

# Light scattering in solutions with two double critical points

L. A. Davidovich, É. K. Kanaki, and I. I. Shinder

*Department of Thermophysics, Academy of Sciences of the Uzbek SSR*

(Submitted 23 June 1989)

Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 3, 120–123 (10 August 1989)

Measurements of the intensity of Rayleigh scattering of light in a three-component solution with two double critical points are reported. A model incorporating three phase transitions is proposed for describing the temperature dependence of the optical scattering coefficient.

Recent studies<sup>1–3</sup> of phase transitions in a system with one double critical point have shown that the phase transition near the double critical point has several specific features: changes in the values of the effective critical indices, effects of a superposition of critical phenomena stemming from the close spacing of phase transitions with upper and lower critical points near the double critical point, etc. In addition, it has been shown theoretically<sup>4</sup> that more than one double critical point can be observed in solutions containing hydrogen bonds. The presence of two double critical points in a system should result from three phase transitions with both upper ( $T_{cu}$ ) and lower ( $T_{cl}$ ) critical stratification temperatures.

We have found that two double critical points are observed in the 2-butanol-water system with a propanol admixture. The phase diagram of this solution (Fig. 1) in the

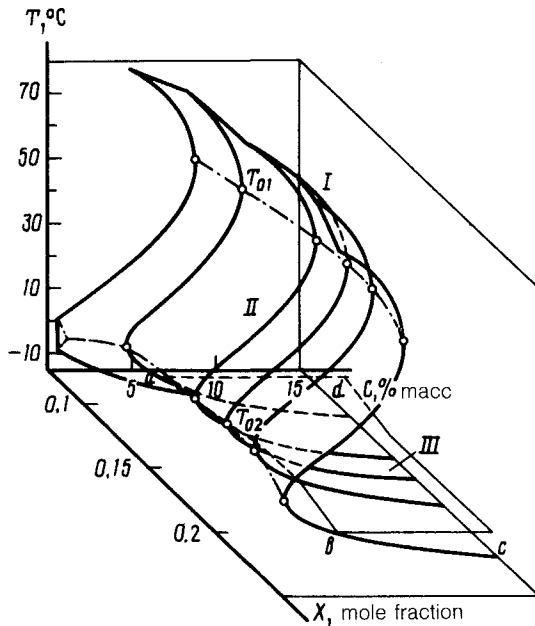


FIG. 1. Phase diagram of the 2-butanol-water + propanol solution.  $T_{01}$ ,  $T_{02}$ —Upper and lower double critical points; dot-dashed lines—lines of “double” points; plane abcd—melting points.

composition region studied is a convex-concave surface in  $TXC$  space ( $X$  is the concentration of the host components, and  $C$  is the admixture concentration). To the left and right of this surface, respectively heterogeneous and homogeneous states of the solution coexist. On the coexistence surface one can distinguish two lines of double points (the dot-dashed lines), which divide the entire surface into three parts: I and III, which are the surfaces of the upper stratification points, and II, which is that of the lower stratification points. The positions of the double critical point on the corresponding lines of double points are marked  $T_{01}$  (the upper double critical point) and  $T_{02}$  (the lower double critical point). The parameters of the double critical point ( $T_0, X_0, C_0$ ) were found to have the following values by the method described in Ref. 3:

$T_{01} = 51.85^\circ\text{C}$ ,  $X_{01} = 0.1$  mole fraction (m.f.) of 2-butanol in water,

$C_{01} = 9.404\%$  (mass);

$T_{02} = 2.7^\circ\text{C}$ ,  $X_{02} = 0.16$  m.f. of 2-butanol in water,

$C_{02} = 3.979\%$  (mass).

The upper double critical point differs from the lower one in a number of ways. For example, while the former is a point of return from a homogeneous state to a homogeneous state of the solution, the latter is, on the contrary, a point of return from a heterogeneous state to a heterogeneous state; or, while the former is characterized by a stratification gap with an upper position  $T_{cu}$  and a lower position  $T_{ci}$ , the former has a mixing gap with a lower position  $T_{cu}$  and an upper position  $T_{ci}$ . Consequently, the lower double critical point may be thought of as the inverse of the upper one. Nevertheless, the boundary curves in the  $TC$  plane near the lower and upper double critical points can be described well by a scaling law in terms of an order parameter:

$$(T_c - T_0)/T_0 = M |(C - C_0)/C_0|^{\beta_0} \quad (1)$$

For all of the  $TC$  cross sections studied, the value of  $\beta_0$  is 0.5.

We undertook an experimental study of the behavior of Rayleigh scattering of light in this system, with its two double critical points. The intensity of the angular scattering of light was measured in a cell 5 mm in diameter in a cylindrical constant-temperature chamber with optical windows. The chamber was filled with ethyl alcohol, which doubled as a temperature-regulation medium and an immersion liquid. The small-diameter measurement cell allowed us to ignore the corrections for multiple scattering. Experiments were carried out over the temperature range 20–70 °C, with an error of 0.02 °C.

Figure 2 shows results on the scattering of light over a temperature range which spans all three phase transitions which are observed in the system, for the concentration  $X = 0.1$ . This concentration corresponds to the upper double critical point. Various values of the impurity concentration were studied. The results show that the curves of  $R_{90}$  versus  $T$  ( $R_{90}$  is the coefficient for the scattering of light at an angle of 90°) have three regions of an anomalous growth in the light scattering, each associated with a corresponding phase transition. Curves 4–6 correspond to a region of homogeneity (with  $C > C_{01}$ ) and have a finite maximum

$$R_{90} \sim |(C - C_{01})/C_{01}|^{-1.23} \quad \text{at} \quad T \approx T_{01}.$$

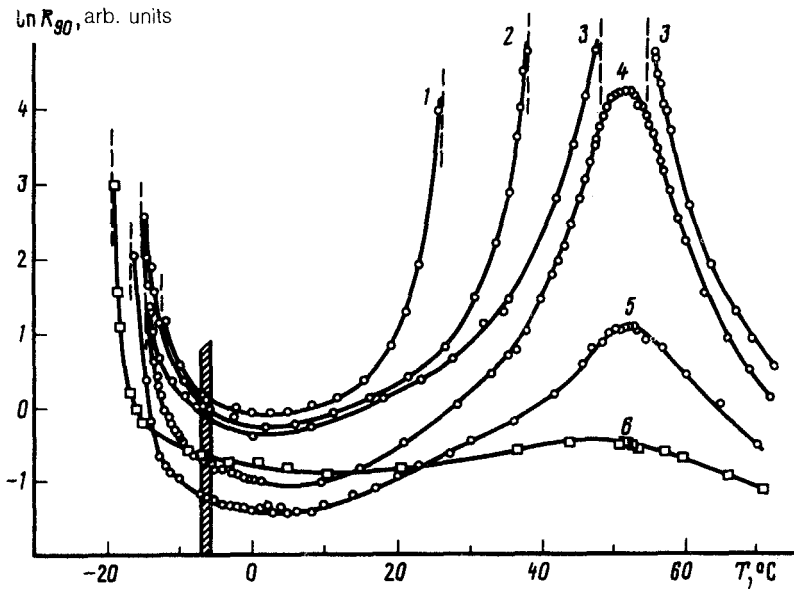


FIG. 2. Temperature dependence of the light scattering coefficient  $R_{90}$  for a concentration  $X_{01} = 0.1$  mole fraction of 2-butanol in water and for various values of the impurity concentration  $C$  (mass%): 1—6.99; 2—8.691; 3—9.359; 4—9.420; 5—10.0; 6—14.0. The points are experimental, and the solid lines are theoretical (see the text proper), calculated for the following parameter values. Curve 1)  $\gamma_1 = 1.21$ ,  $\gamma_2 = 0.825$ ,  $K = 0.55$ ,  $T_u = -12.1^\circ\text{C}$ ; 2)  $\gamma_1 = 1.22$ ,  $\gamma_2 = 0.91$ ;  $K = 0.67$ ,  $T_u = -14^\circ\text{C}$ ; 3)  $\gamma_1 = 1.23$ ,  $\gamma_2 = 0.804$ ,  $K = 0.65$ ,  $T_u = -14.55^\circ\text{C}$ ; 4)  $\gamma_1 = 1.23$ ,  $\gamma_2 = 0.904$ ,  $K = 0.37$ ,  $T_u = -14.5^\circ\text{C}$ ; 5)  $\gamma_1 = 1.23$ ,  $\gamma_2 = 0.801$ ,  $K = 0.26$ ,  $T_u = -15.25^\circ\text{C}$ ; 6)  $\gamma_1 = 1.23$ ,  $\gamma_2 = 0.712$ ,  $K = 0.62$ ,  $T_u = -18.4^\circ\text{C}$  ( $M = 1.0331$ ).

Another specific feature of this system is its tendency toward a supercooling of tens of degrees upon crystallization, so that the low-temperature phase transition with the upper critical stratification temperature  $T_u$ ) and the associated critical phenomena are in a region of a supercooled metastable state of the system. The hatched band in Fig. 2 corresponds to the melting point  $T_m$  for these systems (the plane abcd in Fig. 1 has the same meaning). The light scattering curves which lie below  $T_m$  refer to the metastable state.

Following the superposition principle proposed in Ref. 3, we can write the following expression for the three phase transitions in this system:

$$R_0 = K \left( \tau^2 - \frac{C_{01} - C}{MC_{01}} \right)^{-\gamma_1} \left| \frac{T - T_u}{T_u} \right|^{-\gamma_2}. \quad (2)$$

Here  $\tau = (T - T_0)/T_0$ , and  $\gamma$  is the critical index of the compressibility.

The solid lines in Fig. 2 were calculated from expression (2). The parameter values used in these calculations are shown in the figure caption. The correction of  $R_0$  to  $R_{90}$  was carried out on the basis of the Ornstein-Zernike relation. We see that the agreement is extremely satisfactory, particularly since a discrepancy between the val-

ues found here for the indices and the Ising values is observed in only those cases in which the corresponding phase transition ( $T_u$ ) for the given composition of the system is not critical.

<sup>1</sup>A. A. Sobyenin, *Usp. Fiz. Nauk* **149**, 325 (1986) [*Sov. Phys. Usp.* **29**, 570 (1986)].

<sup>2</sup>V. P. Zaitsev *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 85 (1986) [*JETP Lett.* **43**, 112 (1986)].

<sup>3</sup>L. A. Davidovich and I. I. Shinder, *Zh. Eksp. Teor. Fiz.* **95**, 1289 (1989) [*Sov. Phys. JETP* **xx**, xxx (1989)].

<sup>4</sup>J. C. Wheeler and G. R. Andersen, *J. Chem. Phys.* **73**, 5778.

Translated by Dave Parsons