

## Sound propagation and Raleigh scattering in solutions with one and two "double" critical points

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Measurement results on the absorption coefficient, speed of sound, and Raleigh light-scattering intensity in two stratified solutions containing one and two "double" critical points are presented. A model describing the temperature dependence of the sound absorption coefficients and light scattering, considering the superposition of all phase transitions existing in the systems, is proposed.

### INTRODUCTION

It is known that a "double" critical point (DCP) is formed in solutions during merging of upper and lower critical points of stratification.<sup>1-3</sup> Being a critical point of higher order, the DCP [its existence is determined by two necessary thermodynamical conditions  $(\partial\mu^*/\partial X)_{P,T}=0$  and  $(\partial\mu^*/\partial T)_{P,X}=0$ , where  $\mu^*$  is the difference of chemical potentials of the solution components and  $X$  is their concentration] is characterized by certain specific peculiarities and, above all, by an unusually high sensitivity of the system to external effects, including pressure. Such behavior of the system in the DCP range provides favorable conditions for the observation of different critical phenomena and, in particular, dynamical processes connected with sound propagation.

The purpose of the present paper is to study the nature of sound propagation in the neighborhood of DCP in two types of systems (I) containing one DCP and (II) containing two DCP's. For the latter case optical studies of Raleigh light scattering were carried out, in addition to the acoustic investigations.

### OBJECTS OF INVESTIGATION

Two solutions were the objects of our investigations: the first solution was a propanol and water mixture with sodium chloride and the second solution was a 2-butanol and water mixture with propanol.

The study of the phase diagrams of these solutions at atmospheric pressure in the temperature range of  $-20^\circ\text{C}$ – $+80^\circ\text{C}$  showed that in the propanol–water + NaCl solution there is one DCP with the following parameters of the state: concentration of the main components  $X=X_0=0.15\pm 0.01$  mole fraction (m.f.) of propanol in water; impurity concentration  $C=C_0=5.3830$  mass % and  $T=T_0=45.15^\circ\text{C}$ .<sup>14</sup> It is significant that the increase content impurity  $C$  has an effect of separating on the solution components and increases the width of the heterogeneous region  $\Delta T=T_{cu}-T_{cl}$  ( $T_{cu}$  and  $T_{cl}$  are the upper and lower critical temperatures) which follows from the  $TC$  equilibrium diagram (Fig. 1) presented for  $X=X_0$ .

We have found that there are two DCP's in the 2-butanol–water with propanol system. The phase dia-

gram of the solution (Fig. 2) in  $TXC$  space represents a convexoconcave surface, the heterogeneous and homogeneous states of the solution being to the left and to the right of it, respectively. Two lines of double points (dot-dashed lines) can be distinguished on the coexistence surface. These lines divide the whole surface into three parts: I and III are the surface of the upper stratification points and II of the lower stratification points. DCP position on the relevant lines of double points are shown by letters  $T_{01}$  (upper DCP) and  $T_{02}$  (lower DCP). The DCP parameters ( $T_0, X_0, C_0$ ) have been determined according to the method described in Ref. 4 with the following results:  $T_{01}=51.85^\circ\text{C}$ ;  $X_{01}=0.1$  m.f. 2-butanol in water;  $C_{01}=9.404$  mass %;  $T_{02}=2.7^\circ\text{C}$ ;  $X_{02}=0.16$  m.f. 2-butanol in water;  $C_{02}=3.797$  mass %. It should be noted that the authors of Ref. 5 have found two "double" critical points in the impurity-free 2-butanol–water system, but at high pressure. In our case the upper DCP differs from the lower DCP by certain features. The first DCP is characterized by the stratification slit with the upper position of  $T_{cu}$  ( $T_{c1}$ ) and lower  $T_{cl}$  ( $T_{c2}$ ) but the second one is opposite. It has a mixing slit with the lower position of

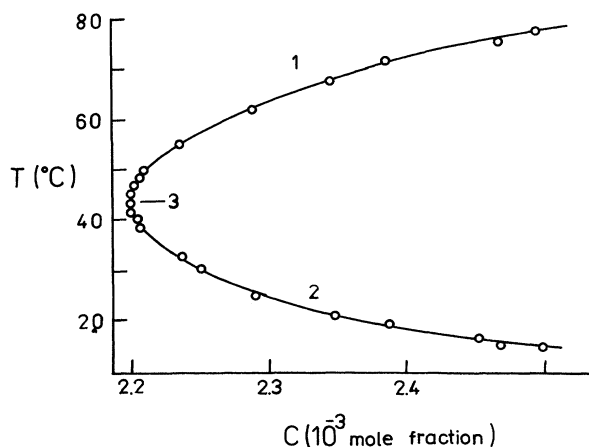


FIG. 1. Equilibrium diagram of the propanol–water + NaCl solution at  $X=X_0$ . 1, line of upper critical temperatures  $T_{cu}$ ; 2, line of lower critical temperatures  $T_{cl}$ ; 3, "double" critical point.

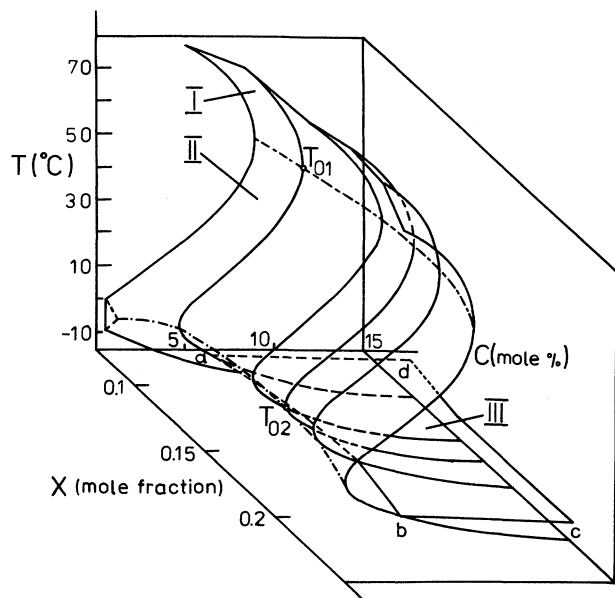


FIG. 2. Phase diagram of the 2-butanol-water+propanol solution. Points  $T_{01}$  and  $T_{02}$  correspond to the upper and lower DCP. Dot-dashed lines are the lines of "double" points. The plane  $abcd$  corresponds to melting points.

$T_{cu}$  ( $T_{c3}$ ) and upper  $T_{cl}$  ( $T_{c2}$ ). Thus the lower DCP can be considered as an opposite one with respect to the upper DCP. However, in the neighborhood of lower and upper DCP the boundary curves in the  $TC$  plane are well described by the scaling law:

$$(T_c - T_0)/T_0 = [(C - C_0)/C_0]^{\beta_0}/M.$$

For all studied  $TC$  sections, the value of the critical temperature index  $\beta_0$  was 0.5.

### SOUND PROPAGATION

Our measurement results for the absorption coefficient  $\alpha$  and sound speed  $\mathcal{C}$  in the neighborhood of DCP of the above-mentioned solution are presented below. To conduct these measurements, it was necessary to overcome some difficulties mainly caused by the very low frequency of relaxation processes in the vicinity of DCP. This seems to be the major reason of the small number of acoustic studies of solutions with DCP (Refs. 6 and 7) and especially in the neighborhood of DCP.

We used two experimental installations to carry out low-frequency acoustic studies: reverberative and resonant ones; they permitted measurement of  $\alpha$  and  $\mathcal{C}$  in the frequency range from 0.02 to 2 MHz. The measuring cell of the reverberative installation described in Ref. 8 had a volume of 70 cm<sup>3</sup> and intrinsic quality factor of 10<sup>4</sup>. The resonant installation was made on the basis of a piezoquartz cylindrical converter with a diameter of 70 mm and inherent frequency of 1.5 MHz. In this case the quality factor of the measuring cell attained the value of 10<sup>6</sup>. The measuring error of  $\alpha$  and  $\mathcal{C}$  over the whole frequency range did not exceed 5% and 0.1%, respectively.

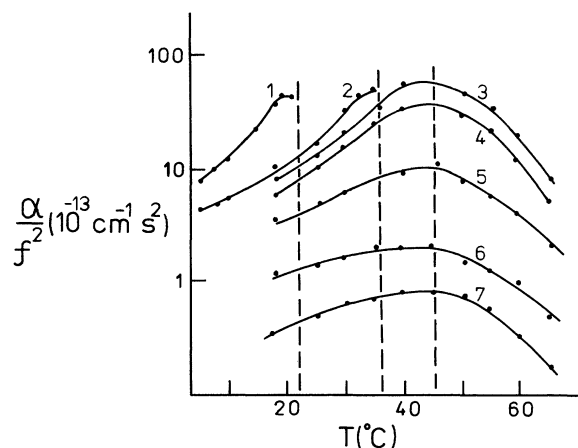


FIG. 3. Dependence of  $\alpha/f^2$  on temperature in the propanol-water+NaCl solution at the frequency of 30 kHz with the following values of NaCl impurity concentration (mass %): 1, 5.877; 2, 5.465; 3, 5.383; 4, 5.329; 5, 5.003; 6, 4.526; 7, 3.819. The points correspond to experimental data and solid lines to the calculations (see the text).

Figures 3 and 4 show the measurement results of temperature dependence  $\alpha/f^2$  obtained for both investigated solutions with the frequency of 30 kHz in the neighborhood of DCP and the presented results for the second solution (Fig. 4) correspond to the neighborhood of the upper DCP.

The measurement results demonstrated that, firstly, the temperature-dependence curve  $\alpha/f^2(T)$  has a maximum at DCP temperature. Secondly, there is an abrupt increase in the  $\alpha/f^2$  value under the approach to the lines with upper  $T_{cu}(C)$  and lower  $C_{cl}(C)$  of critical points. Thirdly, for the external region with respect to the

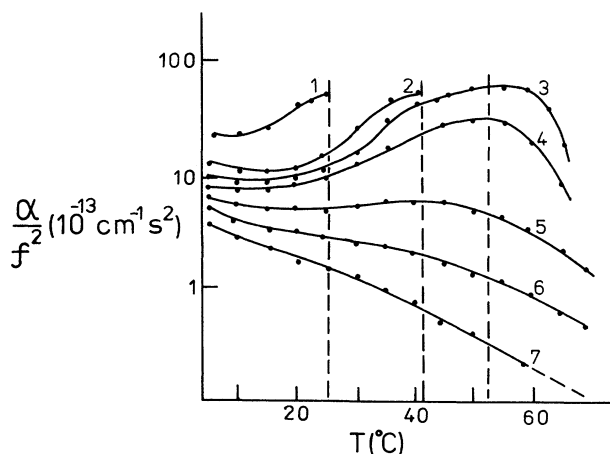


FIG. 4. Dependence of  $\alpha/f^2$  on temperature in the 2-butanol-water+propanol solution at the frequency of 30 kHz with the following values of propanol impurity concentration (mass %): 1, 6.293; 2, 8.801; 3, 9.423; 4, 10.00; 5, 12.00; 6, 14.00; 7, 16.00. The points correspond to experimental data and solid lines to the calculations (see the text).

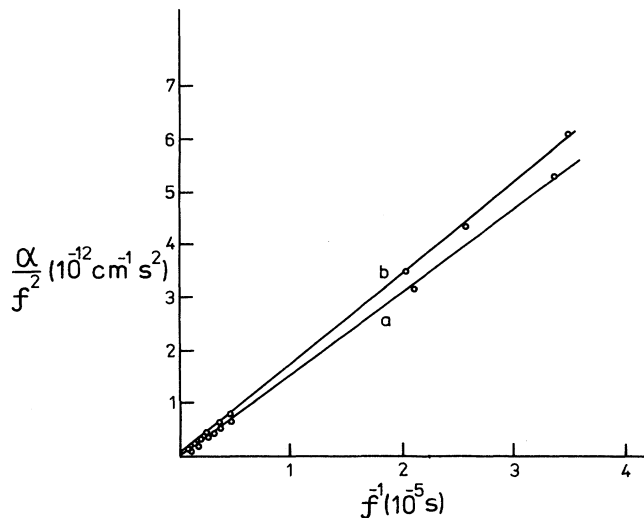


FIG. 5. Dependence of  $\alpha/f^2$  on frequency in DCP in the following solutions: a, propanol-water + NaCl; b, 2-butanol-water + propanol.

stratification line (the region of complete solubility) the maximum on the  $\alpha/f^2(T)$  curves is abruptly decreased. It is significant that with the given frequencies in DCP and on  $T_{cu}(C)$  and  $T_{cl}(C)$  lines the value of the critical absorption remains finite and attains its amplitude value  $\alpha_c$ . All these facts show that the observed anomaly of sound absorption near DCP is connected with relaxation process having a fluctuation origin. A similar conclusion follows from the measurements results of frequency dependence  $\alpha/f^2$  (Fig. 5) obtained in the close proximity to DCP (with  $C=C_0$  and  $T=T_0$ ). Figure 5 shows that this dependence points to a wide region of acoustic relax-

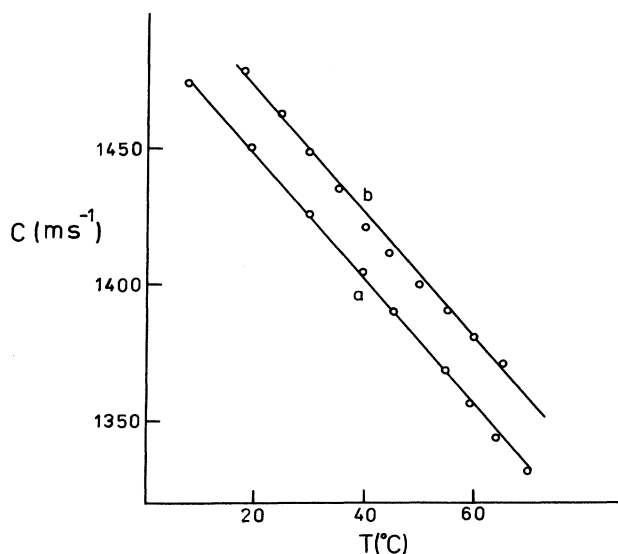


FIG. 6. Dependence of sound speed  $\mathcal{C}$  on temperature in the neighborhood of DCP at  $C=C_0$  in the following solutions: a, propanol-water + NaCl; b, 2-butanol-water + propanol.

ation at very low frequencies  $\ll 1$  MHz.

At the same time, within the limits of the achieved measurement accuracy  $\mathcal{C}$  (0.1%) at the frequency of 30 kHz, the temperature dependence of  $\mathcal{C}$  admits only a linear approximation (Fig. 6). Thus measurements with an accuracy exceeding 0.1% and at lower frequencies are required for a reliable observation of the sound speed anomaly in DCP.

Attention is also drawn to some differences in the behavior of sound absorption temperature dependence in both solutions. It is seen from Figs. 3 and 4 that the maximum shape in the first solution is sufficiently symmetrical and a high asymmetry of  $\alpha/f^2(T)$  curve is observed in the second solution. The analysis showed that this peculiarity is not connected with the contributions of the regular parts of sound absorption in the studied systems and thus can be caused only by another phase transition in the second solution located at low temperatures which makes an additional contribution to the sound absorption. To check this assumption, we studied light scattering in the second solution containing two DCP's in a wide temperature range including comparatively lower temperatures.

#### LIGHT SCATTERING

Raleigh light-scattering intensity was measured only in the solution of 2-butanol-water+propanol with two DCP's as the experiments on light scattering in solution with one DCP were conducted earlier.<sup>14</sup> The intensity of the light scattering was measured in a cell with the diameter of 5mm set into a cylindrical thermostat with optical windows filled with ethyl alcohol, which was thermostatic and immersion liquid at the same time. The use of a small-diameter cell permitted us to neglect the corrections for multiple scattering. The temperature range of measurements was  $-20^\circ\text{C}$ – $+70^\circ\text{C}$  with the accuracy of 0.02.

Figure 7 presents the investigation results of light scattering in the temperature range covering all three

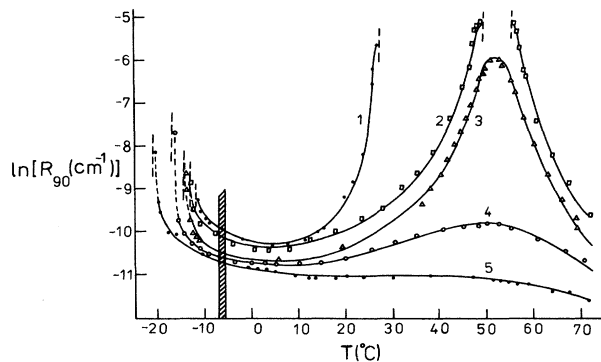


FIG. 7. Temperature dependence of light-scattering coefficient in the 2-butanol-water+propanol solution at  $X=X_0=0.1$  m.f. 2-butanol in water for different propanol impurity concentrations (mass %): 1, 6.99; 2, 9.34; 3, 9.42; 4, 12.00; 5, 16.00. The points correspond to the experimental data, the solid lines to the calculation (see the text).

phase transitions observed in the system with the concentration  $X = X_{01} = 0.1$  m.f. and different values of impurity content. The results showed three regions of anomalous growth of light scattering on the curves  $R_{90}$  of  $T$  ( $R_{90}$  is the light-scattering coefficient at the angle of  $90^\circ$ ). Each region is related to the relevant phase transition. In this case the curves 4,5,6 corresponding to the region of homogeneity (where  $C > C_0$ ) have a final maximum  $R_{90}$  at  $T \simeq T_{01}$ .

Another specific peculiarity of the studied system is its tendency to overcooling during crystallization, so that the low-temperature phase transition with the upper critical temperature of stratification and the critical region related to it appear to be in a metastable state. The cross hatched region of Fig. 7 corresponds to the melting points  $T_m$  for the considered systems (the same is shown in Fig. 2 by means of  $abcd$ ), the light-scattering curves located below  $T_m$  are related to the metastable state.

#### DISCUSSION OF THE OBTAINED RESULTS

According to Refs. 9 and 10 the coefficient of sound absorption in the critical range can be correctly described by means of the universal dynamic function of the frequency  $\mathcal{J}(\omega^*)$  and relaxation time  $\tau_c$  in the following form:

$$(\alpha\lambda)' / \alpha_c \lambda = \mathcal{J}(\omega^*) = \mathcal{J}(2\tau_c \omega), \quad (1)$$

where  $(\alpha\lambda)'$  is an excess coefficient of sound absorption for the wavelength of  $\lambda$ . We have

$$\begin{aligned} \tau_c &= 6\pi r_c^3 \eta, \quad r_c = r_0 [(T - T_c) / T_c]^{-\nu}, \\ \eta_s &= \eta_r [(T - T_c) / T_c]^{-\nu}, \\ \mathcal{J}(\omega^*) &= 2/\pi(1+p)\omega^* \\ &\times \int_0^\infty X^4(1+X^2)(1+X^2)^{p-2} \\ &\times [\omega^{*2} + X^4(1+X^2)]^{-2p} dX^2. \end{aligned}$$

$\eta_r$  is a regular part of the shear viscosity  $\eta_s$ ;  $r_0$  is a radius of the nearest correlation;  $p = 0.5$ .

However, the processing showed that in the case of DCP Eq. (1) does not describe the temperature dependence of the sound absorption, which implies that the universality of the  $\mathcal{J}(\omega^*)$  function is not maintained along the whole line of critical points.

The most plausible reason for the violation of this universality seems to be the existence of two phase transitions with upper and lower critical temperatures in the vicinity of DCP. In this case the system and the processes occurring in it appear to be influenced by their mutual influence.<sup>4</sup> According to Ref. 3 the square-root dependence of  $T_c(C)$  close to the DCP reflects the parabolic temperature dependence of the coefficient  $\alpha$  in the functional of the Landau free energy:

$$\begin{aligned} F = F_0 + \int \left[ \frac{\alpha(T, C)}{2} \eta^2 + \frac{\mathcal{L}(T, C)}{4} \eta^4 \right. \\ \left. + \dots + \frac{\mathcal{L}}{2} (\nabla \eta)^2 \right] dV, \end{aligned}$$

where  $\eta$  is the order parameter, and  $\mathcal{L}$  and  $\mathcal{L}'$  are positive coefficients. The coefficient  $\alpha$  at each of the critical points vanishes so that it must have a minimum between these points:

$$\alpha(T, C) = a_m(C) + a_1(C)[T - T_m(C)]^2.$$

Under the condition that  $|T - T_m|/T_m \ll 1$  and it is possible to neglect the higher terms in the expansion in  $|T - T_m|$ , the temperature  $T_m(C)$  is equal to

$$T_m(C) = [T_{cu}(C) + T_{cl}(C)]/2.$$

Here the coefficient  $\alpha$  can be written in the form

$$\alpha = -a_c(C)[T - T_{cu}(C)][T_{cl}(C) - T].$$

It then follows from the given expression that

$$\begin{aligned} \eta^2 &= -a/2b \\ &= [a_2(C)/2b][T - T_{cu}(C)][T_{cl}(C) - T]. \end{aligned}$$

If  $(T_{cu} - T_{cl})/(T_{cu} + T_{cl}) \ll G$ , where  $G$  is the Ginzburg number, the entire stratification region is located inside the fluctuation region. In this case the functional changes its form in the following way:

$$\begin{aligned} F = F_0 + \int \left[ \frac{a_0}{2} \left| \frac{a}{a_c} \right|^{2\nu - \sigma - 1} \eta^2 + \frac{b_0}{4} \left| \frac{a}{a_c} \right|^{v-2} \eta^4 \right. \\ \left. + \frac{\mathcal{L}_0}{2} \left| \frac{a}{a_c} \right|^{-\sigma} (\nabla \eta)^2 \right] dV, \end{aligned}$$

where  $\sigma \approx 10^{-2}$  is a small critical index which characterized the behavior of the correlation function at  $\alpha = 0$ ;  $a_c \equiv (3k_B T b / 8\pi d^{3/2})^2$ . In that case we have for the existence curve:

$$\eta \sim [(T_{cu} - T)(T - T_{cl})]^\beta.$$

The correlation radius depends on the temperature in the following way:

$$\begin{aligned} r_c &= r_0 [(T - T_{cu}) / T_{cu}]^{-\nu} [(T - T_{cl}) / T_{cl}]^{-\nu} \\ &= (t_1 t_2)^{-\nu}. \end{aligned} \quad (2)$$

Taking account of (2), Eq. (1) can be written as

$$(\alpha\lambda)' / \alpha_c \lambda = \mathcal{J}(\omega^*) = \mathcal{J}[3\omega\eta_r r_0^3 (t_1 t_2)^{2-\alpha} / k_B T], \quad (3)$$

where  $\alpha$  is a critical index of heat capacity.

The points in Fig. 8 show experimental values  $(\alpha\lambda)'$  obtained in the propanol-water + NaCl solution according to the reduced frequency  $\omega^*$ ; the solid line represents a calculation by formulas (3). The graph shows that Eq. (3) correctly describes the dependence of the sound absorption on the temperature and frequency both close to and far from DCP. It is significant that all parameters in Eq. (3) were obtained in independent experiments:  $\alpha_c \lambda = 0.0204$  was defined from the frequency dependence of the sound absorption,  $r_0 = 3.1 \text{ \AA}$  and  $\nu = 0.63$  from measurements of light scattering and  $\nu = 0.4$  from viscosimetric measurements.<sup>4</sup>

Equation (3) can be generalized to the case of external factor variation, i.e., of  $C$  impurity and  $P$  pressure. Con-

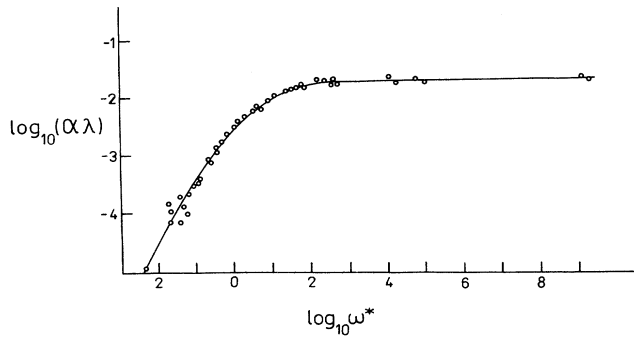


FIG. 8. Sound absorption dependence on  $\omega^*$  in the propanol–water + NaCl solution in the temperature range 10–80°C and impurity concentration from 0 to 6 mass %.

sidering the fact that

$$(t_1 t_2)^{2-a} = (\tau^2 - \Delta\tau^2)^{2-a} \quad (4)$$

and<sup>4</sup>

$$M[(T - T_0)/T_0]^2 = (H - H_0)/H_0,$$

where

$$\tau = (T - T_0)/T_0, \quad \Delta\tau = (T_{cu} - T_{cl})/2T_0. \quad (5)$$

$H = PC_0 + P_0C$  is a generalized parameter of the effect of external factors;  $H_0 = C_0P_0$ . We obtain

$$(\alpha\lambda)' / \alpha_c \lambda = \mathcal{J}(\omega^*) = \mathcal{J}\{3\omega\eta_r r_0^3 / k_B T \times [\tau^2 - (H_0 - H)/MH_0]^{2-a}\}. \quad (6)$$

The calculations showed that Eq. (6) within the experimental accuracy well describes the dependence of  $\alpha/f^2$  on  $T$  not only near the critical point line but also in the region of complete solubility when the impurity of NaCl,  $C < C_0$  (see Fig. 3). Thus the analysis of the acoustic measurement results in the propanol–water + NaCl system shows the validity of Eqs. (4) and (6) considering the effect of mutual influence (superposition) of the two phase transitions near DCP.

It is interesting to use this principle of superposition in

the three phase transitions taking place in another studied system, 2-butanol–water + propanol. According to Ref. 4 the coefficient of light scattering for the case of three phase transitions can be expressed as follows:

$$R_0 \sim \prod_{i=1}^n R_i, \quad (7)$$

$$R_0 = K[\tau^2 - (C_{01} - C)/MC_{01}]^{-\gamma} [(T - T_{c3})/T_{c3}]^{-\gamma}.$$

For a direct comparison with experimental data obtained in the system with the preset composition  $X = X_{01} \neq X_{c3}$  ( $X_{c3}$  is the composition of the third, with the lowest critical temperature, phase transition) we used the expressions obtained from (7) taking account of a simplified “linear model” of the scaling equation of the state:<sup>11,12</sup>

$$R_0 = A[\tau^2 - (C_{01} - C)/C_{01}]^{-\gamma} [(T - T_{cr})/T_{cr}]^{-\gamma}, \quad (8)$$

$$r = r_0(t_1 t_2)^{-\nu} f(X/X_{c3}) t_{cr}^{-\nu}, \quad (9)$$

where  $\gamma = 1.23$  is the critical index of susceptibility,  $T_{cr}$  is the reduced critical temperature,  $f(X/X_{c3})$  is the constant depending on  $X$ , and  $A = Kf(X/X_{c3})$ .

The results of calculations according to formulas (8) and (9) are presented in Fig. 7 by solid lines. The parameters used in calculations are given in Table I.  $R_0$  was reduced to  $R_{90}$  by the Ornstein-Zernike ratio. As is seen from Fig. 7, a satisfactory agreement of the expression (8) with the experiment has been obtained.

Accordingly, for three phase transitions, the sound absorption is

$$(\alpha\lambda)' / \alpha_c \lambda = \mathcal{J}(\omega^*) = \mathcal{J}\{3\omega\eta_r r_0^3 f(X/X_{c3}) \times [\tau^2 - (C_{01} - C)/MC_{01}]^{2-a} \times [(T - T_{cr})/T_{cr}]^{2-a}\}. \quad (10)$$

The calculations with use of Eq. (10) are presented in Fig. 4 by solid lines. Figure 4 shows that these calculations are in agreement with the results of the sound absorption measurements. As in the case of the first solution, the values of all parameters of the expression (10) were defined from independent measurements including the value of  $A$  (see Table I) found from optical measurements

TABLE I. Parameters used in the calculations using Eqs. (8) and (9).  $R_{90,max}$  is a light-scattering coefficient on the line of critical points;  $M = 40.346$ .  $T_{s3}$  is a temperature of stratification for the third phase transition.

$N/N$	Impurity concentration	$A$ (cm <sup>-1</sup> )	$R_{90,max}$ (cm <sup>-1</sup> )	$T_{cr}$ (°C)	$T_{s3}$ (°C)	$r_0$ (Å)
1	6.92	$0.797 \times 10^{-8}$	$2.578 \times 10^{-3}$	-15.8	-11.7	1.32
2	8.69	$1.031 \times 10^{-8}$	$2.803 \times 10^{-3}$	-15.4	-13.6	1.21
3	9.36	$1.686 \times 10^{-8}$	$5.630 \times 10^{-3}$	-19.8	-14.1	1.25
4	9.42	$0.989 \times 10^{-8}$	$2.745 \times 10^{-3}$	-20.8	-14.6	1.26
5	12.0	$1.430 \times 10^{-8}$	$5.660 \times 10^{-3}$	-22.4	-16.5	1.13
6	14.0	$1.560 \times 10^{-8}$	$5.660 \times 10^{-3}$	-24.2	-18.3	1.24
7	16.0	$2.770 \times 10^{-8}$	$5.660 \times 10^{-3}$	-26.6	-20.6	1.49

and  $\alpha_c \lambda = 0.0248$  from acoustic data. It is worth noticing the invariability of the critical absorption amplitude  $\alpha_c \lambda$  along the line of the critical points, including DCP, while the value of the critical part of heat capacity,  $\Delta C_p \rightarrow 0$ , in

DCP. This result implies that the thermal nature of acoustic relaxation in the critical point turns into the "bulk" one in DCP where  $dT_c/dP \rightarrow \infty$ , characterizing the system susceptibility to pressure, approaches infinity.

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