Miscibility dome of guaiacol-glycerin solutions and increased transparency of heterogeneous solutions after shaking

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A closed-loop phase diagram forms when small amounts of water are added to a guaiacol-glycerin solution, and the miscibility dome of the two phases is investigated. The upper and lower critical points lie on curves that intersect at the bottom of the inverted dome. If traces of phenol, isopropanol, or ethanol are added, the closed-loop diagram becomes smaller and disappears completely; the closed loop becomes larger if acetone or benzene are added. When a laser beam passes through a solution with a closed-loop diagram at a temperature shifted slightly to the inside part of the loop, the droplets that form during the nucleation process diffract the laser light so that a bright ring forms on a screen placed behind the cell. The solution becomes homogeneous again when shaken, after which the nucleation process is repeated. The time behavior of the ring at constant temperature is discussed, and the radius of the droplets is estimated.

Many binary solutions have been studied in which the components segregate at an upper or lower critical point, and a few solutions are known to have a closed-loop phase diagram.[1] The behavior of these solutions is described by phase diagrams in the C, T plane, where C is the concentration of one of the components and T is the temperature.

If the pressure is increased or if traces of a third component are added, the closed-loop phase diagram may expand or contract, and in some cases it can shrink to a single point A.[2] In the latter case the components do not segregate into separate layers, but C fluctuates with anomalously large amplitude near A. The phase diagram for these solutions is dome-shaped when plotted as a function of C, T, P or C, T, C_x, where P is the pressure and C_x is the concentration of the third component (Fig. 1). The solution is homogeneous outside the dome but heterogeneous inside it.

In this paper we analyze the three-dimensional phase diagram, find the critical points, and describe the optical behavior of a guaiacol-glycerin solution for varying temperature and component concentrations.

We initially decided to study guaiacol-glycerin solutions because the data in Ref. 3 indicate that guaiacol-glycerin has a closed-loop diagram at temperatures that are readily accessible experimentally, and we wanted to investigate the bahavior of the upper and lower critical points simultaneously.

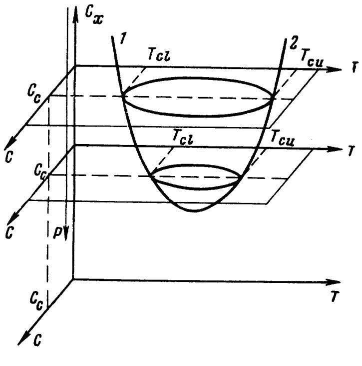

FIG. 1. Three-dimensional phase diagram for a solution with a miscibility dome: C_c is the critical concentration, T_{cl} and T_{cu} are the temperatures of the lower and upper critical points. 1) locus of lower critical points; 2) locus of upper critical points.

However, we found that there was no closed phase diagram for solutions prepared from pure, dehydrated glycerin and guaiacol—a closed loop formed only when at least 2.1% of water by volume was addded to the glycerin, and the loop became larger as the water content increased. We also found that the closed loop for guaiacol-glycerin solutions formed by adding water became smaller if phenol, isopropanol, or ethanol were added. The amount of these materials required for the closed loop to disappear was several times less than the amount of water needed to form the loop. A closed loop also formed after benzene or acetone were added.

We measured the stratifiction temperature T_s by means of a thermostatted glass tube which contained eight cells filled with solutions of different concentrations. The tube was kept at constant temperature by immersing it in circulating water from a U-3 thermostat, and the temperature of the solutions was measured by a mercury thermometer. The time at which stratification occurred was determined visually by noting when the solution in each cell became opaque. The error in measuring T_s ranged from 0.1 and 0.2 °C.

The analytical-grade glycerin was desiccated in vacuum for 6 h at 98 °C. The residual water content deduced from viscosity measurements was 0.45% by volume. The guaiacol was purified by repeated distillation and recrystallization from a melt; the recrystallization was carried out at $T = 26$–27 °C. Twice-distilled water was added to the solution in order to form a closed phase loop.

We did not detect any concentration fluctuations immediately prior to the homogeneous → heterogeneous phase transition for C well away from the critical concentration C_c—the transition occurred abruptly, and the initially clear solution became turbid and opaque with a grayish tint due to droplet formation. On the other hand, for $C \approx C_c$ the solution became bluish when T was within 2–3 degrees of T_s; this corresponded to the onset of critical opalescence associated with large fluctuations in the concentration. For glycerin concentrations $C_G = 44$–50 vol.% the solution became

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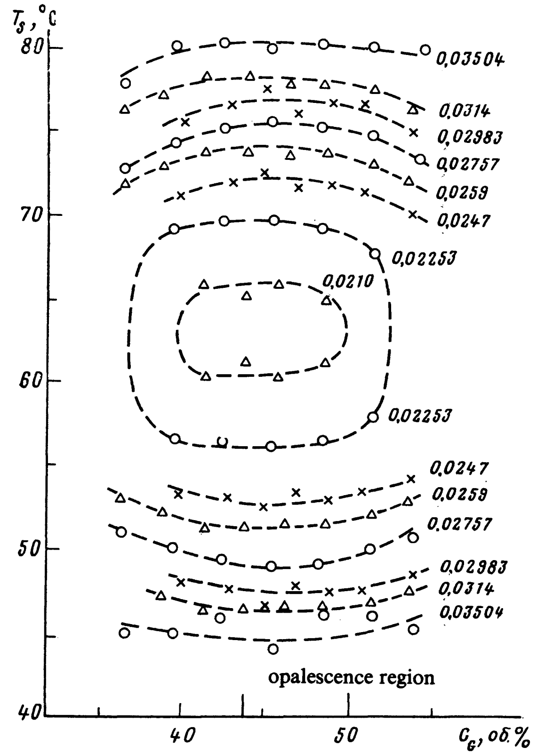

FIG. 2. Phase diagrams for a guaiacol-glycerin solution with a constant water concentration $C_W = \text{const}$ (by volume).

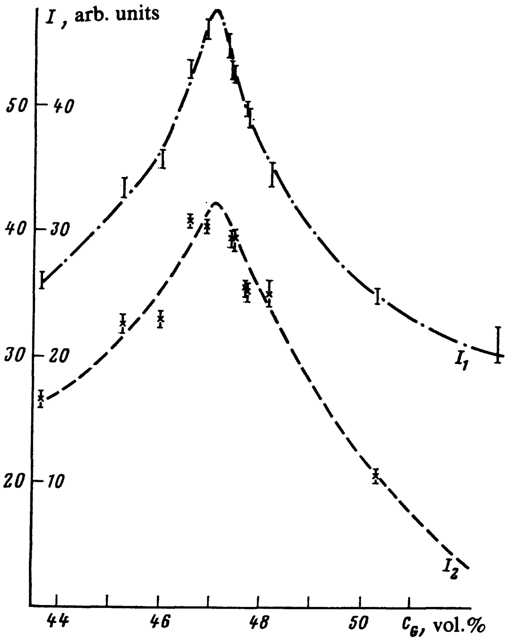

FIG. 3. Relative intensity of scattered laser light vs glycerin concentration C_G for $C_W = \text{const}$ in solutions with $T_{cu} - T_{cl} = 24$ °C. I_1 and I_2 are the intensities recorded for $|T - T_s| = 1°$ on the upper and lower binodals, respectively (T_s is the stratification temperature). The scattering angle was equal to 70°.

turbid and the bluish tint was lost only very close to the critical point. For $C_G = 46$–47.5 vol.% the critical opalescence was so intense that it was difficult to measure the stratification time accurately.

We found it convenient to analyze the miscibility dome in terms of the coordinates T, C_G, and C_W, where T is the temperature, C_G is the volume concentration of glycerin in the dry solution, and C_W is the volume concentration of water in the solution. Figure 2 shows solution phase diagrams for $C_W = \text{const}$. The diagrams are symmetric and resemble the diagrams found theoretically in Ref. 4; the extrema of the binodals lie in the same region where critical opalescence is observed. We note that the concentration interval in which the upper and lower binodals coalesce is so narrow that we were unable to analyze it in detail. In particular, we could not be certain that the minimum of the binodal curve coincides precisely with the critical point for this system. We therefore found C_c by measuring the relative intensity I of light scattered by the solution as a function of the glycerin concentration C_G. We used the device briefly described in Ref. 5, and the scattering angles ranged from 50 to 86°. The cylindrical cell of diameter 15 mm used in the experiment was placed inside a cylinder of diameter 34 mm filled with immersion liquid. Figure 3 shows $I(C_G)$ recorded for $|T - T_s| = 1$ °C on the upper and lower binodals; the scattering angle was 70°. Since the scattered light intensity behaved as

$$I \propto (\partial n/\partial C)^2 \langle \delta C^2 \rangle,$$

where n is the index of refraction, it was necessary to establish whether $\partial n/\partial C$ had a singularity near C_c. We measured $n(C_G)$ for $C_G = 28$–68 vol.% and found that the dependence remained linear to within the measurement error (the relative error in measuring $\partial n/\partial C$ was equal to 3% for $C_W = \text{const}$). Since $\partial n/\partial C = \text{const}$, the critical glycerin concentration corresponded to maximum intensity I and was found to be 47.05 ± 0.10 vol.%

Light transmission through a cell filled with stratified guaiacol-glycerin solution is of considerable interest. We found that there was little light scattering as long as the solution remained homogeneous; in this case, the beam transmitted directly through the cell formed a sharply defined spot on a screen located a distance $L = 43$ cm behind the cell. The spot was slightly elongated in the horizontal direction due to the cylindrical shape of the cell.

When T was changed at a rate of 0.005 °C/s so that the closed loop was entered from the outside, a spotty pattern appeared on the screen when T became equal to T_s, after which a blurred ring formed. This pattern was apparently caused by light diffraction by the small droplets that formed during the initial stage of stratification.[6,7] The spotty ring-shaped structure at first became more intense with time and then became blurred and eventually disappeared. During this time the beam transmitted directly by the cell was attenuated and gradually became indistinguishable from the spotty structure on the screen.

The spots in this case were produced by interference of the light diffracted by the numerous droplets, which were illuminated by coherent laser light. We believe that the physical mechanism of ring formation was the same as for halo formation. Ring formation has also been observed during spinodal decay.[7] The ring was blurred because the diameters of the scattering droplets varied considerably.

We can estimate the effective radius r_{eff} of the droplets from the radius R of the first bright ring, the wavelength λ of the light, and the experimental geometry:

$$r_{eff}=0.81\lambda\,(R^2+L^2)^{1/2}/R.$$

We next chose the solution temperature T to lie inside the closed-loop diagram (heterogeneous phase) by an amount δT equal to a few tenths or hundredths of a °C, so that there was no direct transmission through the cell. When the solution was then shaken vigorously in its thermostat and allowed to sit we noted the following behavior. At first we observed a directly transmitted ray against a dark background, after which a spotty ring-shaped structure formed. As time passed, the ring decreased in radius and became more intense and blurred, while the transmitted ray became weaker and in some cases could not be distinguished from the background. The same behavior was observed after repeated shakings. The time for this process to occur depended on the solution, i.e., on the width Δ of the closed-loop diagram and on the distance δT inside it. The beam disappeared sooner when Δ and δT were increases.

The photographs in Fig. 4 show the vanishing of the transmitted laser beam and the changes in the ring on the screen caused by shaking a guaiacol-glycerin solution with $\Delta\equiv T_{cu} - T_{cl} = 11.8$ °C; δT ranged from 0.04 to 0.13 °C.

For $\delta T = 0.13$ °C the directly transmitted ray disappeared after 5 s, whereas no transmitted ray was observable after shaking for $\delta T = 0.6$ °C. We note that the behavior was the same whether T approached T_s from above or from below for all $C_G = 43$–53 vol.%, i.e., throughout the range of concentrations investigated.$^{1)}$

The turbulence, shear flows, and pressure changes produced by the vigorous shaking may have ruptured the droplets that formed initially during stratification, and this would account for the increased transmission after shaking. Indeed, it was shown in Refs. 8–11 that the phase boundary curve and the critical temperature may change under these conditions. Thus, when the solution is agitated the phase boundary curve shifts toward the heterogeneous phase and then moves back again. Assume that the point A representing the state of the solution in the C_G, T plane lies inside the closed loop by an amount δT along the T axis. If δT is not too large, A may lie either inside or outside the perturbed loop after the solution is shaken. Droplets form in the first case whereas they disintegrate in the second case, the two processes occurring at different rates. If A lies outside the loop (homogeneous solution) no activation energy is needed for the droplets to break up, so that the disintegration is much faster than formation, which has an energy barrier $\Delta\Phi = 4/$

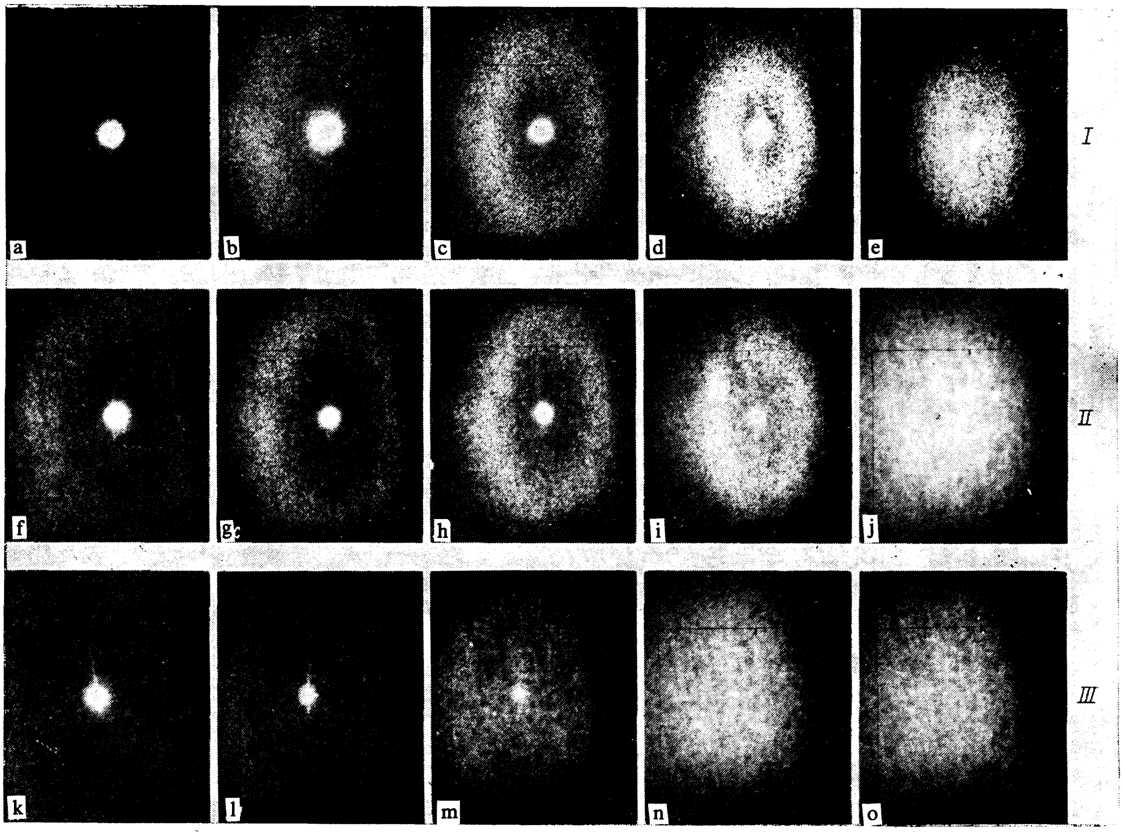

FIG. 4. Photographs showing the increased transmission of a heterogeneous solution after shaking. The formation and evolution of the ring on a screen behind the cell are shown for several values of δT. The width of the closed-loop diagram for this solution was $\Delta\equiv T_{cu} - T_{cl} = 11.5$ °C, $C_G = 47.05$ vol.% I) $\delta T = 0.04$ °C: a) 3s; b) 8 s; c) 25 s; d) 110 s; e) 1200 s. More than 90 min were required for the solution to again become opaque; II) $\delta T = 0.07$ °C: f) 6 s; g) 11 s; h) 17 s; i) 40 s; j) 90 s. The solution became opaque after 130 s. III) $\delta T = 0.13$ °C: k) 3 s; l) 5 s; m) 8 s; n) 15 s; o) 26 s. The solution became opaque after 26 s. The distance from the central marker to the corner of the photographs was equal to 8 cm. The ring is elongated in the vertical direction due to the cylindrical shape of the cell. The effective radius r_{eff} of the droplets deduced from the radius of the experimentally observed rings ranged from $2\cdot 10^{-4}$ to $2.3\cdot 10^{-3}$ cm.

$3 \cdot \rho\sigma r^{*2}$ (Refs. 6, 7; σ is the surface tension and r^* is the critical radius for stable droplets). Periodic shaking can thus rupture the droplets, which are not replaced so that the droplet concentration decreases and the solution becomes more transparent. In addition, the point A in the phase plane may move along the C_G axis toward the boundary of the closed loop if droplet formation is accompanied by a decrease in the concentration of one of the solution components. In this case very weak shaking should suffice to make the solution transparent.

Mechanical agitation was found to make the solutions transparent for a range of temperatures $\Delta T = |T - T_s|$ which increased from 0.09 to 0.7 °C, i.e., as A approached the vertex of the miscibility dome. For comparison we note that ΔT was just 0.02 °C for an aqueous triethylamine solution.

Although the properties of systems with dome-shaped or other types of phase surfaces are of great physical interest, little or no work has been done in this area. In this paper we have analyzed only a few properties, such as the formation of a closed-loop phase diagram when water is added to a guaiacol-glycerin solution, and the vanishing of the loop when ethanol or phenol are added. The physical origin of the observed behavior remains unclear and further experimental and theoretical work is needed.

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[1)] The increased transmission after agitation cannot be due to a change in temperature, because in this case the changes in the transmission would have been different near the upper and lower stratification points, which contradicts our experimental findings.

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