

# VISCOSITY OF SOLUTION NEAR THE CRITICAL MIXING POINT

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To understand many kinetic processes near the critical two-phase equilibrium point, processes connected with the appreciable contribution of the long-wave fluctuations and the increase of the correlation radius of the fluctuations [1 - 3], data are needed on the viscosity of the critical systems. As yet, however, there is still no unified point of view concerning the behavior of the viscosity near the critical point. This pertains both to theory [4 - 6] and experiment [7 - 12].

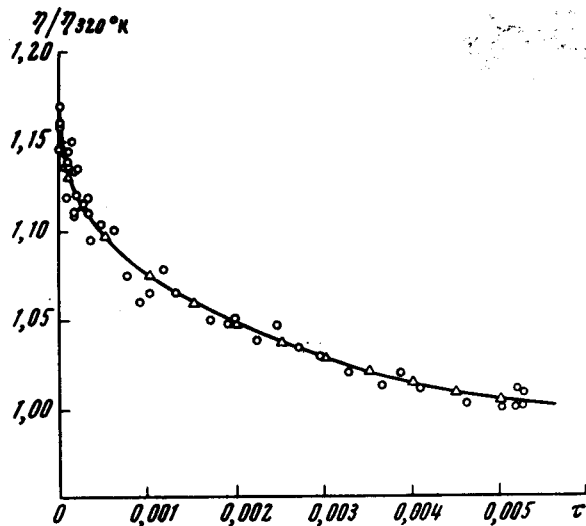


Fig. 1. Viscosity in the single-phase region of the methanol-cyclohexane solution near the critical mixing point: o - experimental points,  $\Delta$  - values calculated from the equation  $\eta/\eta(47^\circ\text{C}) = A - B\tau^\alpha$ .

The present paper reports an investigation of the temperature dependence of the viscosity of a methanol-cyclohexane solution by the vibrating-disc method [8], when the characteristic dimensions of the perturbations in the solution are much larger in this experimental method (for example, the depth of attenuation of the oscillations of the liquid from the surface of the disc) than the radius of correlation of the fluctuations (unlike, for example, in [13]).

The phase-coexistence curve of this solution, plotted in T-C coordinates, was investigated by the method of the vanishing meniscus in order to determine the critical parameters; their values turned out to be  $T = 45.33^\circ\text{C}$  and  $C = 70.8 \text{ wt.}\%$  of cyclohexane [14]. The impurity contents of the methanol and of the cyclohexane did not exceed 0.01 and 0.1%, respectively. The solutions were carefully protected against the absorption of atmospheric moisture.

To measure the viscosity, a

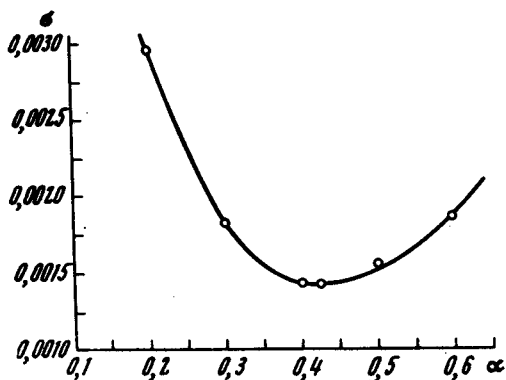


Fig. 2

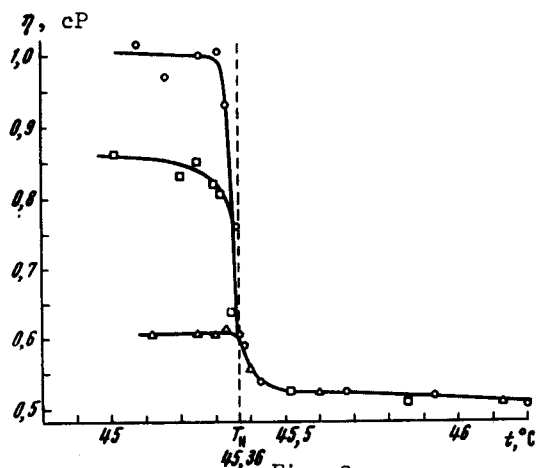


Fig. 3

Fig. 2. Plot of the mean-squared approximation error of the function  $\eta/\eta(47^\circ\text{C}) = A - B\tau^\alpha$ , describing the viscosity near the critical mixing point as a function of  $\alpha$ .

Fig. 3. Viscosity near the critical mixing point. The data in the two-phase region were obtained after intense stirring of the solution: o - immediately after mixing the solution,  $\square$  - 1 minute after stirring,  $\Delta$  - 5 minutes after stirring.

stainless-steel cell was prepared, with two windows, through which it was possible to observe the disc-oscillation amplitude on an external half-meter scale. The disc, of 20 mm diameter and 1 mm thickness, was mounted on a beryllium-bronze suspension. The period of the oscillations was approximately 10 sec. The temperature of the cell was maintained constant accurate to  $0.001^\circ\text{C}$  in a water thermostat. Provision was made for vigorous stirring of the solution in the cell. The solution concentration was determined accurate to 0.5%. The density of the solution, which hardly varied with temperature in the investigated interval, was measured with a pycnometer.

Assuming validity of the Navier-Stokes equation for an incompressible liquid, constancy of the pressure, and small oscillation and infinitesimally small thickness of the disc, an expression was obtained for the damping decrement of two successive disc amplitudes [15]

$$\ln \frac{\theta_n}{\theta_{n+1}} = \frac{\pi^{3/2}}{\sqrt{2}} R \sqrt[4]{\frac{\rho \eta}{T_0}} \quad (1)$$

where  $R$  is the disc radius,  $T_0$  the oscillation period, and  $\rho$  the solution density. Since the experiment deviates from the ideal scheme on which Eq. (1) is derived, the viscosity meter was calibrated using distilled water at different temperature. The calibration curve was plotted in terms of the coordinates  $\eta$  and  $(T_0/\rho)(\ln \theta_n/\theta_{n+1})^2$ . The reliability of the instrument was verified by

measuring the pure components of the investigated solution, the viscosities of which are known. The error in the viscosity measurement amounted to 0.5%.

Figure 1 shows the experimental temperature dependence of the viscosity in the homogeneous region of the solutions with critical concentration. The spread of the critical temperature of the transition to the two-phase state of these solutions, prepared at different times, did not exceed  $0.02^\circ\text{C}$ , and therefore the data are presented in relative coordinates. This dependence was approximated by the following functions:

$$\eta/\eta_{47^{\circ}\text{C}} = B \ln r + A, \quad (2)$$

$$\eta/\eta_{47^{\circ}\text{C}} - 1 = Br^{\alpha}, \quad (3)$$

$$\eta/\eta_{47^{\circ}\text{C}} = A - Br^{\alpha}, \quad (4)$$

where  $\eta/\eta(47^{\circ}\text{C})$  is the viscosity far from the critical point, at  $47^{\circ}\text{C}$ , and  $\tau = (T - T_c)/T_c$ .

The experimental data fit the function (4) with the smallest rms error. The coefficients A and B at a given  $\alpha$  were obtained by least squares. For Eq. (4) their values are  $A = 1.158$  and  $B = 1.530$ . The dependence of the approximation error on  $\alpha$  in the case of the function (4) is shown in Fig. 2. It is seen from this figure that the smallest approximation error occurs when  $\alpha = 0.43$ . Assuming this value of  $\alpha$ , we arrive at the conclusion that it is not the viscosity itself which becomes infinite at the critical point, but its derivative with respect to the temperature, in accord with the formula

$$d\eta/dr \sim r^{\alpha-1}, \quad \text{with } \alpha \approx 0,4 - 0,5.$$

This agrees with the theoretical paper [6].

If the solution that enters the two-phase state is vigorously stirred, then the viscosity of the resultant finely-dispersed system continues to increase with increasing distance from the critical point in the two-phase region, assuming values exceeding the critical value by two or three times.

As the size of the second-phase bubbles increases with time, the viscosity drops to values corresponding to the homogeneous region. This is illustrated by Fig. 3, which shows the experimental viscosity data continued into the two-phase region. It is also seen from this figure that the values of the viscosity measured immediately after intense stirring of the two-phase solutions and 1 and 5 minutes later decreases in time with increasing size of the bubbles. This suggests the reasons for the increase of the viscosity in the homogeneous region namely that the fluctuating formations with dimensions on the order of the correlation radius can be represented as a certain colloidal solution whose viscosity exceeds the viscosity of the binary mixture of the same temperature without fluctuations. Since the experimentally measured viscosity goes over continuously into the two-phase region at the critical point, this indicates, as does the analysis of the approximation functions, that the viscosity is finite at the critical point.

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