CALCULATION OF MOLECULAR DIFFUSION COEFFICIENTS
IN MULTICOMPONENT LIQUID MIXTURES

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A method is proposed for the calculation of practical diffusion coefficients in multicomponent liquid mixtures of hydrocarbons of the paraffin series. The proposed method is used to analyze the effect of nonideality of solution on diffusion in liquid mixtures.

Molecular transport of matter in multicomponent mixtures involves motive forces involving all components and depends essentially in liquid mixtures on the composition of the mixture and the thermodynamic parameters of the system which define its lack of ideality.

Isothermal multicomponent diffusion in accordance with the theory of irreversible processes [1, 5] and the principles of statistical physics [2, 6] is described by a system of phenomenological equations [7]

$$X_i = \sum_{j=1}^{n} F_{ij} C_j (U_i - U_j), \quad i = 1, 2, \ldots, n, \tag{1}$$

where

$$X_i = -\left(\frac{\partial \mu_i}{\partial l}\right)_{T,P}. \tag{2}$$

In practical calculations, the diffusion fluxes J_i are expressed as

$$(J) = -[D]\nabla(C). \tag{3}$$

The relationship between the practical diffusivity D_{ij} and F_{ij} is established by joint solution of Eqs. (1) and (3) for the components $i = 1, 2, \ldots, n-1$ since the X_i are related by the Gibbs–Duheim equation

$$\sum_{j}^{n} C_j X_j = 0, \tag{4}$$

and the fluxes J_i by the frame of reference [7].

In analogy with diffusion in an ideal gas mixture [8] considering that $\sum_{j}^{n} C_j = C_{mix}$ and $(x) = [\mu]\nabla(C)$, we obtain an expression for practical diffusivity in the appropriate frames of reference

$$[D]^{-1} = -[\mu]^{-1} \lceil \overline{C} \rceil^{-1} \{\lceil \overline{U} \rceil + \lceil \overline{F_n} \rceil C_{mix} - \lceil \overline{C} \rceil [B]\}, \tag{5}$$

where $\mu_{ij} = -\partial\mu_i/\partial C_j$, $i, j = 1, 2, \ldots, n-1$; $B_{ij} = F_{ij} - F_{in}$ for the mean-mole frame of reference; $B_{ij} = F_{ij} - F_{in}\overline{V}_j/\overline{V}_n$; for the mean-volume frame of reference, and $U_{ij} = (F_{ij} - F_{in})C_i$.

We designate

$$[K] = \lceil \overline{C} \rceil^{-1} \{\lceil \overline{U} \rceil + \lceil \overline{F_n} \rceil C_{mix} - \lceil \overline{C} \rceil [B]\}, \tag{6}$$

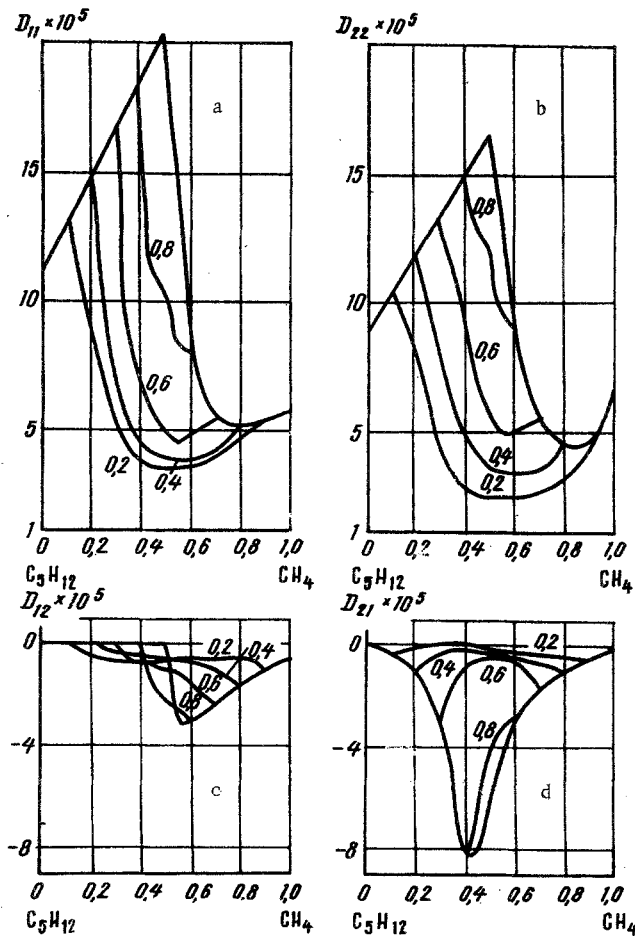where the diagonal elements for the mean-mole and mean-volume frames of reference are respectively

Fig.1. Dependence of practical diffusivity $(\text{cm}^2 \cdot \text{sec}^{-1})$ on the composition in the mean-volume frame of reference. Here, and in Figs.2 and 3, numbers on the curves denote the constant propane component. a, b) Fundamental practical diffusivity; c, d) cross-practical diffusivity.

$$K_{ii}^{\text{mol}} = \sum_{\substack{M=1 \\ M \neq i}}^{n} F_{iM} \frac{C_M}{C_i} + F_{in} \left(\frac{C_n}{C_i} + 1 \right), \tag{7}$$

$$K_{ii}^{\text{vol}} = \sum_{\substack{M=1 \\ M \neq i}}^{n} F_{iM} \frac{C_M}{C_i} + F_{in} \left(\frac{C_n}{C_i} + \frac{\bar{V}_i}{\bar{V}_n} \right), \tag{8}$$

and the nondiagonal elements are

$$K_{ij}^{\text{mol}} = (F_{in} - F_{ij}), \tag{9}$$

$$K_{ij}^{\text{vol}} = \left(F_{in} \frac{\bar{V}_j}{\bar{V}_n} - F_{ij} \right). \tag{10}$$

Theoretical expressions for the F_{ij} in a binary mixture were obtained on the basis of the modified theory of absolute rates [9]

$$F_{ij} = \frac{hN}{C_{\text{mix}} a^2} \exp \Delta G_{ij}/RT, \quad i \neq j. \tag{11}$$

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For linear dependence of activation energy on molar composition,

$$\Delta \dot{G}_{ij} = \sum_{k=1}^{n} N_k \lim_{N_k \to 1} \Delta G_{ij} \tag{12}$$

an expression was obtained for the F_{ij} in a multicomponent mixture in terms of D_{ij}^0 and α_{ij}:

$$F_{ij} = \frac{RT}{C_{\text{mix}}} \left[\prod_{k \neq i,j}^{n} (\alpha_{ij}^k)^{N_k} \right]^{-1} \left[(D_{ij}^0)^{N_j} (D_{ji}^0)^{N_i} \prod_{k \neq i,j}^{n} (D_{jk}^0)^{N_k} \right]^{-1}. \tag{13}$$

The symmetry condition for the F_{ij} made it possible to obtain an equation for independent determination of the α_{ij} [10]:

$$\alpha_{ij}^k = \frac{V_k \left(1 - \dfrac{D_{jk}^0}{D_{ik}^0} \right)}{(V_i - V_j)}. \tag{14}$$

Under the conditions of interest to us, diffusion occurs at boiling and therefore the Chueh—Prausnitz correlation [3] was used for the determination of molar and partial molar volumes.

For a constant total concentration of the mixture, the equation for the elements of the matrix $[\mu]$ are of the form

$$\mu_{ij} = -\frac{\partial \mu_i}{\partial C_j} = \frac{RT}{C_{\text{mix}}} \left[\frac{\partial \ln \gamma_i}{\partial N_j} + \frac{\delta_{ij}}{N_j} \right], \quad i, j = 1, 2, \ldots, n-1. \tag{15}$$

The quantity $\partial \ln \gamma_i / \partial N_j$ for hydrocarbons of the paraffin series can be calculated with the help of the Chao—Seader correlation [4].
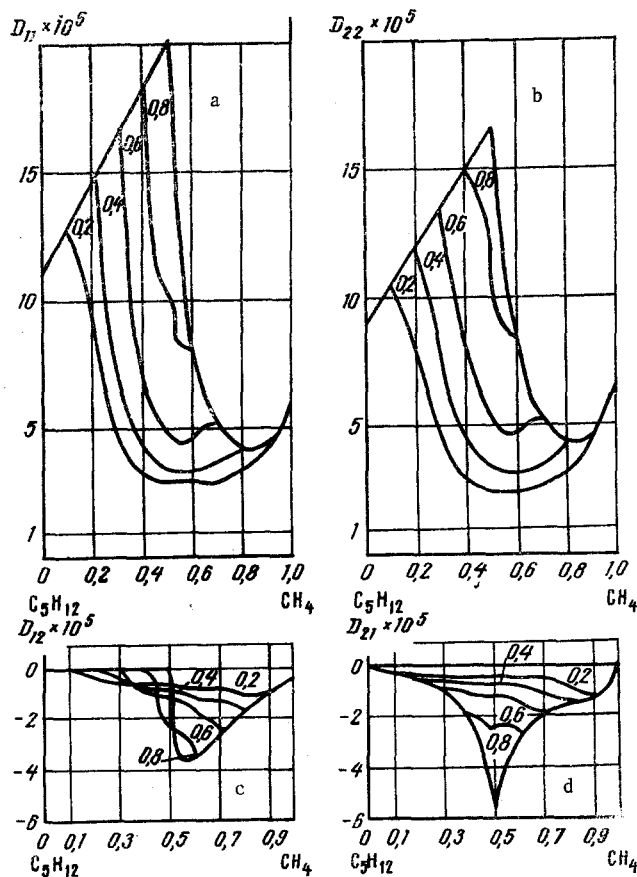

Fig. 2. Dependence of practical diffusivity (cm$^2 \cdot$ sec^{-1}) on composition in a mean-mole frame of reference.
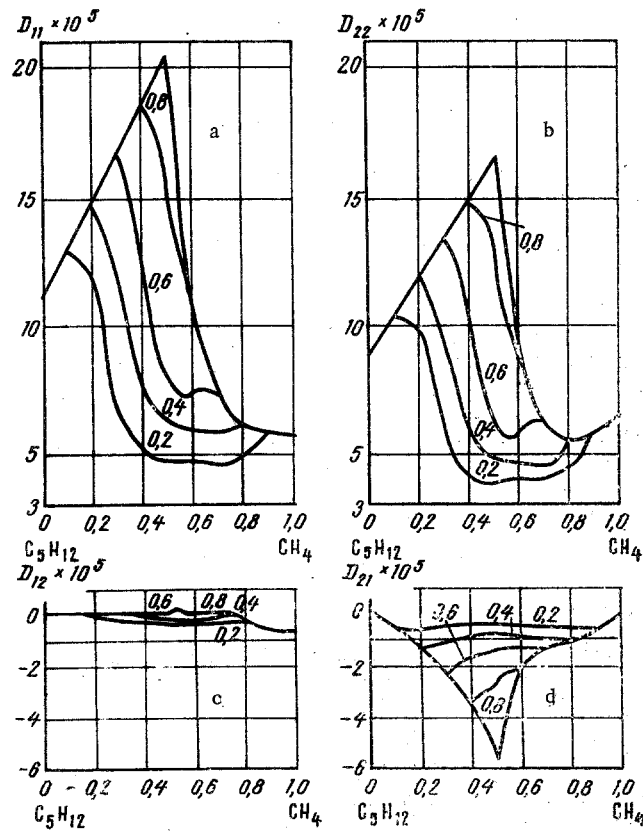
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Fig.3. Dependence of practical diffusivity $(cm^2 \cdot sec^{-1})$ on the composition in the mean-mole frame of reference without allowance for nonideality of solution.

Thus Eqs.(5) and (13)–(15) provide a basis for an algorithm for calculating practical diffusivity.

In studies of multicomponent diffusion, it is of interest to discover the effect of nonideality of solution on practical diffusivity, which is characterized by the extent to which the quantities α_{ij} differ from unity. Expressions for practical diffusivity obtained from the Stefan–Maxwell equation for a mixture of ideal gases [11] can be used to evaluate the effect of nonideality.

For a three-component mixture, these expressions are

$$D_{ii} = \frac{\mathcal{D}_{ik}\left[(1-N_i)\mathcal{D}_{ij} + N_i\mathcal{D}_{ik}\right]}{N_i\mathcal{D}_{jk} + N_j\mathcal{D}_{ik} + N_k\mathcal{D}_{ij}},$$

$$D_{ij} = \frac{N_i\mathcal{D}_{jk}(\mathcal{D}_{ik} - \mathcal{D}_{ij})}{N_i\mathcal{D}_{jk} + N_j\mathcal{D}_{ik} + N_k\mathcal{D}_{ij}}, \tag{16}$$

$$i,\ j = 1,\ 2,\quad i \neq j,\quad k = 3,$$

where

$$\mathcal{D}_{ij} = \frac{N_j}{N_i + N_j} D_{ij}^0 + \frac{N_i}{N_i + N_j} D_{ji}^0, \tag{17}$$

$$\mathcal{D}_{ij} = \mathcal{D}_{ji}.$$

In a three-component mixture where the amount of one component is vanishingly small, the following limiting conditions can be obtained from an analysis of Eq.(3) [12]:

$$\lim_{c_j \to 0} D_{ii} = \mathcal{D}_{ik} = \mathcal{D}_{ki}, \quad \lim_{c_i,c_k \to 0} D_{ii} = D_{ij}^0,$$

$$\lim_{c_j,c_k \to 0} D_{ij} = (D_{ki}^0 - D_{ji}^0)\frac{\bar{V}_j}{\bar{V}_i}, \quad \lim_{c_j \to 0} D_{ij} = 0, \tag{18}$$

$$i,\ j = 1,\ 2,\quad i \neq j,\quad k = 3,$$

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Calculations of practical diffusivity in three-component mixtures were made on the basis of the proposed algorithm. Limitation of the number of components to three derives from the ease of graphical representation of practical diffusivity as a function of mixture composition. Calculations were made by means of a specially prepared computer program for the mixtures methane—ethane—propane, methane—propane—pentane, methane—ethane—pentane, and methane—butane—pentane at a pressure of $34.3 \cdot 10^5$ N/m^2 and saturation temperature of the liquid. Diffusion flux was determined with respect to mean-mole and mean-volume frames of reference.

The present lack of experimental studies of diffusion in mixtures of condensed hydrocarbons of the paraffin series offers no opportunity to compare the calculated results with experimental data; however, the correctness of the calculations was indirectly checked by the satisfaction of the following thermodynamic conditions:

$$F_{ij} = F_{ji}, \quad \mu_{ij} = \mu_{ji},$$

the latter equality being maintained only for constant C_{mix}.

The calculated results for practical diffusivity in a methane—propane—pentane mixture are given in Figs. 1-3; the effect of nonideality of solution on diffusion is equally characteristic for all the mixtures considered.

A two-dimensional representation of the three-dimensional dependence of practical diffusivity on composition [13] is given in Figs. 1-3. The lines in the plots represent the dependence of practical diffusivity on the relative abundance of two components for a constant content of the third component. In our case, the propane content was assumed constant and its value in the mixture is given by the numbers on the curves.

It is clear from the curves that cross-practical diffusivities are comparable with the fundamental diffusivities in the neighborhood of critical parameters of the mixture (Fig. 1a, d). This is evidence of significant superposition effects during diffusion in condensed hydrocarbon systems.

Comparison of Figs. 2c and 3c makes it possible to analyze the effect of nonideality of solution on diffusion.

In the study of practical diffusivity dependence on mixture composition (Figs. 1-3), it was established that the effect of nonideality of solution appears in a marked change in the nature of the cross-practical diffusivity dependence on composition and in the values of fundamental and cross-practical diffusivities as a function of composition. It should be noted that the most important effect of nonideality appears when the mean-volume frame of reference is used (Fig. 1d).

The analysis shows that the calculation of practical diffusivity in condensed mixtures of hydrocarbons of the paraffin series should take into account nonideality of solution.

NOTATION

D_{11}, D_{22}	are the fundamental practical diffusivities;
D_{12}, D_{21}	are the cross-practical diffusivities;
D_{ij}^0	is the binary diffusivity in infinitely diluted solution;
$\mathfrak{D}_{ij}$	is the binary diffusivity;
μ_i	is the chemical potential of i-th component;
l	is the length of diffusion path;
F_{ij}	is the friction coefficient satisfying Eqs. (1), (11), and (13);
C_i	is the molar concentration of i-th component in mixture;
C_{mix}	is the concentration of mixture;
U_i	is the mean absolute velocity vector of i-th component molecules;
J_i	is the molar diffusional flux of i-th component;
$\overline{V}_i$	is the partial molar volume of the i-th component;
h	is Planck's constant;
N	is Avogadro's number;
a	is the distance between two equilibrium positions;
ΔG_{ij}	is the total activation energy of the diffusion process;
R	is the gas constant;
T	is the absolute temperature;

N_i is the mole fraction of the i-th component in the mixture;

V_i is the mole volume of the i-th component;

$\overline{\alpha}_{ij}$ is the thermodynamic factor satisfying Eq.(13);

γ_i is the activity factor of the i-th component;

δ_{ij} is the Kronecker delta.

Subscripts

1   denotes methane;

2   denotes pentane;

3   denotes propane.

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