An investigation of the properties of solutions in the region where the upper and lower critical stratification points merge

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Light scattering and viscosity, and also the phase diagrams in the vicinity of the "double" critical point are investigated both experimentally and theoretically for four multicomponent solutions containing charged or polar impurities. A strong dependence of the effective critical indices on the temperature and the width of the stratification gap in the vicinity of the double critical point is observed. It is shown that this experimental observation is the result of the proximity of two second-order phase transitions. In other words, in the general case the critical properties of the system are functions of the two variables $\tau_u = (T_u - T)/T_0$ and $\tau_l = (T - T_l)/T_0$, where T_u, T_l, and T_0 are the temperatures of the upper, lower, and "double" critical stratification points. Conditions for the determination of the double critical point parameters in three-component systems are found.

A study of systems in which the upper (USCP) and lower (LSCP) critical stratification points coincide is of great interest for a number of reasons. First is the unusual and remarkable fact of the existence of such systems, in which as the pressure, the impurity content, or some other parameter of the state of the system varies, these two critical points (CP) merge into one double critical point (DCP) (see Fig. 1). Second, studies carried out in the vicinity of the CP, enable one to answer the question of the character and the interaction mechanisms of second-order phase transitions. Third, these systems are characterized by an uncommonly high sensitivity to various external influences, creating favorable conditions for a very complete and accurate verification of various fluctuation theories.[1,3] Fourth, theories have recently appeared,[4,5] which, within the framework of the phenomenological approach, make possible the realization of a reliable interpretation of a large number of experimental data for arbitrary systems characterized by the presence of two closely situated points of second-order phase transition of the same nature.

A scale-invariant theory of systems with a double critical point, based on the principle of the isomorphism of critical phenomena, was constructed by Anisimov, Voronel', and Gorodetskii.[4] They showed that the character of the behavior of the thermodynamic quantities for points along the CP line can be found from an expression for the isomorphic thermodynamic potential. In particular, the results of their calculation showed that if the approach of the system in temperature to the given critical point with temperature $T_c(h)$ (h is the parameter of external action) takes place along a path close to the normal to the CP line, then the power-law dependence of various physical quantities on the difference $T - T_c(h)$ is characterized by constant values of the critical indices. If this approach to the point $T_c(h)$ occurs along a path tangent to the CP line, then the values of the critical indices—the order parameter β, the compressibility γ, the correlation radius ν, etc.—bifurcate. The set of those $T_c(h)$ to which the approach in temperature takes place along the tangent include the double critical point.

The theory of systems with a double critical point was developed further by Sobyanin,[5] who showed that the square-root dependence of $T_c(h)$ close to the DCP reflects the parabolic temperature dependence of the coefficient a in the functional of the Landau free energy:

$$F=F_0+\int\left[\frac{a(T,h)}{2}\eta^2+\frac{b(T,h)}{4}\eta^4+\ldots+\frac{d}{2}(\nabla\eta)^2\right]dv; \tag{1}$$

here η is the order parameter, and b and d are positive coefficients. The coefficient a at each of the critical points vanishes so that it must have a minimum between these points

$$a(T,\ h)=a_m(h)+a_2(h)[T-T_m(h)]^2. \tag{2}$$

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

$$T_m(h)=\frac{T_l(h)+T_u(h)}{2}, \tag{3}$$

where T_l and T_u are the temperature of the LDCP and the UDCP. Here the coefficient a can be written in the form

$$a=-a_2(h)[T-T_u(h)][T_l(h)-T]. \tag{4}$$

It then follows from the given expressions that

$$\eta^2=-\frac{a}{2b}=\frac{a_2(h)}{2b}[T-T_u(h)][T_l(h)-T]. \tag{5}$$

If $(T_u - T_l)/(T_u + T_l) \ll \mathrm{Gi}$, where Gi is the Ginzburg number,[6] the entire stratification region is located inside the fluctuation region. In this case the functional changes its form in the following way[5,7]:

$$F=F_0+\int\left[\frac{a_0}{2}\left|\frac{a}{a_c}\right|^{2\nu-\sigma-1}\eta^2+\frac{b_0}{4}\left|\frac{a}{a_c}\right|^{\nu-2}\eta^4+\frac{d_0}{2}\left|\frac{a}{a_c}\right|^{-\sigma}(\nabla\eta)^2\right]dv, \tag{6}$$

where $\sigma \approx 10^{-2}$ is a small critical index which characterizes the behavior of the correlation function at $a = 0$, and $a_c \equiv (3k_B Tb/8\pi d^{3/2})^2$. In this case we have for the existence curve

$$\eta\sim[(T_u-T)(T-T_l)]^\beta. \tag{7}$$

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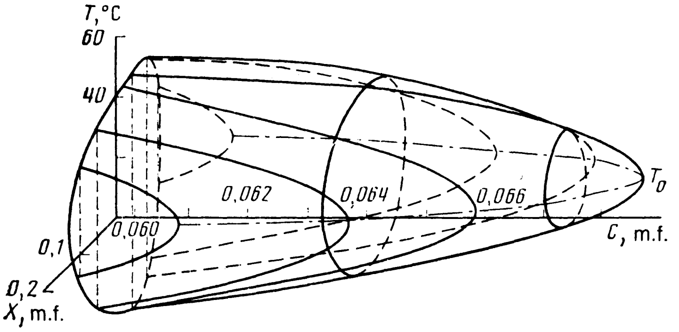

FIG. 1. Phase diagram of the solution butanol–water + HCl. The point T_0 corresponds to the DCP, the dash-dot line is the line of double points.

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

$$r_K \propto (|T_u - T||T - T_l|)^{-\nu}. \quad (8)$$

The idea of the parabolic shape of the dependence of $a(T)$ in the expression for the thermodynamic potential of the system was recently successfully applied to a quantitative description of the anomalous temperature behavior of a large number of properties of a segnet salt.[8,9] As to multicomponent solutions with a double critical point, a detailed investigation of their properties was initiated in Refs. 10 and 11, where a solution of guaiacol–glycerol + water served as the object of study.

The aim of the present article was, first of all, to carry out a study of fairly new classes of solutions which have a double critical stratification point, including systems with various charged impurities, which provide not only the effect of merging of the critical points, but also their separation, and secondly, to carry out an experimental investigation of the dependence of the shape of the coexistence curves, and of light scattering and viscosity, as a function not only of temperature, but also of the concentration of the impurities. As systems with charged impurities we used the solutions I) propanol–water + NaCl, and II) butanol–water + HCl; as specimens with uncharged impurities, the systems III) methy ethyl ketone–water + 1,4-dioxane, and IV) fluorobutanol–water + propanol.

1. PHASE DIAGRAMS

Phase diagrams of these systems were obtained by visual observation of the formation of a meniscus in a closed vessel located in a thermostat. The accuracy of measurements of the phase transition temperature was ± 0.1 K. The temperature range of the measurements was − 30 °C to 150 °C. Reagents of chemically pure grade were used as the components of the indicated systems and were subjected to additional purification and redistillation.

Figure 1 shows the X, C, T-phase diagram (X is the concentration of the first component in water in mole fractions (m.f.), C is the concentration of the impurity in the solution in m.f., and T is the temperature). In the T, C coordinate plane are shown the lines of the upper and lower stratification points, which taken together form a closed surface isolating the two-phase, ordered region–stratification gap from the single-phase, distorted region. A characteristic feature of these diagrams is the presence of lines of double points (the dash-dot line in Fig. 1), separating the stratification surface into two parts with upper T_u and T_l stratification temperatures.

The position on the line of double points of the double critical point DCP, at which the upper and lower critical points merge, has not been previously determined, and, as a rule, it does not coincide with the vertex of the surface of the stratification points. Thus, the determination of the parameters of the DCP (T_0, X_0, and C_0) is an independent experimental problem. For the solution of this problem we made use of the condition that the DCP coincide with the "folding" point, i.e., the point of intersection of the lines of the double points and the critical points, which is characterized by a composition of the solution X_0 such that the phase mixture passes through the middle of the volume as the temperature varies.[12]

We found the temperature T_0 of the DCP from the plots of the experimental values of the temperatures of the double points T_d vs X, which are shown in Fig. 2. As can be seen from the figures, the position of the DCP on the $T_d(X)$ curve always corresponds to the segment with minimal slope, i.e., it coincides with the minimum of dT_d/dX, at which $d^2T_d/dX^2 = 0$. It may be noted that this condition, being a consequence of symmetrization of the phase diagram in the vicinity of the DCP, was satisfied without exception in a number of other systems which we investigated. It can therefore be used as an accurate and simple method for estimating all of the DCP parameters, no less accurate than the method based on the determination of the folding point. On the basis of our measurements the DCP parameters for normal pressure have the following values:

Solution I: $X_0 = 0.15$; $T_0 = 45.1$ °C; $C_0 = 0.02314$;

Solution II: $X_0 = 0.10$; $T_0 = 26.3$ °C; $C_0 = 0.0683$;

Solution III: $X_0 = 0.21$; $T_0 = 61.1$ °C; $C_0 = 0.0567$;

Solution IV: $X_0 = 0.10$; $T_0 = 51.8$ °C; $C_0 = 0.0392$.

The role of the impurity in these systems is twofold: increasing it can lead both to convergence (solutions II, III, and IV) and to divergence (solution I) of the upper (T_u) and lower (T_l) critical temperatures. It may be noted that for these systems an increase in the pressure P close to the DCP always caused T_u and T_l to draw together into the DCP. Away from the DCP the solution can exist only in the homogeneous state (the region of the absolute solubility).

It has already been noted that the position of the DCP in the systems under investigation does not coincide with the vertex of the bounding surface constructed in the physical coordinates T, X, and C. This is due to the fact that the values of X_0 do not correspond to an extremum point on the equilib-

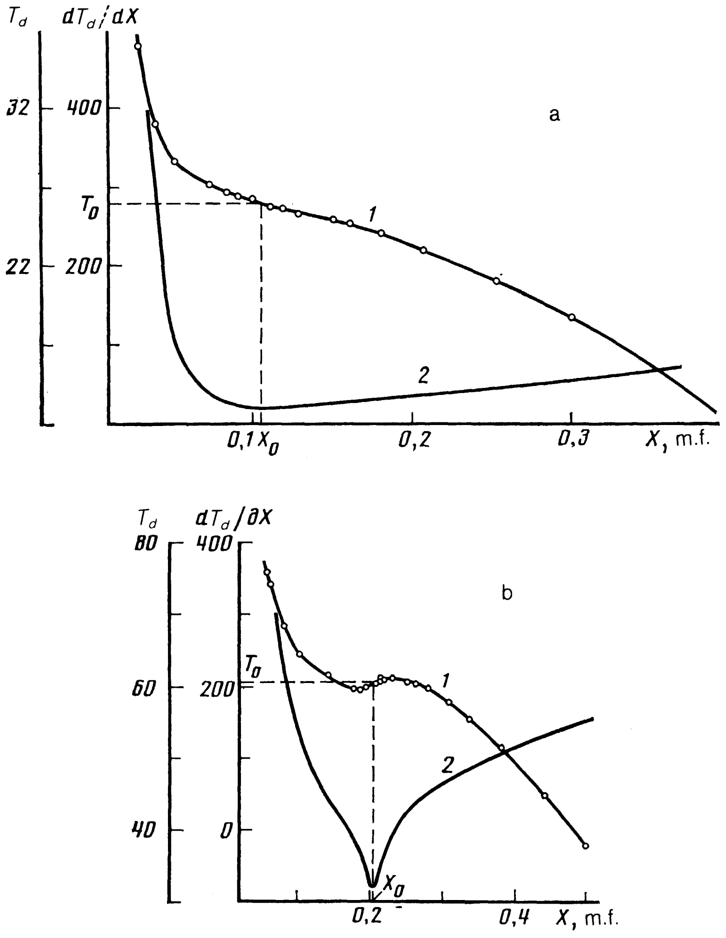

FIG. 2. Dependence of the temperatures of the double points T_d (curve 1) and of dT_d/dX (curve 2) on X: a) solution of butanol–water + HCl. b) solution of methyl ethyl ketone–water + 1,4-dioxane.

rium curve $X(C)$ (Fig. 3). This asymmetry is a consequence of the asymmetric distribution of the concentration of the impurity C between the phases of the solution during its stratification. For the same reason the connecting lines between the points a and b,c and d, and k and l on the curve $X(C)$ (Fig. 3), which correspond to the concentrations of the existing phases, are not parallel to the X axis. Herein lies an important difference between the phase diagram of solutions with impurities and binary systems close to the DCP. In the latter the connecting lines on the $X(P)$ curve are always parallel to the X axis. A solution which contains impurities behaves like a quasibinary solution in the case when the solubilities of the impurity in both components of the solution are the same (this case is extremely rare). We note, however, that the investigated solution of butanol–water + HCl is close to binary since the value of X_0 for this solution differs little from the value of the maximum of the $X(C)$ curve.

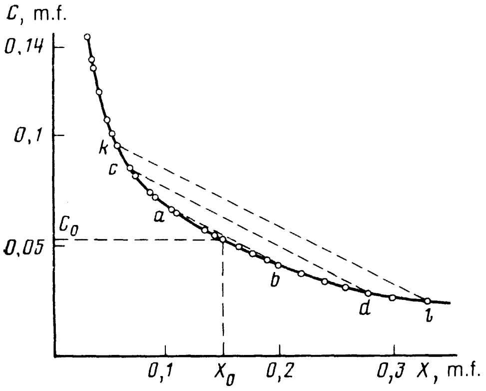

FIG. 3. Dependence of the impurity concentration C on the composition X of the solution propanol–water + NaCl.

In the ideal case of a quasibinary solution the shape of the existence curves in the coordinate X, T; C, X; C,T; and P, T close to the DCP (sections of the phase diagram of the solution butanol–water + HCl, Fig. 1) can be approximated by power laws[13]:

$$(X_a-X_b)\propto(T_c-T)^{\beta_T}, \tag{9}$$

$$(X_a-X_b)\propto(C_c-C)^{\beta_C}, \tag{10}$$

$$(T_c-T_0)=B(C_c-C_0)^{\beta_0}, \tag{11}$$

$$(T_c-T_0)=D(P_c-P_0)^{\beta_P}, \tag{12}$$

where β_T,β_C,β_0, and β_P are the critical indices, T_c,P_c, and C_c are the critical temperature, pressure, and impurity concentration, B and D are constants, $X_a - X_b$ is the difference of the concentrations of the corresponding phases a and b (the order parameter). From this follows the relation between the indices of the order parameter at the DCP

$$\beta_C=\beta_0\beta_T. \tag{13}$$

The results of our experiments (see Table I) and also the results of Ref. 11 show that in all of the investigated systems without exception the index β_0 is equal within the limits of experimental error to 0.5. This result according to

TABLE I.

System	$\beta_{T,1}/\Delta T$, °C	$\beta_{T,2}/\Delta T$, °C	β_P^*	β_0/X, m.f.	B, K/X, m.f.	D, K·Pa$^{-1/2}$
Propanol–water + HCl	0.40/50 0.38/30 0.38/10	0.34/50 0.37/30 0.35/10	0.50	0.51/0.05 0.51/0.10 0.52/0.20 0.50/0.30	–	$6.11\cdot10^{-3}$
Butanol–water + NaCl	0.40/50 0.38/30 0.37/10	0.33/50 0.35/30 0.36/10	0.50	0.50/0.05 0.49/0.07 0.51/0.10	448/0.05 455/0.07 455/0.10 446/0.20	$5.1\cdot10^{-3}$
Methyl ethyl ketone–water + 1,4-dioxane	–	–	0.50	0.50/0.10 0.45/0.15 0.50/0.20 0.51/0.30	372/0.20	$9.0\cdot10^{-3}$

* for $X=X_0$.

Eq. (13) implies a doubling of the index β_T, which agrees with the predictions of theory.[4,5,14]

It is obvious that the direct implementation of Eq. (9) to determine the index β_T is difficult. In fact, being the equation of a parabola, expression (9) can be valid only in a very small neighborhood of T_u and T_l and cannot be used for the description of every T–X-diagram close to the DCP, which has a nearly elliptical closed shape (see Fig. 1).

It is natural to assume that the observed shape of the T–X equilibrium curve is due to the proximity of the critical temperatures T_u and T_l which correspond to the two phase transitions and determine the limit of stability of the system. Consequently, the shape of the boundary curve turns out to be a function of two variables which depend on the proximity of the system temperature T to T_u and T_l. In this case a description of the boundary curve in the T-X plane which is in complete agreement with Eq. (7) can be based on the expression

$$A(X_a-X_b)=|T_B-T|^{\beta_{T,1}}|T_H-T|^{\beta_{T,2}}. \tag{14}$$

In the particular case when the system is found at T_0 and $\beta_{T,1}=\beta_{T,2}=\beta_T$ we have $A(X_a-X_b)=|T_B-T_0|^{\beta_T}|T_l-T_0|^{\beta_T}=|T_0-T_c|^{2\beta_T}$; assuming that

$$L(X_a-X_b)=(C_c-C_0)^{\beta_C},$$

we obtain

$$(T_0-T_c)=\frac{A}{L}(C_c-C_0)^{\beta_C/2\beta_T};$$

and since $\beta_0=0.5$, $\beta_C=\beta_T$. As the investigations have shown, the shape of the boundary curve in the TX plane which was obtained experimentally in the solution butanol–water + HCl is quite accurately described by Eq. (14).

Thus, Eq. (14), which expresses the principle of superposition of phase transitions, allows a description of the T–X phase diagram in which the value of β_T remains unchanged.

However, in order to obtain the true values of the critical indices in a real solution which contains an impurity as its third component, it is necessary when finding the boundary curve to maintain those experimental conditions which hold when the composition of the solution in the two-phase region is varied along the connecting line (see e.g., Fig. 3) i.e., when the chemical potential of the system at constant temperature μ_T is kept constant, but C varies (the condition $\mu_T=$ const is automatically satisfied in the case of a binary solution). Since the determination of such compositions in a three-component system does not yield to calculation, the problem was solved experimentally. First, a solution with prescribed value of $\Delta T=T_u-T_l$ was prepared. Its stratification into two phases and their separation were carried out in a thermostat at constant temperature T_0. Solutions prepared in this way with different concentrations of the components, but equal values of μ_T, served as the starting solutions. By mixing them in different proportions it was possible to obtain compositions of intermediate concentrations which satisfied the condition $\mu_T=$ const. The determination of the concentrations of the components in the starting solutions, which was needed for the calculation of the intermediate compositions, was carried out by methods of qualitative chemical analysis.

The composition–stratification temperature diagrams thus obtained are shown in Fig. 4, and the values of the critical indices of the order parameters $\beta_{T,1}$, $\beta_{T,2}$, β_P, and β_0, and also the coefficients B and D, which were determined by

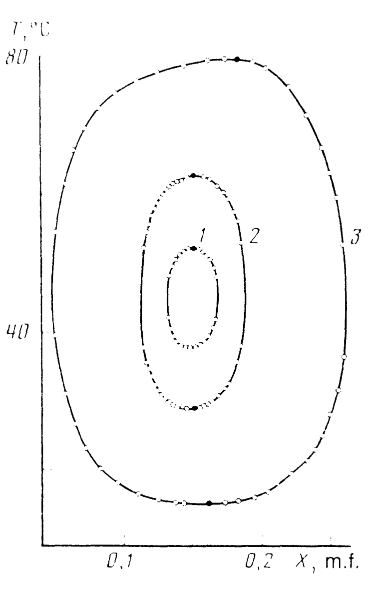

FIG. 4. T–X-Diagram of the equilibrium of the solution propanol–water + NaCl. The curves correspond to $\Delta T=14.5$ °C (1), 34 °C (2), and 64.2 °C (3).

approximation by formulas (12),(14), are displayed in Table 1. The range of values of $\tau_c = (T - T_c)/T_c$ of the approximation was 10^{-3}–10^{-1}.

It follows from Table I that a) in all of the investigated systems the index β_T lies within the limits 0.34 to 0.38 and is close to the value 0.36 obtained for the binary impurity-free solution butanol–water, b) within the limits of experimental error the numerical values of the indices were preserved both near the DCP and far from it, c) it is characteristic that the values of β_T for the upper critical points, and d) the critical indices of the external action β_0 and β_P are equal. Generalizing from this, it is possible to conclude that the region of the DCP, like the region of connected upper and lower critical points, is described by fluctuation theory.

2. LIGHT SCATTERING

In the investigations of the concentration and temperature dependences of light scattering we used a cuvette with a diameter of 40 mm, and in the investigations of its pressure dependence we used a tubular cell with outer diameter 10 mm and inner diameter 3 mm which possessed the necessary mechanical strength. The pressure in the cell was produced by a compressed gas and transferred to the liquid across a flexible fluoroplastic membrane. The accuracy of measurement of the pressure was 0.05 atm. The accuracy of thermostasis was 0.01 °C. The scattering indicatrix was measured at the wavelengths 546 and 632.8 μm for scattering angles from 20° to 160° for vertically polarized light. As a result of the measurements, a correction was introduced to the light extinction. Benzene and acetone were used as calibrating liquids.

The measurements showed that the angular distribution of the reciprocal of the coefficient of light scattering R_θ in the investigated solution obeys the Ornstein–Zernike formula:

$$R_\theta^{-1}=R_0^{-1}+R_0^{-1}r^2\left(\frac{4\pi}{\lambda}\right)^2\sin^2\frac{\theta}{2}, \qquad (15)$$

where r is the correlation radius, λ is the wavelength of the incident light, θ is the scattering angle, and R_0 is the coefficient of light scattering at $\theta = 0$.

According to fluctuation theory, the intensity of light scattering

$$R_0 \sim \tau_c^{-\gamma} \qquad (16)$$

where $\tau_c = (T - T_c)/T_c$ is the reduced temperature, γ is the critical index, and T_c is the critical stratification temperature (upper or lower).

It is of interest to explain the applicability of relation (16) in vicinity of the DCP. Figure 5 shows the results of our measurements of the dependence of $\ln R_0$ on $\ln \tau_c$; the values were found by extrapolation of the experimental values of R_θ to zero scattering angle by Eq. (15). On the same figure are shown the results obtained in Ref. 11.

Note that the dependence of $\ln R_0$ on $\ln \tau_c$ deviates from a straight line and that the deviation is significantly greater than the experimental error. This fact points to the fact that Eq. (16) is inapplicable in the DCP region since γ becomes a variable quantity which strongly depends on both $\Delta\tau = (T_u - T_l)/2T_0$ and τ_c.

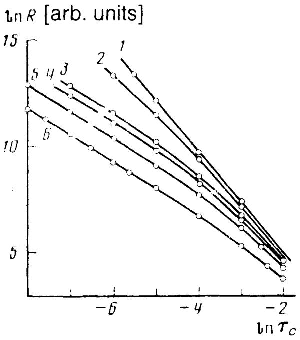

FIG. 5. Dependence of the logarithm of the coefficient of light scattering on $\ln \tau_c$. The curves correspond to $\Delta\tau = (T_u - T_l)/T_0 \approx 0(1)$, 0.029 (2), 0.04 (4), 0.078 (5), and 0.196 (6).

It is natural to suppose that the above-noted fact of the inapplicability of expression (16) in the DCP region is a consequence of the proximity of the two phase transitions corresponding to the upper and lower critical points, as a result of which the system finds itself under their combined influence. One can further hypothesize that the critical parameters of the system near the DCP are functions of the independent variables, namely $\tau_1 = (T_u - T)/T_0$ and $\tau_2 = (T - T_l)/T_0$, which characterize the proximity of the system to the critical states with the upper and lower critical temperature, respectively. Hence we have

$$R_0=K\tau_1^{-\gamma}\tau_2^{-\gamma}. \qquad (17)$$

Analysis has shown the universality of expression (17), which with a high degree of accuracy describes the temperature dependence of light scattering over the entire vicinity of the DCP (Fig. 6). As can be seen from Fig. 6, the values of $\ln(R_0/K)$ for various values of $\ln(\tau_1\tau_2)$ lie on a single straight line which is characterized by one and the same critical index $\gamma = 1.24 \pm 0.03$.

Thus, the universality of relation (17) confirms our initial hypotheses about the superposition of critical phenomena in the vicinity of the DCP which are due to phase transitions in solutions with upper and lower critical points.

Let us generalize expression (17) for the case in which both the external action and the temperature vary. For this purpose we write relation (17) in the form

$$R_0=K(\tau^2-\Delta\tau^2)^{-\gamma}, \qquad (18)$$

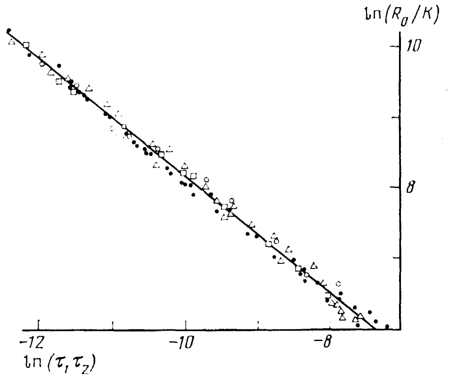

FIG. 6. Dependence of the reduced values of the logarithm of the coefficient of light scattering R_0/K on the logarithm of the product $\tau_1\tau_2$ for solutions (●) butanol-water + HCl, (○) propanol-water + NaCl, (△) methyl ethyl ketone–water + 1,4-dioxane, (□) guaiacol–glycerol-+ water.

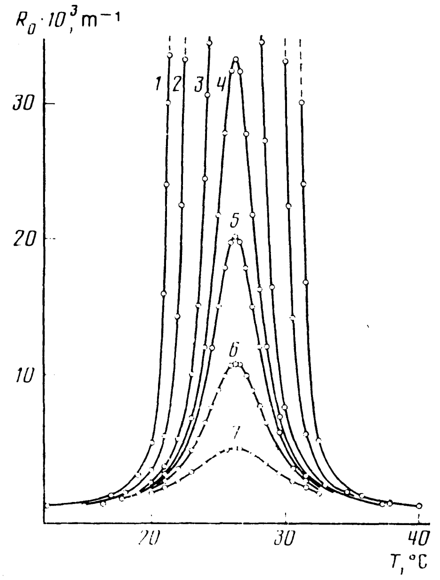

FIG. 7. Temperature dependence of the coefficient of light scattering R_0 in the vicinity of the DCP for various values of the external-action parameter $H \cdot 10^{-6}$, Pa; 1) 37.401, 2) 37.431, 3) 37.467, 4) 37.478, 5) 37.483, 6) 37.492, and 7) 37.520. The solid lines correspond to theory, the points represent the results of experiment for the solution butanol–water + HCl.

where $\tau = (T - T_0)/T_0$. Further, taking into account the relation

$$M\left(\frac{T-T_0}{T_0}\right)^2 = \frac{H_0-H}{H_0},$$

where $H = PC_0 + CP_0$ is the generalized action parameter and $H_0 = C_0P_0$, we have

$$R_0=K\left(\tau^2 - \frac{H_0-H}{MH_0}\right)^{-\gamma}; \qquad (19)$$

and in particular case of fixed $\tau = 0$, i.e., for $T = T_0$, we obtain

$$R_0=K\left(\frac{H-H_0}{H_0M}\right)^{-\gamma} = q\left(\frac{H-H_0}{H_0}\right)^{-\gamma}. \qquad (20)$$

It proved to be the case that expression (19) describes the temperature dependence of the light scattering not only near the UDCP, the LDCP, and the DCP, but also in the region of absolute solubility.

Figure 7 shows an analysis of the experimental data based on Eq. (19) in which the curves which have a finite maximum (4, 5, 6, 7) correspond to the region of absolute solubility, the divergent curves 3 correspond to the DCP, and curves 1 and 2 correspond to the stratification region.

It should be noted that the temperature dependence of the intensity of the scattered light in the region of absolute solubility can also be described with the help of Eq. (18). In this case the last term of Eq. (18) should satisfy the condition $\Delta\tau^2 < 0$, which requires the introduction of imaginary upper and lower critical temperatures. The appearance of imaginary upper and lower critical temperatures can signify the existence of a complex phase diagram which is a continuation of the real phase diagram into the region of absolute solubility, in which the lines of the upper critical temperatures lie below the lines of the lower critical temperatures. This condition can signify the absolute solubility of the components of the solution.

Taking into account the Ornstein–Zernike approximation $R_0^{-1}r^2 = \text{const}$ and relation (17), we obtain an expression for the dependence of the correlation radius on the temperature in systems with upper and lower critical points:

$$r=r_0(\tau_1\tau_2)^{-\gamma/2}=r_0(\tau_1\tau_2)^{-\nu}. \qquad (21)$$

In Table II are displayed the calculated values of the radius of close correlation r_0 and also the values of the scaling coefficients.

Thus, the constancy of the numerical values of the index γ and the correlation radius r_0 near the DCP on the lines of the USCP's and the LSCP's which correspond to the three-dimensional Ising model of fluctuation theory points to the isomorphism of the chosen thermodynamic variable $\tau_1\tau_2$.

3. SHEAR VISCOSITY

Studies of the temperature and concentration dependence of the shear viscosity η_s allow the validity of the predictions of dynamic scaling in the vicinity of the DCP to be verified and values of the characteristic relaxation times of the concentration fluctuations to be calculated (from the data on the correlation radius). In addition to this, we set ourselves the goal of verifying the universality of the principle of superposition of phase transitions in the vicinity of the DCP.

We measured the viscosity with a capillary viscosimeter with a suspended level which was modified for measurements in stratified systems; its accuracy was 0.2%. The accuracy of thermostasis was ± 0.01 °C, and was ensured by a two-circuit scheme of thermostasis using liquid thermostats.

In order to transform the results of the viscosimetric measurements into values of the dynamic viscosity η_s, pycnometric and dilatometric measurements of the density ρ were made. The accuracy of the measurements, $\Delta\rho/\rho$, was $\sim 10^{-5}$. The results of the measurements showed that to within the indicated limits of accuracy the behavior of the density in the vicinity of the DCP has no noteworthy peculiarities and obeys a linear law.

The results of measurements of the viscosity as a function of temperature at $X = X_0$ and various ΔT in the solutions showed that two well-defined maxima are observed on

TABLE II.

System	$K \cdot 10^8$, cm^{-1}	C_0, m.f.	P_0, MPa	M	r_0, Å
Butanol–water + HCl	14	0,068	543	6.26	**4,1**
Propanol–water + NaCl	3.7	0.023	177	−15,64	**3,1**
Methyl ethyl ketone–water + 1,4-dioxane	1,8	0,057	80	13,8	**2,9**

the viscosity curve, which correspond to the upper and lower stratification points, and that as ΔT decreases the two maxima merge into one, which corresponds to the DCP. It is typical that the total width of the fluctuation region, including the two maxima, increases with approach to the DCP (with decrease of ΔT). Far from the stratification points the dependence of the logarithm of the viscosity on the inverse temperature is described by a trace which is close to a straight line, i.e., it is characterized by a temperature dependence of Arrhenius type.

In the solution under consideration the temperature is not the only thermodynamic variable of the system, but the concentration of the impurities, which can be considered as sources of a field which modifies the structure of the solution and causes the phase transition, is also a thermodynamic variable of the system. In this connection we carried out investigations of the behavior of the viscosity as a function of the concentration of the impurities C. As the measurements showed, close to C_0 an anomalously sudden growth of the viscosity is observed, however in the immediate vicinity of the DCP the experimental values of the viscosity remain finite (reasons limiting the growth of the viscosity in the vicinity of the DCP will be discussed below). The maximum value (obtained in the experiments) of the excess part of the viscosity $\Delta\eta$ with respect to the regular viscosity η_P was 15%. Upon variation of the composition of the solution by varying the concentration X by the graph of $\Delta\eta_s$ passes through a narrow maximum at $X = X_0$.

An initial analysis of the results was carried out in terms of the theory of interacting modes,[15,16] predicting a divergence of the viscosity near the critical point:

$$(\eta_s-\eta_P)/\eta_P=\chi_\eta \ln(q_D r)=\ln R-V\ln\tau_c, \qquad (22)$$

where $R = q_D r_0$ is a constant, V is the critical index of viscosity, $r = r_0(r_c)^{-\nu}$ is the correlation radius in the critical region, ν is the critical index of the correlation radius, q_D is a constant which has the dimensions of inverse length, and $\chi_\eta = V/\nu$.

An analysis of the results of the viscosity measurements based on Eq. (22) was carried out in the range of values where the secondary effect responsible for the finiteness of the values of the viscosity at the CP has still not appeared. This effect is connected with the interaction between the concentration fluctuations and the gradient of the viscous flow velocity, which arises when the viscosity is measured.[17] In our experiments this region was $10^{-3}<\tau_c<10^{-1}$ at $\Delta T\approx 0$ and $10^{-5}<\tau_c<10^{-1}$ as $\Delta T\to\infty$ (the case of a combined critical point). Analysis shows that the effective index V which was obtained in the investigated solutions increases as the width of the stratification region ΔT decreases. The dependence $V(\Delta T)$ in the solution propanol–water + NaCl (Fig. 8) turned out to be analogous to a previously obtained dependence[10] for the solution guaiacol–glycerol + water, which has a double critical point. As can be seen from the results presented in Fig. 8,

$$\lim_{\Delta T\to\infty}\frac{V(0)}{V(\Delta T)}=2.$$

Hence it is possible to speak of a doubling of the critical index at the DCP.

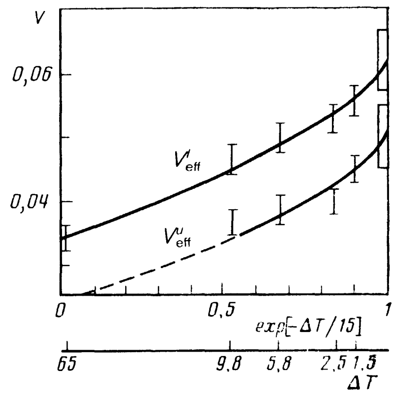

FIG. 8. Dependence of the effective indices of viscosity for the upper and lower critical points V^u_{eff} and V^l_{eff} on the width of the stratification region ΔT in the solution propanol–water + NaCl.

The behavior of the excess viscosity $\Delta\eta/\eta$ of the system during the measurement of the impurity concentration C was approximated by formula (22), in which the quantity

$$\tau(C)=(C-C_c)/C_c.$$

served as the thermodynamic variable.

The region of approximation near the DCP correspond to the interval $10^{-3}<\tau(C)<10^{-1}$, and the values of the quantities V and R were respectively 0.034 ± 0.004 and 0.9. These results show that when the state of the system is varied by varying the concentration of the impurities the value of the critical index of viscosity coincides to within the experimental error with its critical value. The results of the viscosity measurements were analyzed further with the help of the formula

$$\eta_s=\eta_P(\tau_1)^{-V}(\tau_2)^{-V}, \qquad (23)$$

where

$$\eta_P=\eta_0\exp a_P(T+b_P)^{-1}, \qquad (24)$$

which follows from the theory of the renormalization group[18] and was generalized by us to the case in which two phase transitions are superposed in solutions with a DCP.

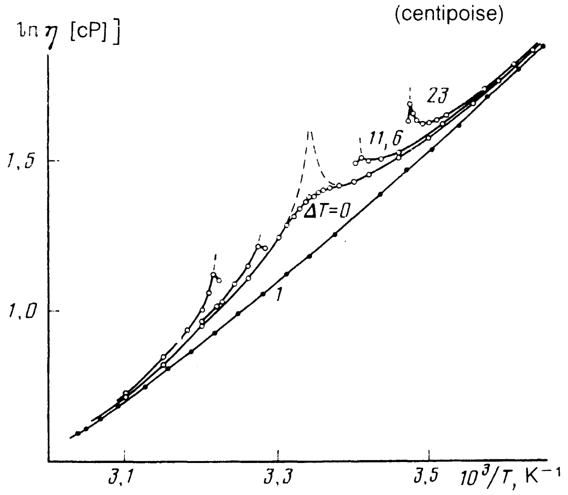

FIG. 9. The viscosity in the solution butanol–water + HCl for various values of ΔT.

Figure 9 shows the results of approximation by Eq. (23) of the data obtained in the solution butanol–water + HCl. It can be seen that the approximation gives good agreement with experiment over a wide interval about the DCP with the exception of the immediate vicinity of the critical temperatures, where the phase transition is smeared out under the influence of the viscous flow which is necessary to allow the shear viscosity to be measured. The regular part of the viscosity, represented in the form (24), was determined experimentally in a solution containing an admixture of HCl in an amount slightly greater than that necessary to bring on the DCP. In this case the viscosity of the solution, which was in the region of absolute solubility of the components, did not contain a singular component (curve 1, Fig. 9).

Analysis of the experimental data shows that the temperature dependence of the viscosity in the solution butanol–water + HCl in the vicinity of the DCP can be described by a law which allows for the proximity of the state of the system to the two phase transitions corresponding to the upper and lower critical points in the form (23) with a fixed value of the critical index $V = 0.038 \pm 0.002$ and numerical values of the constants $\eta_0 = (2.35 \pm 0.10)$ cP, $a_P = (560 \pm 40)$ K, and $b_P = (128 \pm 5)$ K.

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