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A comparison of pressure induced and concentration induced smectic A–nematic–isotropic triple points

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Optical microscopy in mixtures of di-octylazoxybenzene (8AB) and dinonylazoxybenzene (9AB) reveals that a smectic A–nematic–isotropic triple point occurs at $71.5 \pm 0.5^\circ\text{C}$ and 38 ± 2 wt% 8AB. Although this concentration induced triple point is different from the pressure induced triple point known to exist in pure 9AB at elevated pressure, analysis of the data from both the mixing and pressure experiments reveals that the phase transition surfaces in temperature–pressure–concentration space for this system are nearly planar.

1. Introduction

It is well known that additional liquid-crystalline phases and important thermodynamic points can often be obtained either by applying pressure to a liquid crystal or by mixing a liquid crystal with another substance. Classic examples include a pressure induced [1] and concentration induced [2] reentrant nematic phase, as well as a pressure induced [3] and concentration induced [4] nematic–smectic A–smectic C (NAC) triple point. Pressure and mixing experiments have yielded a great deal of new information about both the liquid-crystalline phases involved and the transitions between them. In those cases where the two types of experiments have been performed on similar systems, the results have been consistent.

In spite of a good deal of work under pressure and with mixed systems, relatively few investigations have studied the thermodynamic behaviour when both pressure and concentration are varied. Certainly there are reasons to suspect that some systems should behave quite differently when mixed with another material as opposed to being put under pressure. For example, adding a dissimilar compound to a pure sample means that solubility effects, concentration fluctuations, and complex impurity interactions are likely to be important. Such effects do not come into play when the pressure on the pure sample is varied. On the other hand, these effects might be very small if the added compound is very similar to the pure compound and possesses similar phase transition temperatures.

The purpose of this article is twofold. First, a new concentration induced smectic A–nematic–isotropic triple point is reported for a system where a pressure induced triple point is known to exist. Second, although there are quantitative differences between the two phase diagrams, close analysis reveals that they are consistent with phase transition surfaces in temperature–pressure–concentration space which are nearly planar. For this system, therefore, changes in the pressure and changes in the concentration produce analogous effects over a wide range of the thermodynamic variables.

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2. Theory

In a two component system, the chemical potential is a function of the temperature (T), pressure (P), and concentration of one component (X). The chemical potential function is different for each phase, so at any point in temperature–pressure–concentration (T, P, X) space, the phase with the lowest chemical potential is the stable phase. Phase transitions occur along two-dimensional surfaces where the chemical potential functions of two phases are equal. Likewise, triple points exist along one-dimensional curves where three chemical potential functions are equal. To both illustrate this point and anticipate the experimental results, figure 1 shows the three phase transition surfaces and curve of triple points for a system with an isotropic phase (I), nematic phase (N), and smectic A phase (S_A).

In order to visualize what happens in a pressure experiment where the concentration is kept constant, one need only imagine a slice through (T, P, X) space parallel to the (T, P) plane at the proper concentration. This slice intersects the phase transition surfaces and triple point curve, producing phase transition curves and a triple point in the plane of the slice. This is the phase diagram obtained in a pressure experiment. Figure 1 shows such a phase diagram for a pressure experiment performed with $X = 0$.

Similarly, a mixing experiment at constant pressure corresponds to a different slice through (T, P, X) space, namely the one parallel to the (T, X) plane with the proper pressure. This slice intersects the phase transition surfaces and triple point curve to produce a different phase diagram. This is also shown in figure 1 for a mixing experiment performed at $P = 0$. The important point is that these two phase diagrams result from two very different slices through (T, P, X) space. The two slices intersect along the line parallel to the temperature axis with P equal to the pressure of the mixing

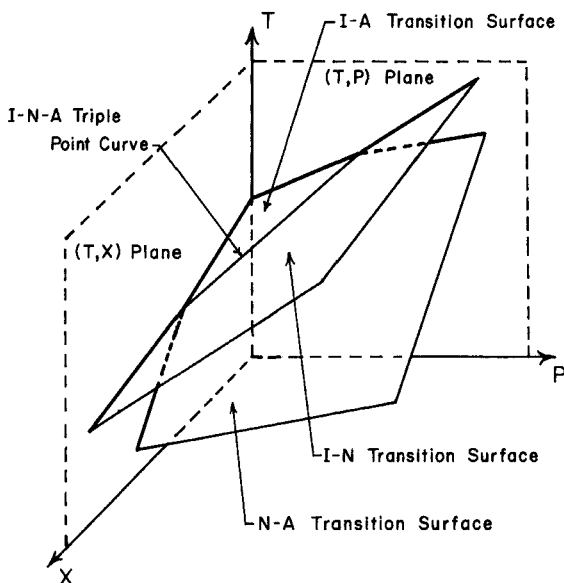


Figure 1. Illustration of three phase transition surfaces and a curve of triple points. The I, N, and S_A phases exist in the regions above, between, and below the surfaces, respectively. The phase diagram for a pressure experiment and mixing experiment are shown by the bold lines on the (T, P) plane and (T, X) plane, respectively.

experiment and X equal to the concentration used in the pressure experiment. This line is the only part common to both phase diagrams. Thus, even though the two phase diagrams might possess the same phases and even the same basic topology, there is no reason to expect that quantitatively the two diagrams are similar.

3. Experimental

Two members of the same homologous series were used in this investigation, di-octylazoxybenzene (8AB) and di-nonylazoxybenzene (9AB). Both liquid crystals were purchased from Frinton Laboratories. The transition temperatures for the 9AB compound agreed with the highest literature values, so it was used without additional purification. The 8AB transition temperatures were a degree or so low, so it was recrystallized from ethanol. This brought its transition temperatures up to values consistent with the literature values.

9AB possesses a solid, smectic A, and isotropic phase at atmospheric pressure, but a previous experiment determined that a nematic phase appears between the smectic A and isotropic phases under pressure [5]. The phase diagram resulting from this work is shown in figure 2. A triple point occurs at $103 \pm 2^\circ\text{C}$ and $92 \pm 6 \text{ MPa}$. Since the solid-smectic A transition was not investigated, the solid phase has been omitted from the phase diagram. It would probably occupy a region in the lower right corner of figure 2.

Since 8AB does possess a narrow nematic phase at atmospheric pressure, addition of 8AB to 9AB should cause a nematic phase to appear at some concentration, similar to what happens under pressure. This hypothesis was investigated by preparing mixtures of 8AB and 9AB with precisely determined concentrations. The transition temperatures for each mixture were measured by placing the sample in an Instec HS-1 hot stage and viewing it with a Leitz Laborlux 12 polarizing microscope. Transition

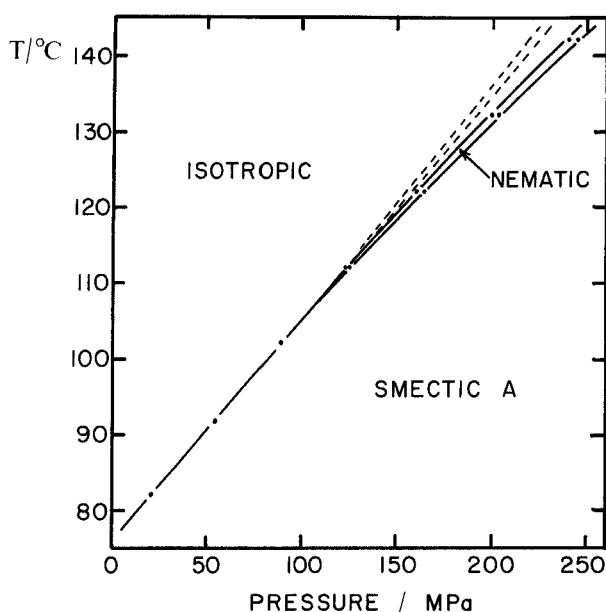


Figure 2. Temperature–pressure phase diagram for 9AB (taken from [5]). A triple point occurs at $103 \pm 2^\circ\text{C}$ and $92 \pm 6 \text{ MPa}$. The solid–smectic A transition curve is not shown. As explained in the text, the dashed lines are the phase transition planar curves extrapolated from the temperature–concentration data of figure 3 assuming planar phase transition surfaces.

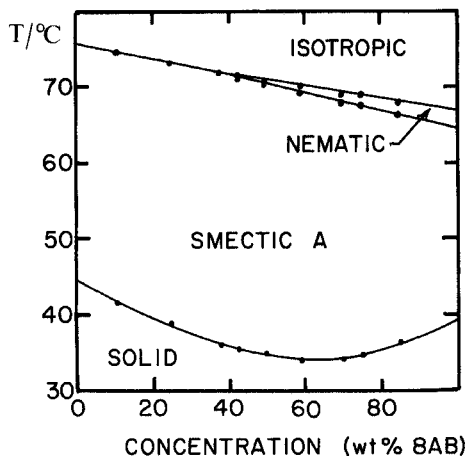


Figure 3. Temperature-concentration phase diagram for the 9AB/8AB system. A triple point occurs at $71.5 \pm 0.5^\circ\text{C}$ and $38 \pm 2 \text{ wt}\% \text{ 8AB}$.

temperatures were determined to the nearest 0.1°C for the solid-smectic A transition and to the nearest 0.01°C for the other transitions. The results of these measurements are shown in figure 3. As suspected, a nematic phase is present with a triple point at $71.5 \pm 0.5^\circ\text{C}$ and $38 \pm 2 \text{ wt}\% \text{ 8AB}$.

4. Discussion

The two phase diagrams are similar in that the same phases are present and the relationship between them is the same. The most apparent difference is that the coexistence curves meeting at the triple point have a positive slope in figure 2 and a negative slope in figure 3. The positive slope in figure 2 is typical of just about all liquid crystals, but the slope in a phase diagram such as figure 3 depends on whether the added compound has higher or lower transition temperatures than the original compound. In this case, 8AB has lower transition temperatures than 9AB, so the coexistence curves slope downward.

Besides the different slopes, there is another way these two phase diagrams are quantitatively different. Since both phase diagrams share a common point (76°C , atmospheric pressure, and $0 \text{ wt}\% \text{ 8AB}$) which is connected to a triple point by either a change in concentration and temperature or a change in pressure and temperature, the magnitude of these changes can be used to scale each of the phase diagrams for comparison purposes. If the scaled phase diagrams are nearly identical, then one could argue that the two phase diagrams are not only qualitatively similar, but quantitatively similar in that they differ by simply the scale factor relating pressure changes to concentration changes. Obviously, other scaling procedures are possible. This one is offered as simply one way to compare the two phase diagrams quantitatively.

To perform the scaling, all temperatures, concentrations, and pressures are measured relative to the point common to both phase diagrams. In other words, 76°C is subtracted from all temperatures, all concentrations remain as $\text{wt}\% \text{ 8AB}$, and atmospheric pressure is subtracted from all pressures. Then each measurement is divided by the change in temperature, concentration, or pressure between the common point and the triple point on the particular phase diagram. After the scaling, therefore,

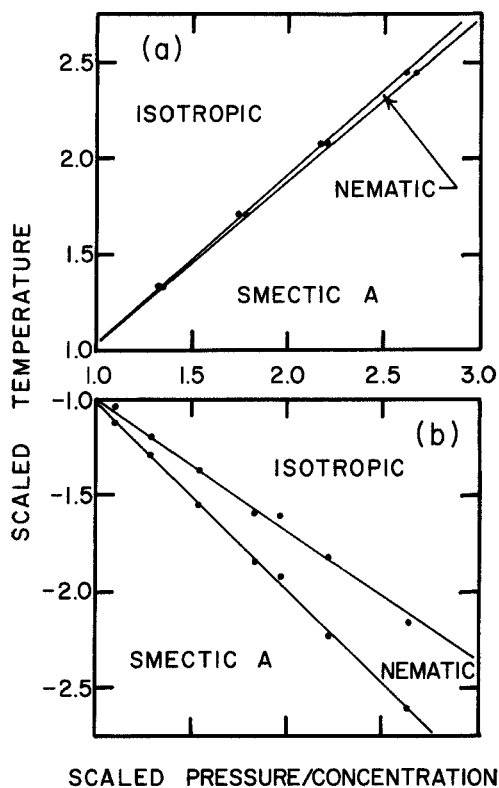


Figure 4. Temperature–pressure (a) and temperature–concentration (b) phase diagrams using scaled variables as explained in the text. The triple point is located at (1, 1) in (a) and (1, -1) in (b). Only the part of the phase diagrams containing the nematic phase is shown.

the point common to both phase diagrams occurs when all three scaled variables are zero, and the triple point occurs when the scaled concentration equals 1 and the scaled temperature equals -1 or when the scaled pressure equals 1 and the scaled temperature equals 1. Since the isotropic to smectic A transition curve is identical after the scaling process, figure 4 only shows the nematic region of both scaled phase diagrams. Notice that in spite of the scaling process, the width of the nematic phase differs appreciably in these two diagrams. Therefore, the conversion factor which relates temperature and concentration changes to temperature and pressure changes for the appearance of the nematic phase is not the same as the conversion factor for the widening of the nematic phase.

It is interesting to ask whether the quantitative differences between the two phase diagrams are due to the fact that the phase transition surfaces for this system are curved, or due to a particular orientation of planar phase transition surfaces. Since the phase transition curves in the (T, X) plane are very linear, each one together with the triple point in the (T, P) plane can be used to define hypothetical phase transition planes. These three planes intersect the (T, P) plane to produce extrapolated phase transition lines. How close do these lines correspond to the actual phase transition curves in the (T, P) plane? To answer this question, least square linear fits to the data shown in figure 3 together with the triple point in the (T, P) plane were used to define three hypothetical

phase transition planes. The intersection of these planes with the (T, P) plane are shown as dashed lines in figure 2 (the S_A - I transition line is virtually identical to the line drawn through the data, so it is not shown). Notice that except for the curvature present in the real data, the extrapolated phase transition lines closely resemble the real data. For this system, therefore, where the two compounds are very similar and have phase transition temperatures which are not too different, the thermodynamics is such that the phase transition surfaces are fairly planar over a wide range of temperature, pressure, and concentration.

5. Conclusion

A concentration induced smectic A -nematic-isotropic triple point has been found in a system which is known to possess a similar pressure induced triple point. Although there are some quantitative differences between the two phase diagrams, these differences result from the fact that the two experiments probe different regions of a simple (possessing nearly planar phase transition surfaces) temperature-pressure-concentration space.

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