Nonlinear diffusion and intermolecular interactions: experimental verification

V. Obukhovsky, O. Ilchenko, V. Nikonova, A. Kutsyk
National Taras Shevchenko University of Kyiv, Faculty of Radiophysics, 64 Volodymirskira Str., 01601 Kyiv, Ukraine, E-mail: vobukhovsky@yandex.ru

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:

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

$$\sum_n U_n = 0, \quad \sum_n \bar{J}_n = 0, \quad \sum_n S_n = 0.$$

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 1\textsuperscript{st} component is:

$$\bar{J}_1^{\text{tot}} = -D_1^e(N_1) \cdot \nabla U_1^{\text{tot}} \quad \text{(here} \quad U_1^{\text{tot}} = U_1 + \eta_{13} U_3, \quad \text{where} \quad U_3 - \text{relative volume of chemical complex,} \quad \eta_{13} - \text{share of 1}\textsuperscript{st} \text{component in complex “3”)}.$$

It was shown: if the dependence of the effective diffusion coefficient $D_1^e(N_1)$ 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] ≡ 1, [B] ≡ 2 the concentration dependence $N_3(N_1)$ of molecular complexes [AB] ≡ 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.