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Figure 1

Figure 1: Figure 1

Abstract

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PHYSICAL CHEMISTRY

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SCATTERING ASYMMETRY AND THE DEVELOPMENT OF FLUCTUATIONS IN NON-STRATIFYING SOLUTIONS

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The phenomenon of critical opalescence in liquid mixtures is well known. The cause of the strong optical inhomogeneity manifested in opalescence is the extremely intense development of concentration fluctuations near the stratification temperature T_k. The theory of critical opalescence developed by Debye (1) predicts, in this case, the appearance of angular asymmetry of opalescence. Angular scattering asymmetry has indeed been observed near T_k, both in mixtures of low-molecular liquids (2) and in polymer solutions (3, 4).

Comparatively recently it was established that, on the concentration and temperature curves of the scattering intensity of certain non-stratifying low-molecular liquid mixtures, sharp maxima occur (5–7). Thermodynamic consideration shows that such solutions are at the limit of stability (6, 7). This gives grounds for considering that the maxima on the scattering curves of such mixtures are caused by the intense development of concentration fluctuations in the corresponding region of compositions and temperatures. An important question is whether the level of fluctuation development in non-stratifying systems reaches the level of fluctuations existing in stratifying systems near T_k. If so, then in non-stratifying solutions, in the region of concentrations and temperatures corresponding to the scattering maximum, measurable scattering asymmetry should also be observed. In an attempt to detect it, we chose the system β-picoline—water, in which, according to the data of work (7), the scattering intensity has a particularly sharp maximum at a picoline concentration of 0.06 mole and a temperature $\approx 70°$.

Fig. 1. Dependence of the scattering intensity $I_{90°}$ of a 0.06 M solution of β-picoline in water (in relative units; solid curve) and of the scattering asymmetry $z = I_{45°}/I_{135°}$ (dashed curve) on temperature.

Figure 2

Figure 2: Figure 2

Fig. 2. Dependence of the scattering asymmetry z of a solution of β-picoline in water (0.06 M) on temperature near the scattering maximum (different points denote different series of measurements).

Measurements were carried out on a photoelectric nephelometer $^{(8)}$ with a cuvette and thermostat described in $^{(9)}$. The thermostat was supplemented with a platinum resistance thermometer connected into a sensitive bridge, which made it possible to measure the temperature of the solution with an accuracy of up to 0.003°. The temperature stability was ±0.003°.

Figure 1 presents the temperature dependence of the scattering intensity I_{90° of a 0.06 M solution of β-picoline in water and the asymmetry of its scattering $z = I_{45^\circ}/I_{135^\circ}$. At a temperature of 69.48°, corresponding to the maximum of the I_{90° curve, there is a sharp spike in the scattering asymmetry, which is equal to unity at all other temperatures. The dependence of z on T is shown in Fig. 2 on a larger scale. The asymmetry z differs from 1 in a narrow interval $\Delta T \simeq 0.3^\circ$ and has a maximum value of 1.5. For comparison, we note that in $^{(2)}$, for the phase-separating system carbon tetrachloride—perfluoromethylcyclohexane, an asymmetry $z = 1.56$ corresponded to a temperature 0.15° away from the phase-separation point T_k. A study of the character of the angular dependence of the scattering intensity I_θ in the temperature region corresponding to the maxima of the curves in Figs. 1 and 2 reveals a rectilinear dependence of the quantity I_θ^{-1} on $\sin^2\theta/2$ (θ is the scattering angle)—Fig. 3.

Fig. 3. Dependence of the quantity I_{90°/I_θ on $\sin^2\theta/2$ at temperature T near the maximum of the curve in Fig. 2.

A theory relating scattering asymmetry to parameters characterizing the degree of development of fluctuations in the system (as has been done for phase-separating solutions $^{(1)}$) has not yet been created for non-phase-separating mixtures. One may, however, suppose that the asymmetry z corresponding to a given level of fluctuations (for example, to the mean correlation length between fluctuations $^{(1)}$) has, in both cases, the same order of magnitude. In that case it may be considered established that there exist non-phase-separating solutions in which the development of concentration fluctuations reaches (at a certain composition and temperature) a level corresponding to phase-separating systems that are at a distance $\Delta T \approx 0.15^\circ$ from the critical phase-separation temperature.

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