Nonlinear diffusion and intermolecular interactions: experimental verification

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Peculiarities of diffusion in the mixture of molecular liquids are connected with intermolecular interactions. Theory of nonlinear diffusion takes into account the effect of molecular complexes generation in solutions. Process of diffusion mass-transfer is described by the following system of equations:

$$\frac{\partial U_n}{\partial t} + \operatorname{div} \vec{J}_n = S_n, \qquad \vec{J}_n = \sum_m d(m,n)[U_n \nabla U_m - U_m \nabla U_n],$$

$$\sum_n U_n = 0, \qquad \sum_n \vec{J}_n = 0, \qquad \sum_n S_n = 0.$$

Here U_n is a relative volume of n-th component; S_n – source functions (determined by interactions between molecules in the solution).

Under some conditions (matter-transfer is slow, but generation of the complex is fast), Fick's law of diffusion takes place. However, the coefficients of diffusion become dependent on the component concentrations. For example, if two liquids are mixed, then total flow of the 1st component is: $\vec{J}_1^{tot} = -D_1^{ef}(U_1^{tot}) \cdot \nabla U_1^{tot}$ (here $U_1^{tot} = U_1 + \eta_{13} U_3$, where U_3 – relative volume of chemical complex, η_{13} – share of 1st component in complex "3"). It was shown: if the dependence of the effective diffusion coefficient $D_1^{ef}(N_1)$ on concentration N_1 was found then the concentration of molecular complexes N_3 in the solution can be calculated.

Several binary mixtures ($[A] + [B]$) were investigated experimentally: acetone-chloroform, benzene-cyclohexane and methyl alcohol-water. For mixtures $[A] \equiv 1, [B] \equiv 2$ the concentration dependence $N_3(N_1)$ of molecular complexes $[AB] \equiv 3$ was found in two independent ways: a) from diffusion measurements, and b) from Raman spectra of solutions. Both types of results coincide with satisfactory accuracy.

1. V.V. Obukhovsky, V.V. Nikonova. Ukr. J. Phys., v. 55, No. 8, pp. 891–896, 2010.