Correlation radius near the critical points of a guaiacol-glycerin solution

V. P. Zaĭtsev, S. V. Krivokhizha, I. L. Fabelinskiĭ, A. Tsitrovskiĭ,
L. L. Chaĭkov, E. V. Shvets, and P. Yani
P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

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The temperature dependence of the correlation radius for fluctuations in a critical guaiacol-glycerin solution has been studied. The critical index ν has been determined for this solution for various sizes of the stratification region.

1. The temperature dependence of the correlation radius for concentration fluctuations in stratifying binary solutions with an upper critical stratification point has been the subject of many studies, and there have been slightly fewer studies of solutions with a lower critical stratification point.[1–3] To the best of our knowledge, there has been only one study[4] of a solution with a closed stratification region.[1)]

In the latter case, there is a closed stratification region in the plane of the temperature T and the concentration C; in this region, the solution separates into two phases, while outside this region the solution is homogeneous.

Of particular interest are binary solutions in which the stratification region can increase or decrease or disappear entirely under the influence of an external pressure or the addition of a small admixture of a third component.[5] In this case, the phase diagram is a dome-shaped surface in the space T, C, P, where P is the pressure, or in the space T, C, C_W, where C_W is the concentration of the third component. There are

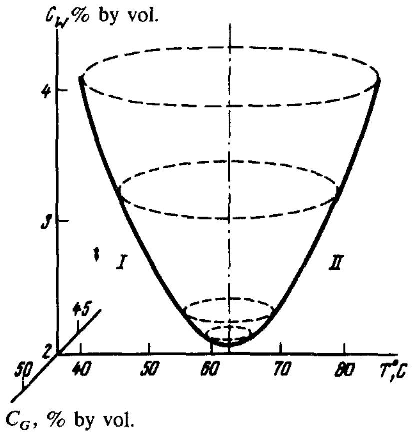

FIG. 1. Coexistence surface of a guaiacol-glycerin solution with a water admixture. C_W—concentration of water in the glycerin; C_G—concentration of glycerin in the dry solution; I—line of lower critical stratification point; II—line of upper critical stratification point.

lines of an upper critical stratification point and a lower critical stratification point on this coexistence surface (Fig. 1).

Our purpose in the present study was to determine the temperature dependence of the correlation radius for concentration fluctuations in guaiacol-glycerin solutions with admixtures of small amounts of water. The water initially gives rise to a closed stratification region, while at higher concentration it causes this region to expand. The guaiacol-glycerin phase diagram is a dome-shaped surface,[6] as shown in Fig. 1. The correlation radius is determined near the upper and lower critical points with the following widths of the stratification region along the temperature scale: 39.70 °C, 32.67 °C, 7.84 °C and 1.32 °C.

2. The correlation radius r_c is determined from the measured width (Γ) of the central polarized Rayleigh optical scattering line and the shear viscosity η_s. The measurements of Γ are taken by the method of self-beats of the scatter light with the help of a Malvern K 7023 correlator and the apparatus described in Ref. 1. The solution is prepared from analytic-grade glycerin, dried under vacuum for 6 h at 97–99 °C. The residual water content in the glycerin is about 0.45% by volume. The guaiacol is purified by repeated alternating vacuum distillation and recrystallization from the melt at 26–27 °C. The small admixtures of water are doubly distilled water. The critical concentration of the glycerin is 47.05% by volume in the dry solution. The water concentration C_W is varied from 2.1% to 4.1% by volume of the water in the glycerin. Dust is removed from the solutions by filtering in an atmosphere of dry nitrogen in a hermetically sealed container. In the experiments we use cylindrical glass cells 15 mm in diameter in a quartz cylinder 34 mm in diameter, filled with glycerin as an immersion fluid.

The temperature is regulated within 0.02 °C. The temperature difference Δt is measured within $(0.01 + 0.002\,\Delta t)$ °C. At each temperature, Γ is measured for at least three scattering angles between 26° and 86°. The accuracy of the Γ measurements is no worse than 2.5%.

Estimates of the effect of multiple scattering based on the results of Ref. 7 show that this effect is much smaller than the experimental error in our experiments and can be ignored. The viscosity is measured with a Höppler viscosimeter within 0.2%; the refractive index is measured by an Abbe refractor within 0.001.

3. In determining the correlation radius from our measurements, we use an expression for Γ from the theory of mutually coupled modes[8,9]:

$$\Gamma = \Gamma_r + \Gamma_c = D_r q^2 (1 + q^2 r_c^2) + D_c q^2 \frac{1}{q^2 r_c^2} R K_0(q r_c). \tag{1}$$

Here Γ_r, D_r and Γ_c, D_c are the regular and critical parts of the line width and of the diffusion coefficient D, respectively; $R = 1.027$ is a constant; $\bar{\mathbf{q}} = \bar{\mathbf{k}}_s - \bar{\mathbf{k}}_l$ is the wave vector of the Fourier component of the fluctuations; $\bar{\mathbf{k}}_s$, $\bar{\mathbf{k}}_l$ are the wave vectors of the scattering and exciting light;

$$K_0(x) = \frac{3}{4}\left[1 + x^2 + (x^3 - x^{-1}) \arctan x\right]; \quad \text{and} \quad D_c = \frac{kT}{6\pi\eta_s r_c},$$

where k is the Boltzmann constant, η_s is the shear viscosity, and $x = q r_c$. Expression (1) gives a good description of experimental data on Γ for x between 0.01 and 50 (Refs. 10 and 11).

This method of determining r_c from Γ is applicable only at $x < 1$, since at $x \gg 1$ the value of Γ becomes independent of r_c. At $x < 1$, we can expand $K_0(x)$ in a power series in x and determine D_c and r_c from measurements of Γ and η_s:

$$D_c = \frac{\Gamma}{2Rq^2(1+\delta)}\left\{1 + \sqrt{1 - \frac{2(1+\delta)Rq^4}{\Gamma}\left(\frac{kT}{6\pi\eta_s}\right)^2\left[\left(\frac{3}{5} + \delta\right) - \frac{(q r_c)^2}{7} + \frac{(q r_c)^4}{15}\right]}\right\}$$

$$r_c = \frac{kT}{6\pi\eta_s D_c}; \qquad \delta = \frac{D_r}{D_c R}. \tag{2}$$

The ratio D_r/D_c is given by[9]

$$\frac{D_r}{D_c} = 0.65 \exp\left\{-\frac{1}{x_\eta}\frac{\eta_s^c}{\eta_s}\right\},$$

where η_s^c is the critical part of the viscosity, and x_η is the critical index of the shear viscosity. Values of η_s^c/η_s for various temperatures and various widths of the stratification region are found from measurements of the viscosity,[12] with corrections for the interaction of the velocity gradient that arises in the measurement of the viscosity with the fluctuations having a nonzero r_c (Ref. 13). From the results of these measurements we find $x_\eta = 0.063 \pm 0.003$. Since D_c appears on both the left and right sides of (2), we calculate D_c by a method of successive approximations.

4. Figure 2 shows the temperature dependence found for r_c for solutions with various widths (ΔT) of the stratification region. These curves are approximated by the

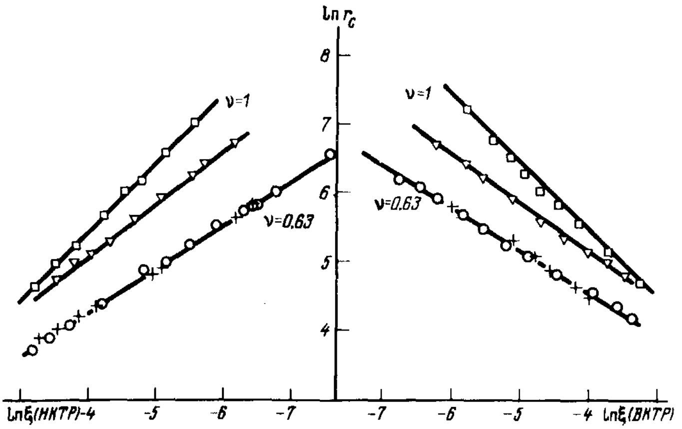

FIG. 2. Change in the correlation radius as the critical temperature is approached for solutions with stratification regions of various sizes. □—$\Delta T = 1.32$ °C; ∇—$\Delta T = 7.84$ °C; +—$\Delta T = 32.67$ °C; ○—$T = 39.7$ °C.

standard formula

$$r_c = r_0 \epsilon^{-\nu}; \quad \epsilon = (T - T_c) / T_c ,$$

where r_0 is a constant, and T_c is the critical temperature found experimentally from the loss of transparency of the solution.

From this approximation we find the values listed in Table I for the upper and lower critical stratification points. It can be seen from these results that the critical index ν of the solution increases with decreasing size (ΔT) of the stratification region, i.e., as we approach the top of the dome. Near the top of the dome, with $\Delta T = 1.32°$, the critical index increases to unity. The top of the stratification dome for the guaiacol-glycerin solution with a small water admixture is essentially flat,[6] so that a solution with a stratification region $\Delta T = 1.32°$ is in the immediate vicinity of an extremum of the stratification dome.

5. It follows from our measurements that as we move away from the stratification region with $\Delta T = 39.7°$ toward the extremum of the stratification dome ($\Delta T = 1.32°$),

TABLE I.

ΔT	ν_{UCSP}	ν_{LCSP}	$r_{0\ \text{UCSP}}$	$r_{0\ \text{LCSP}}$
39.7	0.60 ± 0.02	0.64 ± 0.02	8.7 ± 0.7	5.3 ± 0.5
32.67	0.67 ± 0.03	0.61 ± 0.03	6.4 ± 0.7	6.1 ± 0.05
7.84	0.75 ± 0.05	0.74 ± 0.02	8.8 ± 0.6	8.0 ± 0.7
1.32	1.00 ± 0.03	1.01 ± 0.02	4.1 ± 0.4	3.9 ± 0.4

for the lower and upper critical points, the critical index ν changes from $\nu = 0.63$ to unity. This conclusion is at odds with the predictions of the theory of Refs. 14–16.

At $\Delta T > 0$, very small admixtures of alcohols lead to $\Delta T = 0$, and the solutions become homogeneous.

[1)] After this paper had been prepared for publication, we learned of the appearance of Ref. 17, which reports a study by a different method of the change in the correlation radius in a guaiacol-glycerin solution.

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