Temperature dependence of the correlation radius of concentration fluctuations in guaiacol-glycerin solution near the double critical point

S. V. Krivokhizha and O. A. Dugovaya

P. N. Lebedev Physics Institute, Russian Academy of Sciences

(Submitted 22 June 1992)
Zh. Eksp. Teor. Fiz. **103**, 115–124 (January 1993)

The temperature dependences of the viscosity and correlation radius of concentration fluctuations in guaiacol-glycerin solutions with different phase-separation regions, right up to $\Delta T = 0.01$ °C, were obtained. It is shown that the critical exponent ν of the correlation radius ranges from 0.63 for $\Delta T = 39$ °C to 0.53 for $\Delta T = 0.01$ °C. The measurements were performed by the correlation-spectroscopy method.

1. INTRODUCTION

Critical solutions with an upper critical point have been studied experimentally for a large number of solutions, and the basic physical features of this phenomenon have been determined qualitatively and quantitatively.[1–4] Solutions with a lower critical point have also been studied, though there are fewer such works.[4–8] Solutions (or mixtures) having a closed phase-separation region or loop in the temperature (T) versus concentration (C) plane have been studied even less. Such systems have both upper and lower critical points. Examples are Rochelle salt,[9] a mixture of gases (Ne–Xe),[10] as well as liquid solutions[11–13] such as β-picoline in water with additions of salts or heavy water,[14–17] higher alcohols in water with an addition of salts,[18] and glycerin-guaiacol.[19–25] The latter solution has a number of remarkable properties, some of which are still not understood and are apparently typical of all other systems of this type. It is this solution that became the subject of our experimental investigation, described below.

It should be noted that if the solution components are pure and, most importantly, as much water as possible is removed from both components, then the glycerin-guaiacol solutions are homogeneous for any concentration and temperature. If, however, a small amount of water is added to the glycerin-guaiacol solution, then there appears in such a solution a closed region within which the solution separates into two phases, and the more water added, the larger the region in the (T, C) plane is.

Thus, in the case under consideration, in the coordinates (T, C, C_W), where C_W is the water concentration, the coexistence curve of the separated and homogeneous media is no longer planar but a three-dimensional surface.[19]

The upper and lower critical points become the upper and lower lines of critical points, and the point at which these lines meet forms the double critical point.

Thus a glycerin-guaiacol solution and solutions similar to it are valuable objects for studying critical phenomena in the region of the upper and lower lines of critical points and in the immediate vicinity of a double critical point.

Our aim here is to investigate the behavior of the correlation radius r_c of the concentration fluctuations near the upper and lower critical points in a glycerin-guaiacol solution by the method of correlation spectroscopy for phase-separation regions of different sizes (with respect to the temperature and the critical concentration of the guaiacol), to study experimentally in such samples of solutions the behavior of the shear viscosity η near the upper and lower lines of critical points and especially near the double critical point, to determine the background viscosity, and to determine the qualitative effect of some external conditions on the sizes (with respect to the temperature) of the phase-separation regions.

The temperature dependence of the correlation radius of the concentration and viscosity fluctuations cannot be measured directly, but to determine them it is necessary to use definite models and modern-theory formulas which follow from these models. If it was found that the experimental results could be analyzed by two different methods, both methods were used.

Since new approaches to the analysis of the experimental data may appear in the future, we present the experimental data as completely as possible.

In our experiments the correlation functions were measured and the widths of the central or Rayleigh line in the scattered-light spectrum were extracted from them. The temperature dependence of the shear viscosity was measured viscosimetrically.

2. EXPERIMENT

The temperature dependence of r_c was investigated in eight solutions with the help of light scattering. The shear viscosity was also measured in eight solutions. The sizes of the regions of phase separation are given below in Tables I and II.

Analytical grade glycerin, dried by evacuation at a temperature 97–99 °C for 6 h, was used to prepare these solutions. The residual water content in the glycerin was 0.45 vol.%. The guaiacol (commercial sample) was purified by repeated, successive vacuum distillation and recrystallization from the melt at 26–27 °C. (We note that glycerin absorbs water avidly while guaiacol is virtually insoluble in water.) Twice-distilled water was used as a small additive forming a closed region of phase separation in the (T, C) plane.

We determined the critical density of the glycerin from the maximum intensity of scattered light from 1 °C up to the phase-separation temperature. It was found to be 47.05 vol.% in a dry solution.

1063-7761/93/010062-06$10.00

TABLE I. Results of analysis of the viscosity measurements.

ΔT, °C	$X_\eta \nu \cdot 10^{-2}$	$X_\eta \ln (Q_0 r_0)$	X_η	Q_0^{-1}, Å
0 (DCP)	−3,25±0,19	−0,225±0,014	0,0664	115,5
1,41	−3,95±0,07	−0,224±0,006	0,0666	54,9
2,90	−3,97±0,11	−0,222±0,009	0,0648	49,8
3,20	−3,81±0,16	−0,208±0,013	0,0620	45,8
5,87	−4,19±0,13	−0,218±0,012	0,0671	37,1
8,73	−3,98±0,15	−0,200±0,014	0,0632	32,9
25,7	−3,56±0,23	−0,169±0,019	0,0565	26,9
40,0	−3,50±0,13	−0,154±0,010	0,0553	21,06

Dust was removed from the solutions in a dry-nitrogen atmosphere filtered through Millipore FGLP teflon filters with pore diameter 0.20 μm. Optical cells, made from optically quality quartz tubes 2.8 cm in diameter, were filled with the same solution.[1)] The solutions in the cells were frozen and the vessels were evacuated with a forevacuum pump and sealed. The solution-filled cells were placed in a thermostat.

The half-width Γ of the Rayleigh line, which, near the critical points, depended strongly on the correlation radius of the concentration fluctuations, was determined by measuring the correlation functions of the scattered light with the help of a Malvern Instruments K7023 correlator, as described previously in Refs. 8 and 24.

The temperature dependence of the viscosity was measured to within 0.2% with the help of a Hoeppler viscosimeter and the refractive index was measured to within ± 0.001 with the help of an RF-22 Abbe refractometer.

During the measurements of Γ and η the temperature was maintained constant to within 0.02 °C. The temperature difference ΔT was measured to within $(0.01 \pm 0.002\ \Delta T)$ °C. The value of Γ was measured for each temperature at several scattering angles θ. The accuracy of the measurements of $\Gamma(\theta)$ was not worse than 2.5%.

The effect of double scattering, estimated on the basis of the results of Ref. 26, is significantly smaller than the experimental error and can be neglected.

The critical phase-separation temperatures were determined on the basis of the vanishing of a beam passing through the cell or on the basis of the solution becoming opaque.[2)] The cell temperature changed by not more than 0.1 °C/min, and as a rule the rate was an order of magnitude slower.

3. THE DEPENDENCE OF THE WIDTH OF THE CENTRAL RAYLEIGH SCATTERING LINE ON THE VISCOSITY AND ON THE CORRELATION RADIUS OF THE CONCENTRATION FLUCTUATIONS: BASIC FORMULAS OF THE THEORY

The interacting-mode theory[27–34] an the renormalization-group theory[35] yield a basic relation between the half-width Γ of the central Rayleigh line of the light scattered in the solution in the critical region, and other physical quantities which can be measured or computed.

This basic relation can be written as follows:

$$\Gamma = \Gamma_B + \Gamma_C = D_B q^2 (1 + x^2) + D_C R q^2 K(x). \qquad (1)$$

Here Γ_B, Γ_C, D_B, and D_C are, respectively, the background (B) and critical (C) parts of the linewidth Γ and the background and critical mutual diffusion coefficients D; $q = |\mathbf{q}_S - \mathbf{q}_L|$, where $\mathbf{q}_S$ and $\mathbf{q}_L$ are the wave vectors of the scattered and exciting light, respectively; $x = qr_c$, where r_c is the correlation radius of the density fluctuations; $R = 1.027$; 2.36, $K(x)$ is the Kawasaki function:[27,28]

$$K(x) = {}^3/_4 x^{-2} [1 + x^2 + (x^3 - x^{-1}) \arctan x], \qquad (2)$$

$$D_C = \frac{kT}{6\pi\eta r_c}. \qquad (3)$$

The background part of the mutual diffusion coefficient, obtained in Ref. 37, is described by the relation

$$D_B = \frac{kT}{16\eta_B r_c} \frac{1}{q_c r_c}, \qquad (4)$$

where η_B is the background star viscosity and q_C can be obtained from the relations[37]

TABLE II. Results of analysis of measurements of Γ and the viscosity data ($q_D^{-1} = 4.5$ Å).

ΔT, °C	ν	r_0, Å	X_η	Q_0^{-1}, Å
0,01	0,529±0,005	3,94±0,16	0,0592	113,4
0, 42	0,550±0,008	3,12±0,21	0,0670	99,2
1, 24	0,575±0,005	2,25±0,09	0,0667	59,0
1, 32	0,601±0,006	1,88±0,10	0,0665	59,3
7,74	0,619±0,010	1,46±0,12	0,0650	34,7
32,67	0,651±0,021	1,33±0,19	0,0563	27,0
39,9	0,611±0,011	1,63±0,14	0,0571	24,1
65,5	0,633±0,004	1,17±0,03	0,0539	17,9

$$Q_0^{-1}=2e^{-4/3}q_0^{-1},\quad q_0^{-1}=q_c^{-1}+q_D^{-1}, \tag{5}$$

where the dimension of q_D and Q_0 is that of the wave vector. An estimate of q_D will be given below, and Q_0 can be obtained from the temperature dependence of the viscosity[37]

$$\eta/\eta_B=(Q_0r_c)^{X_\eta}, \tag{6}$$

where X_η is the critical exponent of the viscosity.

It has been established that the formulas of the interacting-mode theory, which have been presented above, describe the experimental data well in a wide range of values of qr_c ($0.1\leqslant qr_c<20$) for solutions[2,3,36] and for individual liquids.[38–40]

4. ANALYSIS OF THE MEASUREMENTS

The correlation radius r_c can be determined with the help of the formulas (1)–(5) from the values of the half-width Γ of the Rayleigh line, the refractive index n, and the temperature dependence of the viscosity, if $qr_c\lesssim 1$. For $qr_c\gg 1$ Γ no longer depends on qr_c and only the dependence $\Gamma\propto q^3$ remains. In order to describe the temperature dependence of r_c we employed the expression[18]

$$\begin{gathered} r_c=r_0(\varepsilon_1\varepsilon_2)^{-\nu},\\ \varepsilon_1=(T_c^L-T)/T_c^L,\quad \varepsilon_2=(T_c^U-T)/T_c^U, \end{gathered} \tag{7}$$

where T_c^L and T_c^U are, respectively, the lower and critical temperatures, r_0 is a constant, and ν is the critical exponent of the correlation radius.

The temperature dependence of the viscosity (6) can be expressed as follows with the help of Eq. (7):

$$\ln(\eta/\eta_B)=X_\eta\ln(Q_0r_0)-X_\eta\nu\ln(\varepsilon_1\varepsilon_2), \tag{8}$$

where the value of η_B was determined from a number of experimentally determined temperature dependences of the viscosity in solutions in which the phase separation regions have different sizes, as well as from the temperature dependences of the viscosity in a dry solution and in a solution with a phase-separation region 2.8 °C, in which this region was "collapsed" by adding 0.7 vol.% ethyl alcohol. It was found that the temperature dependences of the viscosity in a dry solution, where the viscosity does not have a critical part, and in a solution with added alcohol, where the critical part of the viscosity is eliminated artifically, are virtually collinear. These curves are described well by the formula

$$\eta_B=A(T-T_0)^b \tag{9}$$

and can serve as a basis for determining η_B graphically in all solutions which we studied.

The value of η_B was found for each region of phase separation using the formula (9) with three points, two of which were chosen to be farthest from the critical temperature—the extreme experimental points—and the central point was chosen graphically from the condition that the temperature dependences $\eta_B(T)$ for different solutions are collinear.

In analyzing the experimental results we also included the correction due to the interaction of strongly developed density fluctuations near the critical phase-separation temperature with the gradient of the velocity of the liquid in the viscosimeter.[41] Such an interaction results in an effective reduction of the measured viscosity. A method for taking this correction into account for a Hoeppler viscosimeter is presented in Ref. 42.

In our experiments the width ΔT of the phase-separation regions was different in solutions whose viscosity was measured and in solutions for which the angle of Γ was measured. For this reason we first analyzed the viscosity data and then recalculated the viscosity for solutions for which the half-width Γ of the Rayleigh line was studied. To check the correctness of the results, the calculations were also performed for a solution in which the values of ΔT obtained from viscosity measurements were identical with the values of ΔT obtained from measurements of Γ.

In order to determine r_c from the measured values of Γ, n, and η we expanded the formulas (1) and (2) and then solved for D_C:

$$D_C=\frac{\Gamma}{2Rq^2(1+\delta)}\left\{1+\left[1-\frac{4(1+\delta)R^2q^6}{\Gamma^2}\left(\frac{kT}{6\pi\eta}\right)^2\right.\right.$$
$$\left.\left.\times\left(\frac{3}{5}+\delta-\frac{x^2}{7}+\frac{x^4}{15}\right)\right]^{1/2}\right\}, \tag{10}$$

where

$$\delta=\frac{1}{R}\frac{D_B}{D_C},\qquad x=qr_c,\qquad r_c=\frac{kT}{6\pi\eta D_C}.$$

The ratio D_B/D_C was determined from the relations (3)–(5), the quantity Q_0 was obtained from the data on the shear viscosity, and the value of q_c was found from the formulas (5).

The quantity q_D arises in the interacting-mode theory as the upper limit of integration over the wave vectors in the relations for the critical parts Γ_c and η_c. The physical reason for introducing this upper limit is that such an integration can be carried out as long as hydrodynamics is applicable or the medium can be regarded as continuous. We adopted the value $q_D^{-1}=4.5$ Å.

It should be noted that since Q_0^{-1} and therefore q_c^{-1} increase strongly as the phase-separation region shrinks, the accuracy with which q_D^{-1} is determined is not significant for determining r_c near the double critical point (DCP). We verified this by performing a calculation with $q_D^{-1}=7.5$ Å (see Table V below).

In determining r_c from measurements with the help of the formula (10) an iteration procedure was used for each value of the scattering angle and for each temperature, since the right-hand side of Eq. (10) also contains r_c. The value of D_C obtained with $x=0$ was used as the zeroth-order approximation of such calculations of r_c.

The quantities ν and r_0 were determined by fitting the temperature dependence to the formula (7). At the same time, the temperature dependence of the viscosity was fitted to the formula (8); this made it possible to obtain for each solution the quantities X_η and Q_0. This fit was made taking into account the correction due to the interaction of concentration fluctuations with the gradient of the fluid velocity in the viscosimeter.[42] The value of Q_0, refined with the help of the correction, gives in turn refined values of D_B/D_C and r_c

for each temperature. These refined values were once again fitted to Eq. (7) and employed to obtain a new estimate of the correction to the viscosity.[41,42] After five iterations the parameters so obtained no longer varied and these values of ν and r_0 were used to calculate the final value of the viscosity from the formula (8). The results are given in Table II.

To check the convergence of the results of the procedure described above, the quantities X_η and Q_0 presented in Table I were taken as the initial data for obtaining from Γ, n, and the viscosity the entire set of quantities (ν, r_0, X_η, Q_0) characterizing the temperature dependences of r_c [the formula (7)] and the viscosity [the formula (8)] (see Table II). According to Table II, the result of the check of the convergence agrees, to within the limits of error, with the data in Table I.

Another published method for analyzing the results—calculation with $q_D/q_C = \text{const}$—consists of the following:[16,17] a) When describing the viscosity measurements the temprature T_c, as also $X_\eta \ln(Q_0 r_0)$ and $X_\eta \nu$, is assumed to be a variable parameter, and the temperature dependence of the viscosity is linearized by varying T_c in double-logarithmic coordinates in the calculation using the formula (8); the correction due to the interaction of the fluctuations with the gradient of the fluid velocity in the viscosimeter[41,42] is assumed to be small and is neglected. b) The ratio q_D/q_C is assumed to be constant for all regions; specifically, it is assumed that $q_C = 4Q_0$.

If our experimental data are analyzed by this method, we obtain the results presented in Table III and IV (to calculate X_η it was assumed that $\nu = \text{const} = 0.625$).

5. DISCUSSION

In this work we measured experimentally the temperature dependences of the half-width of the Rayleigh line in the scattered-light spectrum, the shear viscosity, and the index of refraction, and we also determined experimentally the temperatures of the upper (T_c^U) and lower (T_c^L) critical points.

The calculation of the critical exponent ν of the correlation radius of the density fluctuations, using the formulas presented in Secs. 3 and 4 required knowledge of the background shear viscosity η_B, which was also found experimentally, as described above.

The product of the critical exponent X_η of the shear viscosity by the critical exponent of the correlation radius ν (7) was determined in the same experiments.

The interacting-mode theory was developed for a continuous medium, and for this reason in the integrals for Γ_c and η_c the upper limit of the integration over the wave vectors cannot be infinite. It must be limited to some value q_D, which must satisfy the requirements of a continuous medium, but otherwise can be arbitrary. Here we set $q_D^{-1} = 4.5$ Å, and this means that the molecular structure of the solution studied will not be felt over linear distances of ~ 30 Å, and for this reason such a medium can certainly be regarded as continuous. We note once again that we also performed calculations for $q_D^{-1} = 7.5$ Å, and we obtained the same result (see Table V) in the region of the double critical point. Thus the numerical value of q_D^{-1} does not play a significant role, but the presence of a cutoff in q is significant, and the chosen value of q_D^{-1} is assumed to be the same for all regions of phase separation.

In our experiments we endeavored to vary the size of the phase-separation region in the (T, C) plane so as to approach as close as possible the double critical point T_c^D, and we came close enough to it so that the width of the phase-separation region was $T = 0.42$ °C. We were even able to reach practically the double critical point itself: $\Delta T = 0.01$ °C.

All measurements performed in this work were made in the regions of both the upper and lower critical points, as well as in the region of the double critical point itself. The results obtained for the temperature dependence of the shear viscosity are presented in Table I, and the results of the measurements of the temprature dependence of the half-width of the Rayleigh line of the scattered-light spectrum are presented in Table II.

The critical exponent ν for the correlation radius r_c of the density fluctuations for the upper, lower, and double critical points in eight different solutions were found from the measurements and the formulas presented above. For large phase-separation regions the critical exponent ν was found to be 0.631 ± 0.004, which is the same as the values of ν obtained in our works[21–24] and in the works of other authors.[16,17,20]

When the phase-separation region is smaller than $\Delta T = 1.5$ °C, however, the critical exponent ν tends to decrease and approaches the value $\nu \approx 0.5$ (Tables I and II and Fig. 1).

This last result indicates that as the double critical point is approached Landau's mean-field theory[43] gives an increasingly better description of the phenomenon. This result is unexpected.

The problem of describing the phenomenon with the

TABLE III. Results of analysis of viscosity measurements by the method of calculation with $q_D/q_c = \text{const} = 1.1$.

ΔT, °C	$X_\eta \nu \cdot 10^2$	$X_\eta \ln(Q_0 r_0)$	X_η	Q_0^{-1}, Å
0 (DCP)	3,69±0,14	−0,166±0,011	0,0590	40,33
1,41	3,28±0,10	−0,172±0,008	0,0525	36,5
2,90	3,47±0,08	−0,186±0,006	0,0556	38,6
3,20	3,15±0,08	−0,166±0,007	0,0504	36,6
5,87	3,87±0,11	−0,197±0,010	0,0619	31,8
8,73	3,51±0,10	−0,173±0,008	0,0561	23,0
25,87	3,23±0,16	−0,144±0,124	0,0517	19,1
40,0	3,25±0,10	−0,141±0,008	0,0521	16,9

TABLE IV. Results of analysis of data on Γ by the method of calculation with $q_D/q_c = \mathrm{const} = 1.1$.

ΔT, °C	ν	r_0, Å	Q_0^{-1}, Å
0,01	0,574±0,005	2,14±0,10	60,0
0,42	0,605±0,009	1,62±0,13	37,0
1,24	0,621±0,005	1,38±0,06	34,0
1,32	0,644±0,007	1,18±0,07	29,5
7,74	0,618±0,009	1,41±0,10	35,6
32,67	0,687±0,024	0,96±0,16	13,8
39,9	0,629±0,011	1,42±0,12	18,7
65,5	0,640±0,005	1,03±0,04	11,8

TABLE V. Results of analysis of Γ measurements with $q_D^{-1} = 7.5$ Å.

ΔT, °C	ν	ΔT, °C	ν
0,01	0,53±0,005	7,74	0,639±0,011
0,42	0,566±0,008	32,67	0,689±0,025
1,24	0,585±0,005	39,9	0,623±0,012
1,32	0,607±0.006	65,5	0,652±0,004

help of the mean-field theory[43] or the fluctuation theory can be solved by calculating the Ginzburg criterion[44,45] (or an equivalent number) or Ginzburg's radius.[24]

For the time being, however, the required quantities contained in the Ginzburg criterion cannot be determined accurately enough in the vicinity of the double critical point, and for this reason no definite conclusion can be drawn about the applicability of one or another theory. This phenomenon requires further theoretical and experimental study.

As far as we know, in our work we have approached closer to the double critical point than in any previous works.

Johnson *et al.*[20] studied the scattering phase function of a guaiacol-glycerin solution in a wide range of angles and for different sizes of the phase-separation region from $\Delta T = 65.9$ to 1.6 °C. The susceptibility and the correlation radius were determined under the Ornstein-Zernike assumption about the angular dependence of the intensity of the scattered light, and the critical exponent ν for the correlation radius was not found from experiment but rather was set equal to 0.63; the value of T_c was adjusted so as to obtain a fit to the data.

The work of Sorensen and Larsen[16,17] is also of interest. They used correlation spectroscopy to study a solution of β-picoline and water. When heavy water (D_2O) is added to such a solution, it acquires a double critical point. The widths of the phase-separation region were varied from $\Delta T = 78.5$ °C to 3.55 °C, and the data for the lower critical point were used to analyze the results. Analysis of the measurements by the method of calculation with $q_D/q_c = \mathrm{const}$ enabled the authors to conclude tht the critical exponent ν can range from 0.665 to 0.52, depending on the values chosen for the ratio q_D/q_c.

Table IV gives the results of the analysis of our measurements performed by the method employed in Refs. 16 and 17. Specifically, it was assumed that the ratio $q_D/q_c = \mathrm{const}$ and the interaction of the gradient of the velocity with the concentration fluctuations was neglected when determining the shear viscosity. As the data in Table IV show, up to the

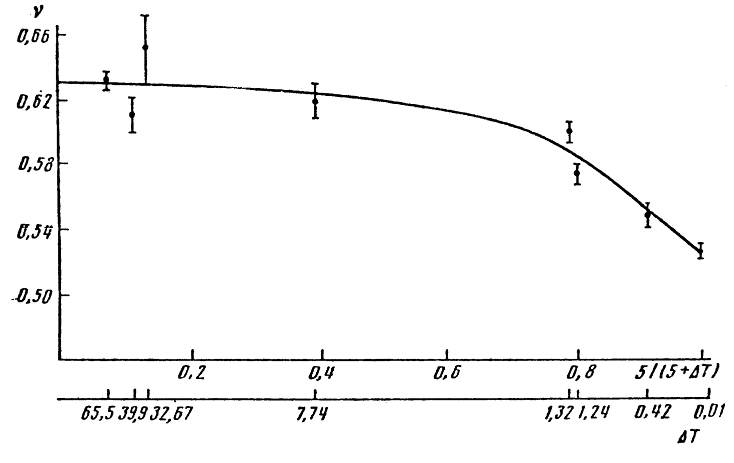

FIG. 1. Critical exponent ν as a function of the width ΔT of the phase-separation region of guaiacol-glycerin solutions.

width $\Delta T = 1.32$ °C of the phase-separation region the critical exponent ν remains practically constant and equal to 0.64 ± 0.01, which agrees with the results of Refs. 16 and 17. For phase-separation regions $\Delta T < 1.32$ °C ν decreases somewhat.

On the other hand, because the ratio q_D/q_c is constant, q_D^{-1} is found to be different for different widths ΔT, and we see no justification for this.

Several solutions for higher alcohols in water with addition of salts were studied by Davidovich and Shinder.[18] The solutions had a double critical point, but the critical exponent for r_c was not measured but rather set equal to $\nu = 0.62$.

The behavior of the shear viscosity in the critical region is of interest in itself. Our value for the critical exponent X_η for wide phase-separation regions agrees satisfactorily with previous results,[46,47] and the product $X_\eta \nu$ remains constant for all phase-separation region (see Table I).

Binary solutions with small additions of a third component, which have closed phase-separation regions and a double critical point, are objects in which small external actions result in serious intemolecular effects. Thus, for example, it was shown that a "dry" guaiacol-glycerin solution does not have a phase-separation region; it is homogeneous for any concentrations and temperatures. The addition of a small amount of water engenders a phase-separation region, while the addition of a drop of ethyl alcohol to this solution "collapses" the phase-separation region, and the solution once again becomes homogeneous.

Our investigations show, in particular, that the results of experimental and theoretical studies of such systems are undoubtedly of interest.

We thank V. P. Zaïtsev for assisting in the experiments.

1) The solution with $\Delta T = 1.32$ °C, studied in a cell to which a teflon plug was clamped with a special clamp, is an exception. We used a cell of 1.50 cm diameter made of NS-3 chemical glass and placed in a 3.4 cm (diameter) immersion cylinder filled with immersion liquid was used.

2) Visual determination of the critical temperature was performed as follows. The filament of an incandescent lamp was viewed through the vessel holding the solution. As the critical temperature was approached, viewed at an angle of 90° (of angle) with respect to the lamp, the solution acquired a bright-blue color; when the filament was viewed through a vessel containing a solution the solution itself became opalescent and the intensity of the light emitted from the incandescent lamp and passing through the vessel decreased. The filament at first turned red, and then it gradually became invisible. The temperature at which the filament of the incandescent lamp is no longer visible, i.e., when the laser beam no longer passes through the vessel, was taken to be the critical temperature.

[1] H. L. Swinney and D. L. Henry, Phys. Rev. **8**, 2586 (1972).

[2] H. C. Burstyn and J. V. Sengers, Phys. Rev. A **25**, 448 (1982).

[3] H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrel, Phys. Rev. A **28**, 1567 (1984).

[4] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Nauka, Moscow, 1987, p. 260.

[5] E. Gulari, A. F. Collings, R. L. Smidt, and C. L. Pings, J. Chem. Phys. **56**, 6169 (1972).

[6] D. Beysens, R. Tufeur, and Y. Garrabos, and J. de Phys. Lett. **40**, L623 (1979).

[7] G. G. Hurker and R. L. Schmidt, J. Chem. Phys. **67**, 332 (1977).

[8] S. V. Krivokhizha, O. A. Lugovaya, and L. L. Chaĭkov, Opt. Spektrosk. **56**, 381 (1984).

[9] A. A. Volkov, G. V. Kozlov, and E. B. Kryukova, Usp. Fiz. Nauk **149**, 331 (1986) [Sov. Phys. Usp. **29** (6), 574 (1986)].

[10] A. Derenberg, J. A. Sgauten, and N. J. Trappeniers, Physica A **103**, 183 (1980).

[11] J. S. Walker and C. A. Vause, Phys. Lett. A **79**, 421 (1980).

[12] J. S. Walker and C. A. Vause, J. Chem. Phys. **79**, 2660 (1983).

[13] M. A. Anisimov, A. A. Voranel', and E. E. Gorotsetskiĭ, Zh. Eksp. Teor. Fiz. **60**, 1117 (1971) [Sov. Phys. JETP **33**(3), 605 (1971)].

[14] G. M. Sneider, Ber. Bun. Gessel Phys. Chem. **76**, 325 (1972).

[15] C. W. Garland and K. Nishigaki, J. Chem. Phys. **65**, 5298 (1976).

[16] G. A. Larsen and C. M. Sorensen, Phys. Rev. Lett. **54**, 343 (1985).

[17] C. M. Sorensen and G. A. Larsen, J. Chem. Phys. **83**, 185 (1985).

[18] S. A. Davidovich and I. I. Shinder, Zh. Eksp. Teor. Fiz. **95**, 1289 (1989) [Sov. Phys. JETP **68**(4), 743 (1989)].

[19] S. V. Krivokhizha, O. A. Lugovaya, I. L. Fabelinskiĭ, and L. L. Chaĭkov, Zh. Eksp. Teor. Fiz. **89**, 85 (1985) [Sov. Phys. JETP **62**(1), 48 (1985)].

[20] R. G. Jonston, N. A. Clark, P. W. Wilzius, and D. S. Cannel, Phys. Rev. Lett. **54**, 49 (1985).

[21] V. P. Zaĭtsev, S. V. Krivokhizha, I. L. Fabelinskiĭ *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 85 (1986) [JETP Lett. **43**, 112 (1986)].

[22] I. L. Fabelinskiĭ, S. V. Krivokhizha, and L. L. Chaĭkov, Usp. Fiz. Nauk **149**, 328 (1986) [Sov. Phys. Usp. **29**(6), 572 (1986)].

[23] S. V. Krivokhizha, I. L. Fabelinskiĭ, and L. L. Chaĭkov, Izv. Vyssh. Uchebn. Zaved., Radiofiz. **30**, 308 (1987).

[24] L. L. Chaikov, Trudy FIAN **207**, 84 (1991).

[25] S. V. Krivokhizha and L. L. Chaĭkov, Kratkie soobsheniya po fizike, FIAN, No. 9, 50 (1985).

[26] R. A. Ferrel and J. K. Bhattacharjee, Phys. Rev. **19**, 348 (1979).

[27] K. Kawaski, *Critical Phenomena, Proceedings of the International School of Enrico Fermi*, edited by H. S. Green, Academic Press, New York, 1971.

[28] K. Kawasaki, Phys. Rev. **50**, 291 (1966).

[29] L. P. Kadanoff and J. Swift, Phys. Rev. **166**, 89 (1968).

[30] K. Kawasaki, Ann. Phys. **61**, 1 (1970).

[31] R. A. Ferrel, Phys. Rev. Lett. **24**, 1169 (1970).

[32] R. Perl and R. A. Ferrell, Phys. Rev. Lett. **29**, 51 (1972).

[33] R. Perl and R. A. Ferrell, Phys. Rev. Lett. **6**, 2358 (1972).

[34] D. W. Oxtoby and M. W. Gelbart, J. Chem. Phys. **61**, 2957 (1974).

[35] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. **13**, 2110 (1976).

[36] S. H. Chen, C. C. Lai, J. Rouch, and P. Tartaglia, Phys. Rev. **27**, 1085 (1983).

[37] J. K. Bhattacharjee, R. A. Ferrell, and R. S. Basu, Phys. Rev. A **24**, 1469 (1981).

[38] J. V. Sengers and P. H. Keyes, Phys. Rev. Lett. **26**, 70 (1971).

[39] A. L. Swinney, D. L. Henry, and H. Z. Cummens, J. de Phys. (Paris) **33**, Suppl. 2-3, C1-81 (1972).

[40] H. C. Burstyn, J. V. Sengers, and P. Esfandiari, Phys. Rev. A **22**, 282 (1980).

[41] G. W. Oxtoby, J. Chem. Phys. **62**, 1463 (1975).

[42] S. V. Krivokhizha, O. A. Lugovaya, and L. L. Chaĭkov, Kratkie soobsheniya po fizika, FIAN, No. 5-6 (1992).

[43] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, N.Y.

[44] V. L. Ginzburg, Fiz. Tverd. Tela 2, 2031 (1960) [Sov. Phys. Solid State **2** (Part 3), 1824 (1961)].

[45] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, *Fluctuation Theory of Phase Transitions* [in Russian], Nauka, Moscow, 1982.

[46] R. F. Berg and M. R. Moldover, J. Chem. Phys. **89**, 3694 (1988).

[47] R. F. Berg and M. R. Moldover, J. Chem. Phys. **93**, 1926 (1990).

Translated by M. E. Alferieff