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HEAT-CAPACITY ANOMALY IN A WIDE VICINITY OF THE CRITICAL POINT OF THE TRIETHYLAMINE–WATER PHASE TRANSITION

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The behavior of the isobaric heat capacity in the triethylamine–water binary system has been investigated experimentally by the adiabatic calorimetry method. The possible physical models of the observed effects are discussed.

Investigation of the behavior of liquid demixing systems in the metastable region and determination of its boundaries are needed for understanding the nature of the critical phenomena and developing a modern theory of phase transitions. The difficulty of such investigations is connected with the wide variety of concrete conditions under which the processes proceed in solutions and the diversity of critical phenomena in them. Despite the development of the experimental basis and theory, some questions connected with the structural transient states in liquid systems remain open. And the nature of the phase transitions in systems with a weak disorder or localized impurities (LI) is still a subject of intensive investigations. This is evidenced by the recent reviews [1–4], where the macroscopic effects of disorder that are always present in real systems are considered. Investigations of the influence of LIs on the universal properties of the critical behavior of substances are of practical importance and are also of interest for the development of basic science. It is in the range of temperatures close to the critical one that even a negligible quantity of impurities can strongly affect the properties of a substance compared to a perfect system. The presence of impurities leads to the appearance of microinhomogeneities responsible for the appearance of phases that are thermodynamically advantageous only in a limited temperature range, usually covering the interval between the critical temperatures of a perfect and a disordered system. In liquid systems, a weak disorder can result from the formation of compact regions with a higher concentration of liquid molecules surrounded by regions with a low concentration. Under definite conditions, e.g., at phase transitions, the LIs begin to interact with concentration fluctuations. They can lead to limited sizes of fluctuations, markedly changing the critical behavior of the system. Despite the numerous investigations of the phase transitions in soft systems, the issues connected with the interactions of LIs with concentration fluctuations or collective order parameters are still not clearly understood. In many biological systems and process liquids, membranes, colloids, and polymer solutions in which molecular complexes are formed, dissolution occurs with a temperature decrease, i.e., they have a lower critical dissolution point. Therefore, in the present paper we focus on the investigation of the influence of LIs on the behavior of the heat capacity of the binary triethylamine–water demixing liquid. As is known, in this system complexes with a hydrogen bond are formed, and segregation into two phases occurs not under cooling but under heating. This is due to the fact that the Brownian mixing intensity and the entropy effects differently depend on temperature. The domination of one effect over another determines the critical behavior of the system.

Experimental Results and Discussion. In the experiments, chemically pure substances were used. Subsequently, purity was achieved by multiple distillation.

Measurements of the isobaric heat capacity were made on the known UNTO low-temperature reference thermophysical facility (heat-capacity measurement error 0.4%). The facility is described in detail in [5].

The investigations have shown that the binary triethylamine–water solution has a number of specific features (Figs. 1, 2). The critical concentration of the solution is very difficult to determine because of the small change in the phase-transition temperature in the range of concentrations from 20 to 50% of weight fractions of triethylamine (Fig.

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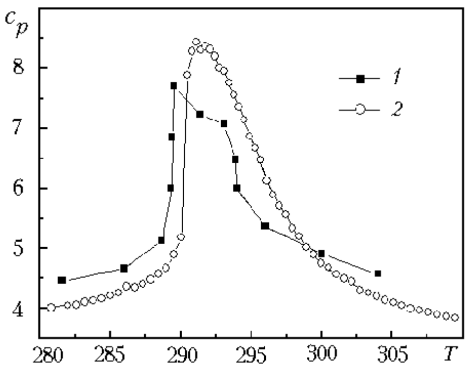

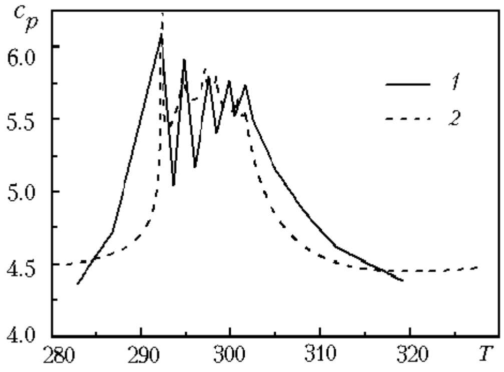

Fig. 1. Heat capacity of the triethylamine–water system at different concentrations: 1) $X = 0.2$; 2) 0.34%. c_p, J/(g·K); T, K.

Fig. 2. Oscillations of the heat capacity of the triethylamine–water system: 1) experiment ($X = 0.4\%$); 2) theoretical curve. c_p, J/(g·K); T, K.

3). To determine the critical parameters, we took measurements of the temperature dependence of the heat capacity of solutions at various concentrations of triethylamine. As is seen from Fig. 1, the jumps of the heat capacity for different concentrations have a different amplitude and peak width. It is known that as the critical point is approached, the jump amplitude of the heat capacity increases and the peak narrows. Therefore, the critical values were found for the concentration $C_{\text{cr}} = 0.34$ ppm and the temperature $T_{\text{cr}} = 290.23$ K in the triethylamine–water system.

As mentioned above, the temperature interval of the phase transition increases with departure from the critical point, and there is an increase in the width of the region of blurring of the heat-capacity jump with the appearance of the characteristic kink point. Multiple heat-capacity measurements have shown that this region exists independently of the experimental conditions for all concentrations of triethylamine except for the critical one. Therefore, we believe that the blurring range of the heat-capacity peak can be considered as a region of metastable states of the triethylamine–water system and the kink point — as a spinodal point.

As the binodal point ($X = 0.2$ ppm of triethylamine) is approached, the heat-capacity value smoothly increases and reaches its peak, and when the system goes into the metastable region, heat-capacity oscillations are observed (Fig. 2, curve 1). Numerous experiments show [6, 7] that the nonlinear oscillations observed in the properties of solutions in the critical region are a characteristic feature of systems with a lower critical dissolution point. In [8], these oscillations are attributed to the action of LIs that are largely determined by the specific interaction between the solution molecules.

It is known that the system disorder created by the presence of LIs shows up as random perturbations of the local critical temperature or random fields [9, 10]. The present paper is devoted to the heat-capacity behavior in a system with a random temperature disorder. The model Ginzburg–Landau Hamiltonian with two coupled order parameters, a concentration field $u(\mathbf{x})$, and an impurity field $\psi(\mathbf{x})$ is of the form

$$H(u, \psi) = \int d^d x \left\{ \frac{1}{2}\left[K_u |\nabla u|^2 + a u^2\right] + \frac{b}{4} u^4 + \frac{1}{2}\left[K_\psi |\nabla \psi|^2 + \psi^2\right] + \frac{1}{4}\psi^4 + \frac{g\psi^2 u^2}{2} + hu \right\}, \quad (1)$$

where

$$u^2 = \sum_{i=1}^{n} u_i^2 ; \quad \psi^2 = \sum_{i=1}^{m} \varepsilon_i \psi_i^2 ; \quad \psi^4 = \sum_{i=1}^{m} \gamma_i \psi_i^4 ; \quad |\nabla u|^2 = \sum_{i=1}^{n} \left|\nabla u_i\right|^2 ; \quad |\nabla \psi|^2 = \sum_{i=1}^{m} \left|\nabla \psi_i\right|^2 ;$$

$$a = \alpha \frac{T - T_{\text{cr}}}{T_{\text{cr}}} ; \quad \varepsilon_i = \beta \frac{T - T_i}{T_i} .$$

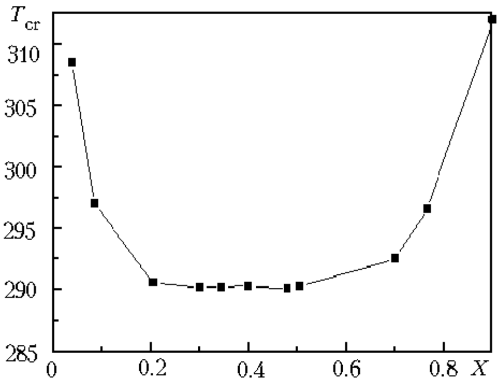

Fig. 3. Critical temperature versus the concentration of the triethylamine–water solution. T, K; X, %.

From the experimental heat-capacity data it is seen that the interaction of LIs with the concentration field $u(\mathbf{x})$ at the critical point weakens. In so doing, in the vicinity of the critical point the contribution of the order parameter $u(\mathbf{x})$ to the free energy of the system is much larger than that of the impurity field $\psi(\mathbf{x})$, whereas beyond it a mixed phase with both coexisting types of ordering are observed. Proceeding from this, let us represent the coefficient g in Eq. (1) in the form (by analogy with the method proposed in [11]) $g = g_0(C_{s2} - C_{s1})^2$, where g_0 is a constant; C_{s2} and C_{s1} are spinodal concentrations, whose values are determined in the zero of the second derivatives of the free energy density with respect to u, and at the critical point $C_{s2} = C_{s1} = C_{\rm cr}$.

Consider the equilibrium distribution ψ_i of localized impurities. Variation of (1) in ψ_i yields

$$\frac{\delta H}{\delta \psi_i} = -K_{\psi_i} \Delta \psi_i + \varepsilon_i^* \psi_i + \gamma \psi_i^3 = 0 \,, \tag{2}$$

where $\varepsilon_i^* = \varepsilon_i + gu^2$. At $d < 4$, this equation has spherically symmetric solutions with the asymptotics [11]

$$\psi_i\,(|\mathbf{x}| \le 1) \cong \psi_i\,(0) \sim 1 \,, \quad \psi_i\,(|\mathbf{x}| \ge 1) \cong \exp\,(-\,|\mathbf{x}|) \to 0 \,.$$

In the approximation used in the present paper, the liquid is incompressible and the fluctuation movements are purely transverse and, consequently, the microinhomogeneity distribution is considered in the direction of the normal, i.e., the z-axis. To investigate the effects of impurities, we use only one scale of lengths, i.e., only the wavelength fluctuations in an infinitely small interval L and $L + \delta L$. Averaging over these wavelength fluctuations gives the free energy F_L for the order parameter u, where only wavelengths larger than $L + \delta L$ are present. Inside the region of $L \pm L + \delta L$ we assume that $u \equiv u_0$. To provide the decaying behavior of system (1) in the absence of external forces (or, in other words, to provide stability of the system) we will require that the coefficient ε^* be less than zero. Then the solution of Eq. (2) is of the form

$$\psi_i\,(z, z_{0i}) = \sqrt{|\varepsilon_i^*|}\left\{\tanh\left[\sqrt{\frac{|\varepsilon_i^*|}{2\gamma_i}}\,(z - z_{0i})\right] - 1\right\} . \tag{3}$$

For graphical representation of the distribution function $\psi_i(z)$, it is convenient to write solution (3) as

$$\psi_i\,(z, z_{0i}, \delta L_i) = \sqrt{|\varepsilon_i^*|}\left\{-\,1 + \tanh\left[\sqrt{\frac{|\varepsilon_i^*|}{2\gamma_i}}\left(z - z_{0i} + \frac{\delta L_i}{2}\right)\right] - \tanh\left[\sqrt{\frac{|\varepsilon_i^*|}{2\gamma_i}}\left(z - z_{0i} - \frac{\delta L_i}{2}\right)\right]\right\} , \tag{4}$$

where δL_i is the size of the region Ω_i; z_{0i} is the coordinate of the center of localized impurities (Fig. 4).

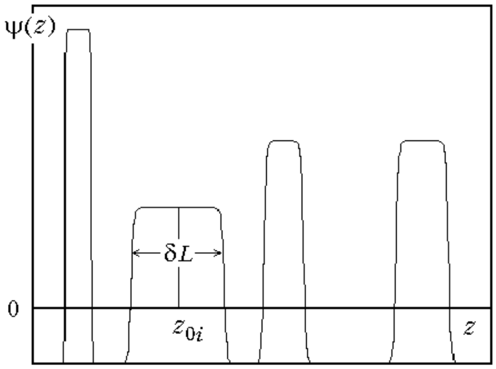

Fig. 4. Distributions of localized impurities given as regions of width δL with a center at point z_0.

From Eq. (4) it is seen that the eigenfunctions $\psi_i(z)$ for m inside the region Ω_i are very close to a constant independent of z and m but dependent on δL_i. Therefore, the quantity ψ^2 is almost exactly equal to its mean value $\langle \psi^2 \rangle$ in the local volume Ω_i of size δL_i. To find the mean distribution of local impurities in the region of $L + \delta L$, it is necessary to calculate the following integral:

$$\tilde{\psi}_i = \langle \psi(\Omega_i)^2 \rangle = \frac{1}{\delta L_i} \int_{L_i}^{L_i+\delta L_i} dz\,\psi(z)^2 =$$

$$= 2\,|\varepsilon^*| - \sqrt{\frac{|\varepsilon^*|}{2\gamma_i}}\,\tanh\left(\sqrt{\frac{|\varepsilon^*|}{2\gamma_i}}\,x\right)\Bigg|_{L}^{L+\delta L} + 2\sqrt{\frac{|\varepsilon^*|}{2\gamma_i}}\,\ln\frac{\cosh\left[\sqrt{\frac{|\varepsilon^*|}{2\gamma_i}}\,(L+\delta L)\right]}{\cosh\left(\sqrt{\frac{|\varepsilon^*|}{2\gamma_i}}\,\delta L\right)}, \tag{5}$$

where the length $\delta L \ll 1$ but is larger than the atomic size.

Substitution of (5) into Hamiltonian (1) and variation in $u(\mathbf{x})$ give the following equation:

$$-K_u \Delta u + \left[a + g\sum_{i}^{m} \tilde{\psi}_i\right] u + bu^3 = h\,. \tag{6}$$

Linearization of (6) with respect to the small deviations of $u = u_0 + u_1$ yields

$$-K_u \Delta u_1 + \left[a + g\sum_{i}^{m} \tilde{\psi}_i + 3bu_0^2\right] u_1 = h\,.$$

Solving this equation for the distribution of u_1 arising from the point source of the field h placed at the origin of coordinates, one can easily obtain the Green function

$$G(z, z_0) = -\frac{1}{2}\exp\left(-\kappa\left|z - z_0\right|\right),$$

where

$$\kappa^{-1} = \xi = \sqrt{\frac{K\psi}{\left(a + 3bu_0^2 + \sum_i^m \tilde{\psi}_i\right)}}\ .$$

Consequently, the characteristic size of the fluctuation turns out to be dependent on the size of local impurities as $\xi \sim \delta L^{-1/2}$, i.e., an increase in the size of the latter leads to a decrease in the correlation radius in the vicinity of the critical demixing point. Then the fluctuation addition to the heat capacity can be found from the expression [13]

$$\Delta c_p = -\frac{\alpha}{2T_{\mathrm{cr}}} \lim_{x\to 0} \frac{\partial}{\partial T} [G(x)] = \frac{\alpha}{2T_{\mathrm{cr}}} \frac{\dfrac{4\alpha}{T_{\mathrm{cr}}} + \dfrac{\partial \sum_i^m \tilde{\psi}_i}{\partial T}}{\sqrt{4a + \sum_i^m \tilde{\psi}_i}}\ . \qquad (7)$$

In the immediate vicinity of the critical point the system demonstrates a specific critical behavior characterized by the competition of two types of ordering. In the region where disorder prevails, a macroscopic amount of spatially inhomogeneous ground states exists. They correspond to the solutions of the saddle equation (2). Physically, the latter correspond to the appearance of phases resembling Griffith phases [12], which appear as a consequence of the existence of ordered "islands" in the temperature range between the critical temperatures of the pure and the disordered systems. Upon introduction of random temperatures in the 292.23–305.5 K range responsible for the sequential decomposition of these "islands" — localized impurities — in (7) at dimensions of u and ψ representations $n = 1$ and $m = 5$, respectively, the behavior of the heat capacity markedly changes and oscillations are observed (Fig. 2, curve 2). Decomposition of microinhomogeneities leads to a local increase in u and the correlation radius ξ, and, as is seen from expression (3), an increase in u causes, in turn, a growth of the impurity field ψ, which stimulates the formation of new microinhomogeneities. In other words, the decomposition of LIs retards the process of phase layering, and this goes on until the intensity of the Brownian movement of molecules begins to predominate over the entropic effect of mixing. Thus, the presence of LIs, such as molecular complexes formed by means of a hydrogen bond, and their interaction with concentration fluctuations can be one explanation of the anomalous behavior of the heat capacity observed in our experiments.

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NOTATION

a, b, g, α, β, ε, ε^*, γ_i, coefficients; c_p, heat capacity at constant pressure, J/(g·K); C_{s1}, C_{s2}, spinodal concentrations, ppm; C_{cr}, critical concentration, ppm; d, space dimension; F, free energy, J; $H(u, \psi)$, Hamiltonian, J; h, generalized external field; K_u, kinetic coefficient of the concentration field; K_ψ, kinetic coefficient of the impurity field; L, characteristic wavelength of the process under consideration; m, n, dimensions of representations; T_i, decay temperature of localized impurities, K; T_{cr}, critical temperature of the phase transition, K; $u(\mathbf{x})$, concentration field; X, concentration, ppm; x, z, coordinate axes; z_{0i}, coordinate of the center of localized impurities; δL_i, size of the region Ω_i; ξ, correlation radius; Ω, range of values; $\psi(\mathbf{x})$, impurity field; $\tilde{\psi}$, mean value of the squared impurity field. Subscripts: cr, critical; p, pressure; s, spinodal.

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