Distinctive features of the phase diagram of a glycerin–quaiacol solution

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The onset of a closed stratification region in a glycerin–guaiacol binary solution upon the addition of a small amount of a third component, soluble in only one component of the solution, has been studied experimentally. The third component was either water, which is soluble in glycerin, or CCl^4, which is soluble in guaiacol. The stratification region disappears when alcohols soluble in both components of the solution are added. A stratification region arises in this solution upon the addition of other liquids which are soluble in only one of the components of the solution. © *1994 American Institute of Physics.*

Research on phase transitions in binary solutions which have closed loops within which the solution becomes stratified has proved rewarding in many ways. Among these solutions are glycerin–guaiacol solutions to which a small amount of a third component, e.g., water, is added. This binary solution has several surprising properties, which have yet to be explained.

Walker and Vause[1–3] have carried out a comprehensive theoretical study of such systems and of the overall problem. They have developed the modern theory, which has allowed them to construct phase diagrams which agree well with experimental results. Systems which have a closed loop within which the solution is heterogeneous have upper and lower critical points simultaneously. By adding the appropriate amount of the third component, one can produce a system in which the upper and lower critical points merge into a one double critical point. At this double critical point, the critical exponent of the correlation radius of concentration fluctuations is quite different from that observed at the upper and lower critical points (see Ref. 4 and the papers cited there). While the existence of an upper critical point can be explained without difficulty on the basis of a minimum of the free energy of the system, which arises because of an increase in the temperature and the entropy, the lower critical point cannot be explained in such a simple way. In an effort to explain it, Walker and Vause[1] introduced an orienting force which lowers the total energy of the solution. In Ref. 1 they specified this force to be the force of a hydrogen bond. In the theory of Ref. 1, the formation of a closed loop in a glycerin–guaiacol solution is explained on the basis that (a) a hydrogen bond between glycerin and guaiacol weakens and (b) some of the guaiacol molecules form hydrogen bonds with water molecules. An orderly system which allows the existence of more than one closed loop and up to five critical points was constructed in Ref. 1. All this was done for various versions of the hydrogen-bond forces in the binary solution.

In the experiments which we have already reported and in further experiments with

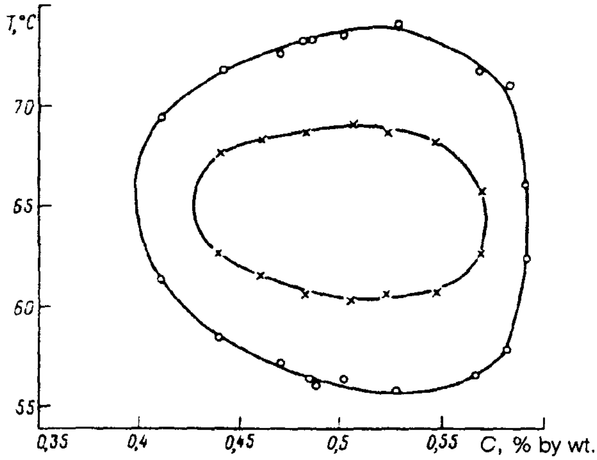

FIG. 1. Phase diagram of the stratification region of a guaiacol–glycerin solution plotted as carbon tetrachloride, CCl_4, is added. Here C is the glycerin concentration. ×) At a CCl_4 concentration of 1.65% by weight in guaiacol; O) at a CCl_4 concentration of 1.73% by weight in guaiacol.

glycerin–guaiacol solutions, we have obtained results and observed features which could hardly be explained by the existing theories.

1. When guaiacol and glycerin, both thoroughly purged of water, are mixed, they form a homogeneous solution at any temperature and at any concentration (a dry solution). Water dissolves only in the glycerin. The addition of water in an amount corresponding to one water molecule per 23 solution molecules gives rise to a stratification loop. We expected that the addition of ethyl alcohol, in an amount smaller than that of the water by a factor of 5, to the solution would increase the "width" of the loop. In fact, the loop disappeared completely, and the solution became homogeneous. We then thought that the alcohol "tore" the water away from the guaiacol and closed the water's hydrogen bonds on itself, causing the solution tobecome"dry."[5] However, that idea is by no means correct.

2. To a "dry" glycerin–guaiacol solution we add, instead of water, carbon tetrachloride (CCl_4). This liquid has no hydrogen or oxygen. In an even smaller amount than in the case of water (one CCl_4 molecule per 180 solution molecules), it gives rise to a closed loop in the solution. If there is a strong hydrogen bond between the glycerin and the guaiacol, a negligible amount of CCl_4 could hardly alter the situation. Nevertheless, a loop arises (Fig. 1). If we now add a drop of ethyl alcohol to the solution, the loop disappears: The solution becomes homogeneous over the entire phase plane. This experiment shows that the matter of importance here is apparently not a hydrogen bond, although it may play a role; the important point is instead some more general mechanism for interactions between molecules.

3. The experiments which we have carried out, at this point still few in number, apparently allow us to conclude that a closed loop can be caused in a homogeneous glycerin–guaiacol solution by a liquid which dissolves in only one component of the solution: water, which dissolves in glycerin, or CCl_4, which dissolves in guaiacol.

According to our observations, benzene and acetone also form a closed loop in the solution; both dissolve in guaiacol alone. Liquids, such as alcohols, which dissolve in both components, do not form a closed loop, but they do annihilate an existing loop, as stated above.

4. It follows from all these results that very small amounts of a third component cause radical changes in the properties of the solution. It is unlikely that such small amounts of water or, especially, CCl_4 could cause such effects as the formation of a closed loop directly.

We would suggest that the third component (water or CCl_4) acts as a trigger. Apparently all these circumstances must be taken into account in a discussion of the results.

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