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MULTICOMPONENT DIFFUSION IN LIQUID MIXTURES

BY CHROMATOGRAPHIC AND NMR TECHNIQUES

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A method of calculating the matrix of the coefficients of multicomponent diffusion in liquid mixtures on the basis of experimental data obtained by chromatographic and pulsed nuclear magnetic resonance (NMR) techniques is devised.

Information about diffusion coefficients in liquid multicomponent mixtures is of theoretical and practical interest. Theoretical methods still do not provide accurate predictions of diffusion in liquids. Diffusion in gases and solids can be calculated fairly accurately, but in the case of liquids rigorous extimates are difficult, since the molecules in liquids are tightly packed and the dynamics of their interaction is multiparticulate.

The results of measurements of diffusion coefficients in liquid systems are sparse, since the widely used classical methods greatly increase the duration of the experiment. Attempts to devise express methods of investigating diffusion in mixtures have recently been made. They include chromatographic and pulsed NMR techniques, the theory and application of which in the investigation of diffusion have been confined so far only to binary gas and liquid mixtures, which are determined by one diffusion coefficient.

For multicomponent mixtures molecular mass transfer is written in the form

$$(\mathbf{J}) = - [D] \, \nabla (\mathbf{c}), \tag{1}$$

where [D] is the matrix of the multicomponent diffusion coefficients (MMDC).

It has been stressed in many recent papers [1, 2] that the values of the nondiagonal MMDC elements may attain values commensurable with the diagonal elements, and that their values depend strongly on the concentration and composition of the mixtures. Hence, there was a need to devise a simple, but accurate, method of obtaining the MMDC.

The chromatographic method consists in the creation of a concentration perturbation in a laminar flow by injection of a sample at the entrance to a long capillary tube followed

TABLE 1. Coefficients of Multicomponent Diffusion of Mixtures into Chloroform

Composition of mixture	$c_1^0 - c_2^0$, %	T, K	$D_{11} \cdot 10^9$, m²/sec	$D_{22} \cdot 10^9$, m²/sec	$D_{21} \cdot 10^9$, m²/sec	$D_{12} \cdot 10^9$, m²/sec
Methanol–acetone	44,2—55,8	299	2,74	2,72	0,21	0,19
Methanol–acetone	31—69	299	2,81	2,82	0,23	0,19
Methanol–acetone	66,8—33,2	299,5	2,60	2,61	0,29	0,32
Heptane–acetone	70,8—29,2	299,5	2,27	2,29	—0,09	—0,11
Heptane–acetone	43,8—56,2	299,5	2,32	2,30	0,08	0,09
Heptane–acetone	22,3—77,7	296	2,20	2,21	0,12	0,12
Hexane–acetone	28,4—81,6	296	2,70	2,70	0,02	0,02
Hexane–acetone	43,2—66,8	299,5	2,11	2,09	—0,16	0,17
Hexane–acetone	68,8—31,2	299,5	2,17	2,16	0,08	0,08
Chlorobenzene–acetone	69—31	299,5	0,81	1,62	1,54	0,85
Toluene–methanol	21—79	295	2,87	2,84	0,15	0,15
Toluene–methanol	39,2—60,8	295	3,20	3,24	0,23	0,25
Tolune–methanol	34,8—65,2	295	3,22	3,19	—0,13	—0,13
Benzene–acetone	36,8—63,2	295,5	1,71	1,71	0,04	0,05
Benzene–acetone	79,8—20,2	295,5	1,38	1,95	2,41	1,12
Benzene–methanol	49,4—50,6	296	1,6	1,27	3,02	0,67
Benzene–methanol	33,2—66,8	296	2,78	2,78	0,02	0,02
Benzene–toluene	55—45	295,5	2,79	2,78	—0,02	—0,02
Benzene–toluene	30,5—69,5	295,5	2,41	2,40	—0,15	—0,15
Benzene–toluene	65—35	295,5	2,91	2,96	0,29	0,29
Methanol–isopropanol	46,5—53,5	296	2,46	2,46	0,1	0,1
Methanol–isopropanol	22,1—77,9	296	2,44	2,44	—0,01	—0,01
Methanol–isopropanol	71,3—28,7	296	2,75	2,70	0,33	0,30
Benzene–carbon tetrachloride	26,6—73,4	294,5	2,24	2,19	0,36	0,40
Benzene–carbon tetrachloride	25,2—74,8	294,5	2,68	2,72	—0,19	—0,18
Benzene–carbon tetrachloride	42,6—57,4	294,5	2,73	2,73	0,24	0,19
Acetone–carbon tetrachloride	25—75	294,5	2,66	2,66	0,40	0,43
Acetone–carbon tetrachloride	66,7—33,3	294,5	3,11	3,11	0,05	0,06
Acetone–carbon tetrachloride	64—36	294,5	2,68	2,68	0,04	0,03

by determination of the distribution profile of the concentrations of all the components at its exit [3].

In the case of binary diffusion with sufficient diffusion time the concentration of injected substance has a Gaussian distribution near the entrance point, which moves with the mean flow velocity. The transition of the instantaneous parabolic concentration profile at the time of entry to a plane profile is effected by radial diffusion in a time that is negligibly small in comparison with the diffusion time [4].

The equations of diffusion in three-component liquid mixtures are written for the chromatographic method and are solved with appropriate boundary conditions. The distribution of concentrations of diffusing components in the moving flow is represented by a system of interdependent nonlinear equations, written in cylindrical coordinates with due regard to the parabolic profile of the flow velocities:

$$\frac{\partial c_i}{\partial \tau} + 2v \left(1 - \frac{r^2}{r_0^2} \right) \frac{\partial c_i}{\partial x} = \sum_j D_{ij} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_j}{\partial r} \right) + \frac{1}{r} \frac{\partial c_j}{\partial r} + \frac{\partial^2 c_j}{\partial x^2} \right], \quad i = 1, 2, \tag{2}$$

which is solved with the following initial and boundary conditions:

$$c_1 = \begin{cases} 0, & -\infty < x < -h, \quad +h < x < +\infty, \\ c_1^0, & -h < x < +h, \end{cases}$$

$$c_2 = \begin{cases} 0, & -\infty < x < -h, \quad +h < x < +\infty, \\ c_2^0, & -h < x < +h, \end{cases} \tag{3}$$

$$c_3 = \begin{cases} c_3^0, & -\infty < x < -h, \\ 0, & -h < x < +h, \end{cases} \quad \frac{\partial c}{\partial r}\bigg|_{r=r_0} = 0.$$
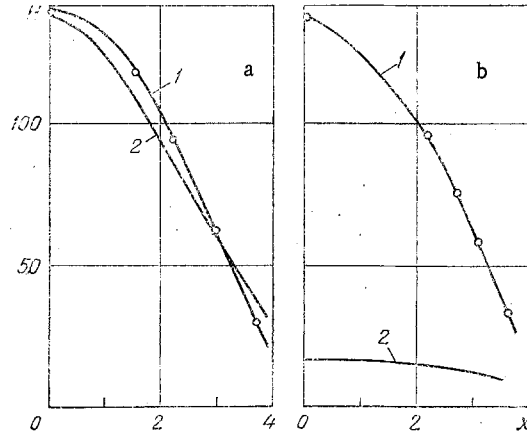
Fig. 1. Comparison of experimental and calculated profiles of concentrations of methanol—acetone—chloroform (a) and benzene—methanol—chloroform (b) mixtures, whose nondiagonal diffusion coefficients are: a) much smaller than the diagonal ones; b) comparable in value with the diagonal elements [1) experimental curve; 2) theoretical curve]. H and x, mm.

Since an accurate analytical solution of this system is impossible, we used Toor's linearization method [5], in which the field of concentrations c_j is replaced by a field of pseudoconcentrations ψ_k:

$$\psi_k = \sum_{j=1}^{n-1} S_{jk} c_j, \qquad (4)$$

and the system of equations (2) reduces to a form analogous to the equation of binary diffusion. The solution of these equations has the form [6]

$$\psi_k(x, \tau) = \frac{V}{fLr_0 \sqrt{4\pi D_a \tau}} \, \psi_i(x_0, \tau_0) \exp(-\Delta x^2 / 4 D_a \tau), \qquad (5)$$

where

$$D_a = D_{1,2}^0 \frac{L^2 r_0^2}{48 D_{1,2}^0 \tau}, \quad a = 1, 2. \qquad (6)$$

In gas mixtures, owing to the high diffusion rate, we can neglect the second term of Eq. (6). In liquids, on the other hand, since the diffusion rate is low, the first term of Eq. (6) is negligibly small. Reverse conversion of ψ_k fields to c_j fields gives the distribution of component concentrations in the flow

$$c_1 = \frac{1}{1 - S_{12}S_{21}} \frac{V}{L\pi \sqrt{\pi} \, r_0^3} \left\{ c_1^0 \left[\sqrt{12 D_1^0 \tau} \exp\left(-\frac{\Delta x^2 12 D_1^0 \tau}{r_0^2 L^2}\right) \right. \right.$$

$$\left. - S_{12}S_{21} \sqrt{12 D_2^0 \tau} \exp\left(-\frac{\Delta x^2 12 D_2^0 \tau}{r_0^2 L^2}\right) \right] + S_{21} c_2^0 \left[\sqrt{12 D_1^0 \tau} \right.$$

$$\left. \left. \times \exp\left(-\frac{\Delta x^2 12 D_2^0 \tau}{r_0^2 L^2}\right) - \sqrt{12 D_2^0 \tau} \exp\left(-\left(\frac{\Delta x^2 12 D_2^0 \tau}{r_0^2 L^2}\right)\right) \right] \right\}, \qquad (7)$$

$$c_2 = \frac{1}{1 - S_{12}S_{21}} \frac{V}{L\pi \sqrt{\pi} \, r_0^3} \left\{ c_2^0 \left[\sqrt{12 D_2^0 \tau} \exp\left(-\frac{\Delta x^2 12 D_2^0 \tau}{r_0^2 L^2}\right) \right. \right.$$

$$\left. - S_{12}S_{21} \sqrt{12 D_1^0 \tau} \exp\left(-\frac{\Delta x^2 12 D_1^0 \tau}{r_0^2 L^2}\right) \right] + S_{12} c_1^0 \left[\sqrt{12 D_2^0 \tau} \right.$$

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TABLE 2. Diffusion Coefficients D_{NMR} of C_7H_8—C_6ClH_5—C_6BrH_5 Mixture in Relation to Composition at $T = 300°K$ (X_1, mole fraction of C_7H_8; X_2, mole fraction of C_6ClH_5; X_3, mole fraction of C_6BrH_5; $\sigma_1 = 6.088$ Å, $\sigma_2 = 6.038$ Å, $\sigma_3 = 6.178$ Å, D_{11}, D_{22} from [10])

Composition X_1—X_2—X_3	$D_{NMR} \cdot 10^9$, m²/sec	$D_{11} \cdot 10^9$, m²/sec	$D_{22} \cdot 10^9$ m²/sec
0,25—0,50—0,25	1,88±0,09	1,85±0,07	1,80±0,08
0,26—0,03—0,70	1,66±0,08	1,57±0,09	1,61±0,11
0,70—0,15—0,15	2,12±0,11	2,13±0,10	2,06±0,11
0,15—0,70—0,15	1,86±0,09	1,85±0,11	1,84±0,11
0,45—0,25—0,30	1,96±0,10	2,01±0,11	1,89±0,11
0,18—0,28—0,54	1,71±0,09	1,77±0,11	1,52±0,11

$$\times \exp\left(-\frac{\Delta x^2 12 D_2^0 \tau}{r_0^2 L^2}\right) - \sqrt{12 D_1^0 \tau} \exp\left(-\frac{\Delta x^2 12 D_1^0 \tau}{r_0^2 L^2}\right)\bigg]\bigg\}, \tag{7}$$

where

$$D_{1,2}^0 = \frac{D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}}}{2}; \quad S_{12} = \frac{D_2^0 - D_{22}}{D_{12}};$$

$$S_{21} = \frac{D_1^0 - D_{11}}{D_{21}}.$$

The inverse problem — determination of the MMDC from the concentration profile — was solved on the basis of a straight line, i.e., on the basis of the experimental concentration profile. To determine the MMDC we compare the theoretical concentration distribution with the experimental chromatograms. The refractometer signal is proportional to the difference in refractive indices of the mixture and flow

$$H = B[(n_1 - n_3) c_1 + (n_2 - n_3) c_2]. \tag{8}$$

A program written in ALGOL was compiled for the solution of the system of equations. The solution was obtained on an M-222 computer. The experimental chromatograms were approximated by the least-squares method. To exclude the possible error of injection of the sample we determined the instrument constant B, which contains the volume of the injected sample as a factor. The error of the approximation was ~6%.

By the described method we obtained the coefficients of diffusion of the following liquid mixtures with different initial compositions and low concentrations of components into a flow of solvent: methanol—acetone, toluene—methanol, hexane—acetone, benzene—acetone, heptane—acetone, benzene—methanol, benzene—toluene, methanol—isopropanol, benzene—carbon tetrachloride, acetone—carbon tetrachloride, and chlorobenzene—acetone. As a solvent we used chloroform. The measurements were made in accordance with the requirements of the chromatographic method [7] at room temperature (295-299°K) and atmospheric pressure. The obtained coefficients of three-component diffusion are given in Table 1.

The diagonal MMDC elements have values of $2 \cdot 10^{-9}$-$3 \cdot 10^{-9}$ m²/sec and are always positive. The nondiagonal elements in the majority of the investigated mixtures lie in the range $0.01 \cdot 10^{-9}$-$0.1 \cdot 10^{-9}$ m²/sec. As already mentioned, there are mixtures for which the nondiagonal elements are of the same order as the diagonal elements — $2 \cdot 10^{-9}$ m²/sec. Such mixtures are benzene—acetone—chloroform, benzene—methanol—chloroform, and chlorobenzene—acetone—chloroform.

The calculated relative error in determination of all the MMDC elements was 8%.

A theoretical examination of diffusion in multicomponent liquid mixtures leads to the following explicit form of the MMDC for a three-component mixture [8]:

$$D_{11} = D_1 - X_1(D_1 - D_3), \quad D_{21} = X_2(D_1 - D_3), \quad D_{22} = D_2 - X_2(D_2 - D_3), \tag{9}$$
$$D_{12} = -X_1(D_2 - D_3).$$

TABLE 3. Diffusion Coefficients D_{NMR} of $CH_4O-C_4H_{10}O-C_3H_8O$ in Relation to Composition at $T = 303°K$ (X_1, mole fraction of CH_4O; X_2, mole fraction of $C_4H_{10}O$; X_3, mole fraction of C_3H_8O; $\sigma_1 = 3.69$ Å, $\sigma_2 = 5.49$ Å, $\sigma_3 = 4.71$ Å; D_{11}, D_{22} from [11])

Composition $X_1-X_2-X_3$	$D_{NMR} \cdot 10^9$, m²/sec	$D_{11} \cdot 10^9$, m²/sec	$D_{22} \cdot 10^9$, m²/sec
0,46—0,24—0,30	1,13±0,06	1,04±0,04	0,88±0,01
0,25—0,11—0,64	0,98±0,05	0,91±0,04	0,72±0,02
0,28—0,57—0,15	0,82±0,04	0,77±0,03	0,62±0,04
0,83—0,08—0,09	1,97±0,10	1,51±0,12	1,38±0,02

In correspondence with expressions (9) and taking into account that within 10 sec with a diffusion time of the order of 1000 sec the concentrations of the injected components become small in comparison with the carrier concentration, we have

$$D_{11} = D_1 = \mathcal{D}_{13} \quad D_{21} \rightarrow 0, \quad D_{22} = D_2 = \mathcal{D}_{23} \quad D_{12} \rightarrow 0. \tag{10}$$

The solution of the direct problem on the basis of the obtained MMDC, with the nondiagonal elements neglected in accordance with (10), leads to satisfactory agreement of the calculated concentration profile with the experimental profile in the case where the nondiagonal elements are much smaller than the main elements (Fig. 1a). When all the elements of the diffusion coefficient matrix have values of the same order, the disagreement of the profiles is pronounced (Fig. 1b).

In accordance with (9) the structure of the explicit form of the MMDC is such that it is determined in terms of partial diffusion coefficients, i.e., in terms of coefficients in a stationary frame of reference [8]. Hence, the most suitable method of investigating them is pulsed nuclear magnetic resonance (NMR), which provides a stationary system of coordinates.

To check the evaluation from (9) and the significance of the effect of the nondiagonal MMDC elements we measured several liquid mixtures by the NMR method on an incoherent pulse NMR spectrometer (spin–echo technique). The spectrometer working frequency was 17 MHz, and the field gradient was produced by Helmholtz coils. The error of the measurements was ∿5%.

According to the theory of the NMR method [9], the decay in amplitude of the transverse magnetization is determined by diffusion of field-labeled particles in an equilibrium thermodynamic system

$$A = \sum_{i=1}^{v} A_{0i} \exp \left[-\frac{2}{3} \gamma^2 G^2 D_i \tau'^3 \right] = A_0 \exp \left[-\frac{2}{3} \gamma^2 G^2 D_{NMR} \tau'^3 \right], \tag{11}$$

where $A_{0i} \sim X_i N_i$ is the initial amplitude of the echo of the i-th component; N_i is the number of resonating nuclei in the molecule of the i-th component; τ' is the time between the 90° and 180° pulses; D_i is the diffusion coefficient of field-"labeled" molecules of the i-th component. Hence, in correspondence with the definition of "partial" coefficient given in [8], the diffusion coefficient of field-labeled molecules of the i-th component in the NMR method and the partial coefficient are identical.

Knowing D_i, which in principle we find from relation (11), we can calculate the MMDC elements on the basis of NMR measurements from expressions (9).

The NMR measurements, however, showed that for most liquid mixtures, all the components of which contain resonating nuclei, we extract only one "effective" coefficient D_{NMR}, since the relation between $\ln(A/A_0)$ and G^2 is practically linear. The latter makes it difficult to obtain all the partial coefficients D_i and to calculate the MMDC elements.

Nevertheless, three-component mixtures with similar interaction potential parameters, according to [8], have close partial coefficients D_i, which, according to (9), leads to zero values of the nondiagonal elements $D_{12} = D_{21} = 0$. Then, from (9) and (11)

$$D_{11} = D_{22} = D_1 = D_2 = D_{NMR}. \tag{12}$$

Thus, in the case of liquid mixtures with close interaction potential parameters the spin-echo method is an express method of quantitative determination of the MMDC diagonal elements (Table 2).

In mixtures with very different force parameters inequality of the MMDC diagonal elements and differences between them and D_{NMR} are possible (Table 3). The latter can provide a basis for explanation of the reported disagreement of the results of NMR measurements with data obtained for particular mixtures by traditional methods.

Thus, on the basis of investigation of diffusion by chromatographic and NMR techniques we have shown that in the general case all the MMDC elements must be used for the correct description of the process.

NOTATION

t, time; B, instrument constant; c_i°, initial concentrations; c_i, component concentrations; H, instrument signal; $2h$, length of region occupied by injected sample; L, length of diffusion tube; n_i, refractive index of i-th component; r_o, radius of diffusion tube; τ, diffusion time; x, coordinate; V, volume of injected sample; X_i, mole fraction of i-th component; γ, gyromagnetic ratio of "resonating" nucleus; G, external magnetic field gradient; D_i, "partial" diffusion coefficient of i-th component; D_{ij}, elements of matrix of multicomponent diffusion coefficients; $\mathcal{D}_{ij}$, binary diffusion coefficients; D_{NMR}, diffusion coefficient measured by NMR method; ν, number of components in mixture; σ_i, interaction potential parameter of i-th component; f, cross-sectional area of diffusion tube; v, mean flow velocity; D_a, "effective" diffusion coefficient; D_1°, D_2°, diffusion coefficients in space of pseudoconcentrations ψ_k.

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