

Anomaly of specific heat and possible phase transition of the ordering type in an aqueous solution

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We observed the λ anomaly of the specific heat in a liquid solution of water and tertiary butanol. A mechanism is proposed for the phase transition responsible for this anomaly, namely, ordering of the alcohol molecules in the quasicrystalline structure of the water.

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The only example of second-order phase transition in simple liquids and their solution are the critical liquid-gas and liquid-liquid critical points.^[1] It is usually assumed that in liquids, unlike in crystals, phase transitions of the order-disorder type are impossible. The situation may turn out to be fundamentally different for liquids that have a quasicrystalline structure (when the short-range crystalline order subtends at least over several intermolecular distances).^[1] It is not excluded that in such liquids phase transitions typical of solids are possible over scales corresponding to crystalline order. In this respect, the most promising object is water near the crystallization point.^[2] M. F. Vuks has called attention to the solution of tertiary butanol (C_4H_9OH) in water, which reveals a number of anomalous properties, particularly strong opalescence, at small concentrations of the alcohol (<10 mol%).^[3]

We have performed similar measurements of the specific heat of this solution in the concentration region <10 mol.% from the crystallization point ($T \approx 262-273$ °K) to $T \approx 330$ °K. The measurement procedure was similar to that used to investigate pure water near the crystallization^[2] and the critical liquid-liquid equi-

librium point.^[4] The error in the measurement of the temperature dependence of the specific heat was $\sim 0.1\%$. In measurements of the concentration dependence, additional errors were introduced because of remounting and filling the calorimeter, and therefore the error reaches $\sim 0.5\%$ in this case. The sample was stirred continuously during the measurements.^[4] The time of establishment of the thermodynamic equilibrium after heating did not exceed several minutes. At a temperature $274-275$ °K and a concentration $\sim 7\%$ of the butanol (Fig. 1 and 2), a sharply pronounced maximum of the specific heat is observed. Is this maximum sharp enough to speak of λ anomaly and consequently of a phase transition? In real samples, phase transitions are always smeared out and the smearing interval, namely the region where the maximum is flattened on the experimental curve, is frequently determined by the object itself and does not depend on the experimental conditions.^[1] This is particularly typical of solids. The only realistic criterion for the presence of a phase transition is the smallness of the smearing interval in comparison with the temperature region in which the anomaly is observed. In our case, the region of anomalous behavior of the specific heat is $t = |T - T_c|/T_c \approx 2 \times 10^{-1}$ and x

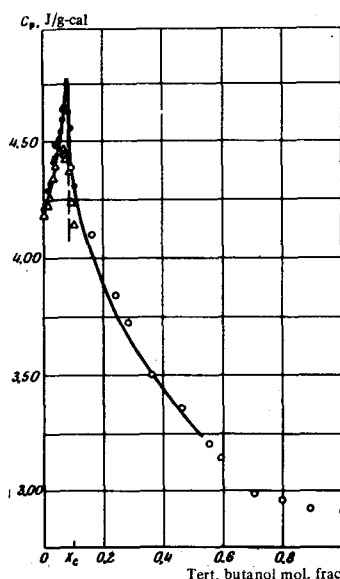


FIG. 1. Dependence of the specific heat of the aqueous tertiary butanol solution on the concentration: \bullet — $T = 275$ °K, Δ — $T = 305$ °K, \circ —results of measurements^[6] at $T = 305$ °K.

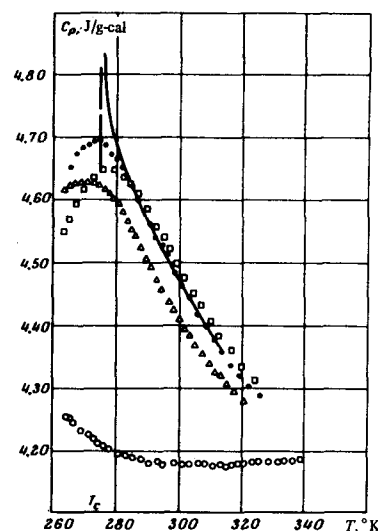


FIG. 2. Dependence of the specific heat of the solution of tertiary butanol in water on the temperature: \circ —pure water supercooled to $T = 264$ °K,^[2] \square —6.6% butanol, \bullet —7.4% butanol, Δ —8% butanol.

$= |X - X_c|/X_c \approx 1$ (Here T_c and X_c are the temperature and concentration at the maximum of C_p), while the smearing region is $t_0 \approx x_0 \approx 10^{-2}$. We can speak of "λ anomaly," naturally, only to the degree of assurance with which the conditions $t_0 \ll t$ and $x_0 \ll x$ are satisfied. Typical of the solution of tertiary butanol in water is the appreciable dependence of the properties on the prior history of the sample. Thus, opalescence is not observed at all if the components are mixed at low temperatures and the subsequent measurements are carried out without stirring.^[5] The sensitivity to the prior history, in our opinion, is also evidence of the presence of a phase transition.

A detailed analysis of the mechanism of the proposed phase transition was the subject of a special study. Here we confine ourselves only to a few remarks of fundamental character. We note first that this transition has no bearing on the critical equilibrium point liquid-liquid. Measurements of the saturated vapor solution^[6] show that at small (<10%) butanol concentrations, the "osmotic compressibility" of the solution ($\partial x/\partial \mu_{PT}$ (μ is the chemical potential), which characterizes the tendency of the solution to stratification, has no anomaly whatever (see also^[3]). Moreover, the mutual dissolution of the components in this concentration region is accompanied by release of energy.^[6] These facts suggest that we are dealing here with an ordering-type phase transition, which is well known for crystalline binary solutions.

Whereas the usual critical point of the solution is a transition of the "ferromagnetic" type (molecules of the same sort are effectively "attracted"), the ordering in binary alloy is a transition of the "antiferromagnetic" type (the molecules of the different sorts are effectively "attracted").^[7] In our case the butanol molecules are apparently ordered in the "lattice" of the water. Since such a phase transition is typical of crystalline bodies, it becomes smeared out in liquids to the extent to which

the crystal structure is smeared out by the thermal motion of the molecules. As soon as the correlation radius of the fluctuations of the corresponding "order parameter," which increases like $r_c = r_0 t^{-\nu}$ (r_0 is the direct-interaction radius and ν is the positive number),^[1,7] which is the characteristic length of the crystalline short-range order, the λ anomaly begins to become smeared out. Let us estimate, by starting from the value of the smearing interval, the scale of the short-range crystal order in a liquid solution of tertiary butanol in water.

Assuming $r_0 = 2-3 \text{ \AA}$, and $\nu \approx 2/3$ ^[1] we obtain $r_c \approx 50 \text{ \AA}$ at $t \approx 10^{-2}$. In a "crystallite" of this type there are contained 10^3-10^4 molecules of water and 10^2-10^3 molecules of butanol, an amount perfectly sufficient to exhibit collective spectra.

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¹⁾We do not have in mind liquid crystals which have, like solids, long-range crystal order.

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