm}$, and ΔV_n . Typical forms of its concentration dependence are shown in Fig. 1. The behavior of $D_{\text{eff}}(M_1^{\text{total}})$ depends strongly on the type of complexes $X^n Y^m$. It is easy to verify that $D_{\text{eff}}(0) = d_{12}$ in the

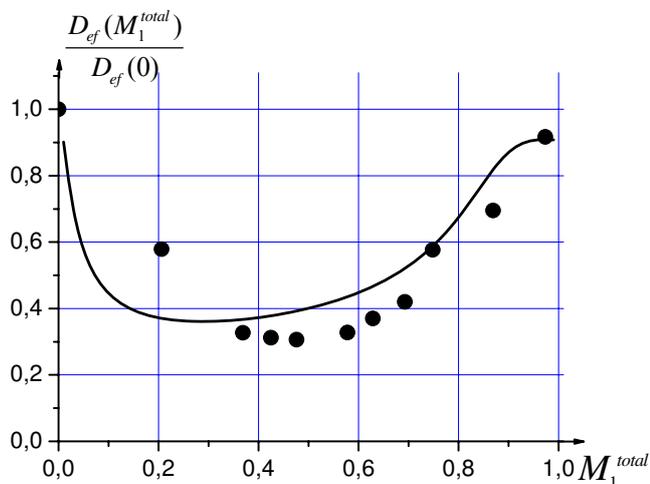


Fig. 2. Concentration dependence of relative diffusion coefficient for ethyl alcohol in water. Points – the experimental data [14], solid curve – is the theoretical calculation. In accordance with [14] effective diffusion coefficient for infinite diluted solution $D_{\text{eff}}(0) = 1.2 \times 10^{-9} \text{m}^2/\text{s}$

case where $n \geq 2, m = 1$ at extremely low concentrations ($M_1^{\text{total}} \rightarrow 0$), and the coefficient $D_{\text{eff}}(1) = d_{12}$ for $n = 1, m \geq 2$ as $M_1^{\text{total}} \rightarrow 1$. For certain relations between the parameters of the system, the function $D_{\text{eff}}(M)$ has extrema. Their relative value and position can be used to determine the qualitative characteristics of complexes.

The diffusion of ethanol in aqueous solutions has studied in many works [14–17]. Below, we will focus on work [14], in which the diffusion was studied at a stabilized temperature. As seen in Fig. 2, the alcohol diffusivity has a non-monotonous dependence with a deep minimum in the region $40 \div 60\%$ (to $\sim 30\%$ of the maximum value of D_{eff}).

As a result of numerical calculations, we determined the optimum values of parameters that characterize the processes of diffusion in the “ethyl alcohol–water” mixture: $n = 2.5, m = 1, d'_{12} = 1.00, d'_{13} = 0.90, d'_{23} = 0.05, \gamma = 65, \eta_1 = 0.78$ (the normalization of the diffusion matrix coefficients is performed by the value $D_{\text{eff}}(0)$, i.e., $d'_{nm} = d_{nm}/D_{\text{eff}}(0)$). Possessing the coefficient η_1 , we assume that alcohol⁵ behaves itself as a monomolecular substance (S_1). Then we obtain

$$\Delta V_W = \left(\frac{1 - \eta_1}{\eta_1} \right) \Delta V_S \cong 92(\text{\AA})^3. \quad (19)$$

⁵ We use the abbreviations $S \equiv \text{spiritus}, W \equiv \text{water}$. Lower indices are the numbers of relevant molecules.

The last value is closest to the volume occupied by a complex⁶ of three molecules of water $\Delta V_W^{(c)} = 3\Delta V_W^{(1)} = 90(\text{\AA})^3$. Therefore, we may assume that, in our case, $Y^1 = W_3$. We note that, according to [21, 22], water particles that move in the process of diffusion (“the diffusing water particles”) are the units from three (on the average) water molecules (trimers).

Thus, it turns out that the averaged (effective) hydrate ethanol complex has the form similar to $\langle S_3W_3 \rangle$. According to [14, 15], hydrates S_1W_3 and S_3W_1 play the major role at medium and high concentrations. The results of our calculations indicate that the “effective hydrate” structure belongs to the same type as the structure of real hydrates⁷.

Despite a substantial simplification of the model as compared with the real case (it is known that many different complexes of alcohol hydrates are present in an “water–alcohol” mixture [15, 23]), the main qualitative features of the measured and calculated effective diffusion coefficient coincide. We note that the numbers n and m describe, in our case, the corresponding averages of molecular units in a molecule of “effective” alcohol hydrate. For more accurate calculations, it should be taken the presence of different types of complexes in a mixture into account.

Recall once again that we focus on experiments⁸ where the total concentration of substance 1 is measured (in the free and chemically bound states). Figure 3 shows M_p , ($p = 1, 2, 3$) versus M_1^{total} at the above-mentioned values of the parameters of substances. As we can see, the number of hydrates (complexes of type X^nY^m – substance 3) has a maximum at the total alcohol concentration $\approx 70\%$ ⁹.

The coefficient γ which is the ratio of the rates of formation/disintegration of complexes can be obtained, generally speaking, from independent experiments [11–13].

Because the “ethanol–water” mixture is not binary, but triple (at the mixing, new compounds such as alcohol hydrates appear), the transport properties of the

⁶ The values of volumes are taken from [17].

⁷ Known type of alcohol hydrates is, e.g., S_1W_{12} , but most of hydrates are unstable formations. Therefore, we may assume that only stable hydrates and the “debris” of unstable hydrates take part in diffusion processes.

⁸ With the use, e.g., the method of evaporation, the method of optical absorption at frequencies corresponding to inner shells, etc.

⁹ Interestingly, the so-called “medical alcohol” (disinfectant with the highest effect) has the same part of alcohol.

system are determined by three coefficients d_{12} , d_{13} , and d_{23} . They can be considered as ordinary diffusion coefficients in the presence of only two (from three possible) components. In reality, it is not possible, may be, to realize these conditions, but a simple description (e.g., with a less number of parameters) is also impossible because of the complexity of the system under consideration.

Finally, we underline that the mass-transfer equation (10) does not depend on the specification of nonlinear flows (2) and source functions (6). Due to the inertia of devices, the characteristics registered by them are usually averaged. For example, the full flow of a substance n can be presented in the form

$$\langle \mathbf{j}_n^{\text{total}} \rangle_\tau \cong -D_n^{\text{eff}}(M_n^{\text{total}}) \nabla M_n^{\text{total}} \quad (20)$$

for any molecular liquids, in which the characteristic time of chemical reactions is small as compared with the diffusion shift time. Thus, the Fick's diffusion coefficient $D_n^{\text{eff}}(M_1^{\text{total}})$ can be introduced not in all the cases, but only if the mentioned condition is satisfied.

The authors thank S. Lukjanets for the indication of the need to study the continuity equation for M_n^{total} , fruitful discussions, and great help in the research.

APPENDIX A

In general, the non-linear dependence (3) is consistent with the equilibrium condition $M_i(\mathbf{r}, t \rightarrow \infty)/M_j(\mathbf{r}, t \rightarrow \infty) = \text{const}$ in a heterogeneous environment¹⁰. Indeed, the gradient

$$\nabla \left(\frac{M_i^\infty}{M_j^\infty} \right) = \frac{M_i^\infty \nabla M_j^\infty - M_j^\infty \nabla M_i^\infty}{(M_j^\infty)^2} = 0,$$

$$(M_n^\infty \equiv M_n(\mathbf{r}, t \rightarrow \infty)) \quad (A-1)$$

can turn into zero only if numerator (4) is zero. As we can see from (3), the flow stops: $\mathbf{j}_i(\mathbf{r}, t \rightarrow \infty) = 0$. In a partial case of homogeneous media, the equilibrium condition is simplified and passes to the normal form: $M_i(\mathbf{r}, t \rightarrow \infty) = \text{const}$.

But the case of two non-interacting molecular liquids is an exception. Indeed, when $M_3 = 0$, then the condition of volume conservation is

$$M_1 + M_2 = 1 \quad (A-2)$$

Hence, we have

$$M_2 = 1 - M_1, \quad \nabla M_2 = -\nabla M_1. \quad (A-3)$$

Substituting (A-2) to (3)

$$\mathbf{j}_1 = d_{12} [M_1(-\nabla M_1) - (1 - M_2)\nabla M_1] \quad (A-4)$$

and taking (A-3) into account, we get a standard diffusion equation in the Fick's form

$$\mathbf{j}_1 = -d_{12} \nabla M_1 \quad (A-5)$$

¹⁰ Especially demonstrative are the cases of inhomogeneous media with fillers.

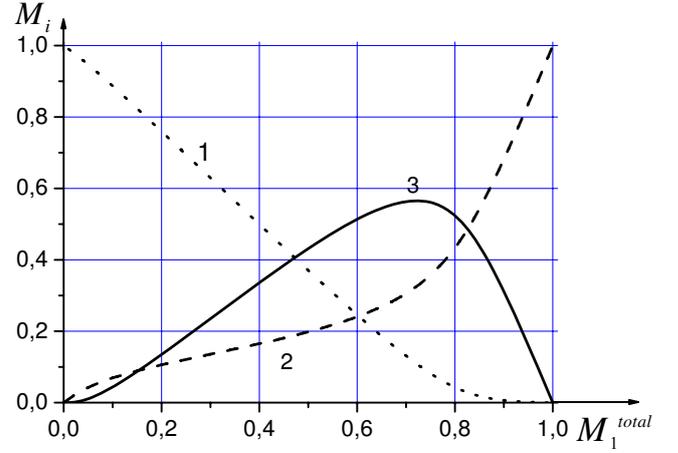


Fig. 3. Dependence of the renormalized concentrations M_1 , M_2 , and M_3 on M_1^{total} (i.e. the full content of a substance in the mixture). Numbers near curves indicate mixture components. The parameters are the same as those in Fig. 2

with the constant diffusivity d_{12} . If each molecule of substance 1 occupies a volume ΔV_1 , then (A-5) yields

$$\mathbf{J}_1 = -D_F^0 \nabla N_1, \quad (A-6)$$

where $\mathbf{J}_1 = \mathbf{j}_1/\Delta V_1$ is the number of particles (molecules) of type 1 which cross a unit surface for unit time, and $N_1 = M_1/\Delta V_1$ is the concentration of particles. As we can see, in the case of chemically inert components of a mixture, the coefficient d_{12} coincides with the usual Fick's diffusion coefficient $D_F^0 = d_{12}$.

APPENDIX B

Consider the reaction



Indices 1, 2, and 3 correspond, respectively, to substances A , B , and C . Let ΔV_i be the volume of molecule "i". For the "molecular complexes", we have

$$\Delta V_3 = n\Delta V_1 + m\Delta V_2. \quad (B-2)$$

Then the "share" of substance 1 in molecule 3 is

$$\eta_1 = \frac{n\Delta V_1}{n\Delta V_1 + m\Delta V_2}. \quad (B-3)$$

As for the derivative, we obtain

$$\frac{\partial M_1^{\text{tot}}}{\partial t} = \frac{\partial M_1}{\partial t} + \eta_1 \frac{\partial M_3}{\partial t} = (S_1 + \eta_1 S_3) - \text{div}(\mathbf{j}_1 + \eta_1 \mathbf{j}_3) \quad (B-4)$$

or

$$\frac{\partial M_1^{\text{tot}}}{\partial t} + \text{div} \mathbf{j}_1^{\text{tot}} = F_1, \quad F_1 = S_1 + \eta_1 S_3. \quad (B-5)$$

Reactions (B-1) are related to the following "source" functions:

$$S_1 = -n\Delta V_1 f_0, \quad S_2 = -m\Delta V_2 f_0, \quad S_3 = +\Delta V_3 f_0, \quad (B-6)$$

where

$$f_0 = \alpha_0 M_1^n M_2^m - \beta_0 M_3. \quad (B-7)$$

Here, α_0 and β_0 are proportional to the synthesis rate and the destruction rate of molecules C . Substituting, we get $F_1 = 0$. In this case, the equation of continuity does not depend on the “source functions” S_n .

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Received 12.02.09

ВЗАЄМОДИФУЗІЯ У ВОДНОМУ РОЗЧИНІ ЕТИЛОВОГО СПИРТУ

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Резюме

Розглянуто взаємодифузю у багатокомпонентних рідких системах в умовах протікання хімічних реакцій. Використано нелінійну модифікацію закону дифузії [8, 9]. Для суміші “етилловий спирт–вода” теоретично проаналізовано залежність коефіцієнта дифузії D_{eff} від вмісту спирту. Показано, що для пояснення експериментально зафіксованої немонотонної залежності D_{eff} від концентрації спирту у розчині (що має глибокий мінімум дифузії в області 40–60 об'ємних відсотків спирту) потрібно враховувати утворення у процесі розчинення молекулярних комплексів (гідратів спирту).