I. L. Fabelinskiĭ, S. V. Krivokhizha, and L. L. Chaĭkov. *Experimental studies of solutions with a "double" critical point.* The report presents the results of experimental studies on the temperature dependences of the correlation radius r_k of concentration fluctuations and of shear viscosity η_s in a solution of guaiacol-glycerin with small amounts of water, that has a "double" critical point.

When expressed in the coordinates C, T, C_w, where C is the concentration of glycerin, T is the temperature, C_w is the water concentration in glycerin, the phase diagram of the solution constitutes a surface in the form of a dome with layers. The section of the dome by a plane parallel to the C, T plane forms a region inside which the solution is stratified. Such a flat phase diagram has the upper (UCPS) and lower (LCPS) critical points of stratification. Thus, the dome has two lines of critical points, which intersect in the extremum point of the dome, forming the "double" critical point (DCP) for $C = 47.05\%$ by volume, $T = 62.7\,^\circ\mathrm{C}$, $C = 2.08\%$ (by volume).[1]

Usually the behavior of a correlation radius in the critical region is described by the expression

$$r_k = r_0 \varepsilon^{-\nu}, \tag{1}$$

where $\varepsilon = (T - T_c)/T_c$, T_c is the critical temperature, r_0 is a constant, ν is the critical exponent for r_k.

In our experiments the correlation radius was determined from the measured values of the width Γ of the central polarized Rayleigh line in the spectra of scattered light. The values Γ and r_k are related by the formula[2–5]:

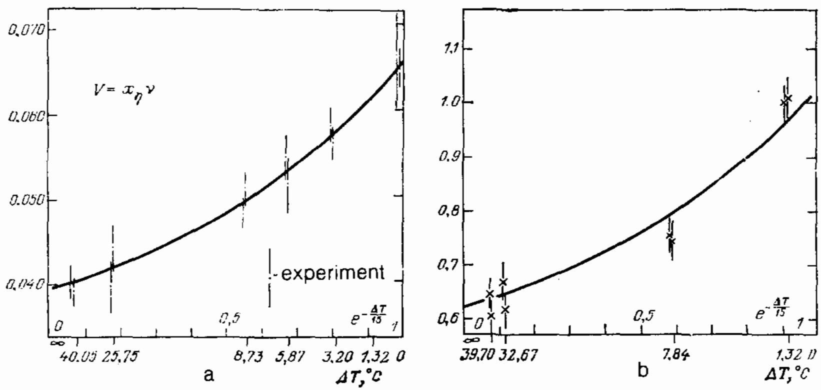

FIG. 1. (a) Dependence of the effective index of viscosity V on the stratification region width ΔT; the curve is drawn through the averaged UCPS and LCPS values of V. (b) Dependence of the effective value of ν on the stratification region width ΔT; the curve represents the values of ν obtained from Fig. 1a (from $\nu(x)$) as $\nu = V/\chi_\eta$, where $X_\eta = 0.063$; ×—the values of ν obtained from the temperature dependences $r_k(T)$.

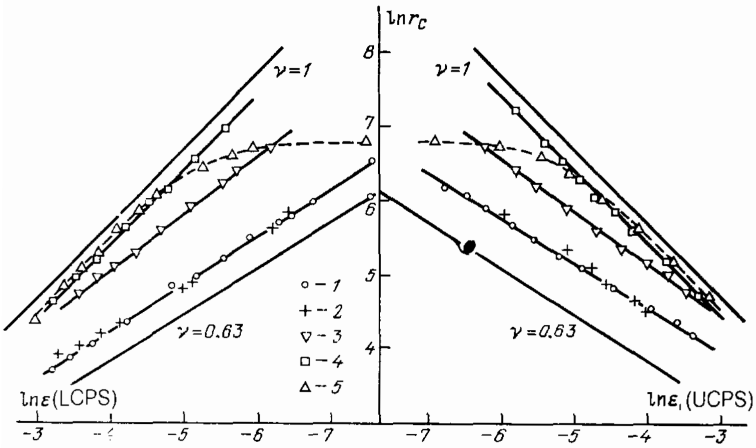

FIG. 2. Temperature dependences of the correlation radius in solutions. 1—$\Delta T = 39.70\ ^\circ$C, 2—$\Delta T = 32.67\ ^\circ$C, 3—$\Delta T = 7.84\ ^\circ$C, 4—$\Delta T = 1.32\ ^\circ$C, 5—solution with a special point. The slope corresponding to $\nu = 0.63$ and $\nu = 1$ is shown by the straight lines.

$$\Gamma = \Gamma_B + \Gamma_c = D_B q^2 (1 + q^2 r_K^2) + 1.027\ D_c q^2 \frac{1}{q^2 r_K^2} K_0 (q r_K), \tag{2}$$

where Γ_B, D_B, and Γ_c, D_c are the regular and critical parts of the line width Γ and of the diffusion coefficient D; q is the wave vector of the Fourier-component of fluctuations under investigation, $D_c = kT/6\pi\eta_s r_k$,

$$K_0(x) = \frac{3}{4} [1 + x^2 + (x^3 - x^{-1}) \operatorname{arctg} x]; \tag{3}$$

k is the Boltzmann constant. The value of Γ_B was determined from[3]:

$$\frac{D_B}{D_c} = 0.657 \exp\left(-\frac{\eta_s^c}{\eta_s X_\eta}\right), \tag{4}$$

where η_s^c is the critical part of viscosity, X_η is the "critical exponent" of viscosity. From the formulas (2)–(4) it follows that in order to find r_k from Γ it is necessary to know the temperature dependence of η_s.

The viscosity η_s was measured by a Hoeppler viscosimeter with an accuracy of 0.2% in a dry solution ($C_W = 0.45\%$ by volume), in the solutions with $C_W = 1.3$ and 2.07% (by volume), that still were not forming areas of stratification, in solutions with DCPs and, finally, the measurements were done for solutions with $C_W > 2.08\%$ (by volume), having the stratification regions with the widths $T = 3.24$; 5.8; 8.75; 25.87 and 40.05 °C; i.e., at a different distance from DCP along the C_W axis. The shape of the $\eta_s(T)$ curve for the "dry" solution was such that it was possible to find graphically the regular part of the viscosity for other solutions.

The results of viscosity measurements were approximated by a formula from the theory of interacting modes[3–6]:

$$\frac{\eta_s^c}{\eta_s} = X_\eta \ln(q_D r_K) = \ln R_0 - V \ln \varepsilon;$$

where q_D is a constant having the dimension Å^{-1}, $R_0 = (q_D r_k)^{X_\eta}$, $V = X_\eta \nu$ is the effective exponent of viscosity.

The above approximation takes into account the interaction of fluctuations having significant r_k, and the velocity gradient arising during viscosity measurements.[7] The dependence of the effective exponent V on the width of the stratification region ΔT is given in Fig. 1a. The value of X_η when $\Delta T \to \infty$ is $X_\eta = V(\infty|\nu(\infty) = 0.063$, and this corresponds to a regular critical point with $\nu = 0.625$.

The measurements of Γ were carried out by the method of self-trapping of scattered light in solutions with the stratification width $\Delta T = 39.70$ °C, 32.67 °C, 7.84 °C, 1.32 °C and in a solution with a "special point," i.e., in a solution which is close to stratification but is not stratified. The dependences $r_k(T)$ obtained from our measurements with the help of formulas (2)–(4) are given in Fig. 2. The r_k was determined in the same solution from measurements of the scattering indicatrix.[8] The obtained values of r_k were close to our data. The dependences of r_k for solutions with stratification regions were approximated by the formula (1). Figure 1b gives the effective values of the "critical exponent" ν_e, determined by using the same approximation, and the values of the same exponent found from measurements of the viscosity $\nu_e = V/X_\eta$. From the figure it follows that for $\Delta T = 0$, i.e., near DCP, $\nu = 1.03 \pm 0.06$.

The temperature dependence of the correlation radius in a solution with a "special" point was approximated by the expression that follows from Landau's theory[9]:

$$r_K = r_0 (\alpha + \varepsilon^2 + \beta\varepsilon^4)^{-0.5};$$

It was found that $r_0 = 5.09$ Å, $\alpha = 4.13 \times 10^{-5}$, $\beta = 371$.

From the theoretical predictions[10–12] it follows that near DCP the effective value is $\nu_e = 2\nu = 1.25$, and this means that near DCP critical phenomena are described by the fluctuation theory.

From the results of our measurements, it follows that near DCP $\nu_e = 1.03 \pm 0.06$, and this corresponds better to Landau's theory.

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