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M. A. Marcus [a]
[a] Bell Laboratories 600 Mountain Ave., Murray Hill, NJ, 07974, USA
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INTERACTION OF MICELLAR ADDITIONS WITH THERMOTROPIC LIQUID CRYSTALS

M. A. MARCUS
Bell Laboratories
600 Mountain Ave.
Murray Hill, NJ USA
07974

Aerosol OT (AOT), a surfactant which forms inverse micelles, was added to a nematogen, 8CB, and cholesterogens having long and short pitches. The effect of the AOT additions on the liquid-crystal state was gauged by studying the phase diagram of the AOT-mesogen system. AOT depressed the clearing point of all mesogens. In 8CB, there was a retrograde solvus on the nematic side, followed by an isotropic liquid-liquid miscibility gap. The solubility of AOT with water added was greater than that of dry AOT. The blue phases of cholesterol butyrate were completely suppressed by 5 wt. % AOT, while the pitch of a cholesterol proprionate - chloride mixture was shortened by AOT.

1. INTRODUCTION

Liquid crystals are generally divided into two main types - thermotropic and lyotropic. The lyotropic mesophases can be again divided into "rods in suspension" and "surfactant-based" types. In this second type, the order involves the formation of micelles whose shape, size, and arrangement determine what the phase is[1]. For example, the common surfactant Aerosol OT (AOT) forms a middle phase when dry, a cubic phase at intermediate water concentrations, and a lamellar phase with larger amounts of added water[2]. This sequence of phases can be described as being due to a change in micelle shape from cylindrical to equilateral to planar. The presence of supramolecular aggregates is what distinguishes surfactant-based lyotropics from thermotropics.

What happens if one tries to combine thermotropic and micellar order? In this paper, I describe the results of some preliminary experiments along this line. The experiments involve the addition of AOT to a nematic and two cholesterics. AOT is known to form inverse micelles when solvated in a hydrocarbon. Thus, in the mesogen, it is probable that the AOT exists as aggregates which present a hydrocarbon surface to the solvent. Support for this theory comes from the fact that AOT with water added to it can be dissolved in 8CB (4,4'-octylcyanobiphenyl) at least as well as can dry AOT. Since 8CB is a relatively non-polar substance, the water could only have been accommodated inside micelles. The AOT-8CB and (AOT-H_2O)-8CB systems will be discussed below.

One way to look at micellar additions is as fine particles. It has been shown that the addition of fine particles to a nematic lowers its clearing point. What happens when the particles are extremely fine, as micelles are?

2. METHODS

AOT was purchased from Riber as a solution containing enough water to put it in the cubic-isotropic phase. This material was used as-is as "wet AOT". The wet AOT was dried by Soxhlet extraction with hexane, followed by warming to its isotropic point in a flow of nitrogen. The resulting material had a clearing point of 195-200°, the uncertainty being due to the slowness of the middle-isotropic transformation. The mesogens were from commercial sources and were used as-is.

The samples were made by mixing appropriate amounts of the components and heating and stirring until all the AOT was dissolved. The mixture was placed between a slide and coverslip and kept for at least a few hours at a temperature such that it was uniformly isotropic before examination. Care was taken to assure that the sample was truly in equilibrium at a given temperature before a decision was made as to its state at said temperature. For example, to find a (nematic+isotropic)-isotropic boundary, I would cool the sample to the point where nematic formed, then warm it slowly to a test temperature and wait at least twenty minutes. If the nematic phase was still present, the temperature was raised. If the nematic was gone, then the temperature was again lowered to nucleate the nematic, after which the sample was heated to a new, lower test temperature. For transitions involving the middle phase, the waiting period was hours, since the kinetics of the growth or dissolution of the middle phase are much slower than those of the nematic.

3. RESULTS

In Figs. 1,2 I show the phase diagram at the nematic end for the 8CB-AOT system. We see that AOT is much less soluble in the nematic phase than in the isotropic. Further, the retrograde solvus shows that the solubility of AOT in the nematic decreases with decreasing temperature. A one-degree drop in temperature produces a halving of the solubility. There is also a miscibility gap in the isotropic phase.

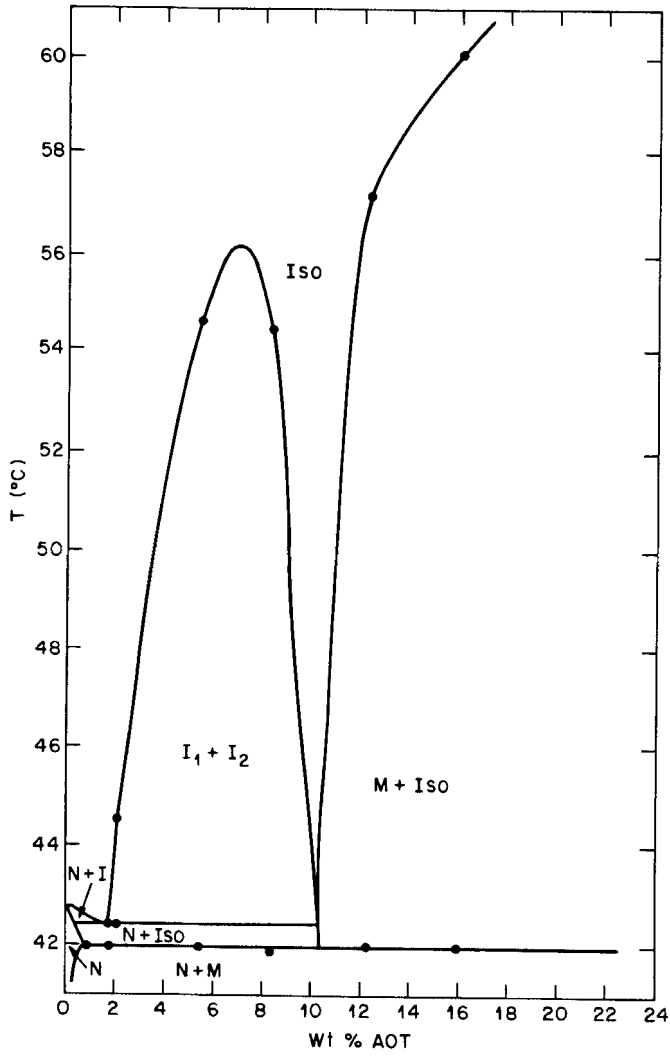

FIGURE 1. Phase diagram for 8CB-AOT system. M = middle phase, I = isotropic, N = nematic, $I_{1,2}$ = separated isotropic phases.

What happens if we use wet AOT instead of dry? The resulting phase diagram is shown in Fig. 3. The qualitative form of the diagram is unchanged by the addition of water, but the solubility of wet AOT in 8CB is greater than that of dry AOT. The wet AOT was doped with a small amount of methylene blue, a dye which is soluble in water but not in 8CB, and I found that only the AOT-rich phases were colored blue, indicating that all the water was solubilized by the AOT.

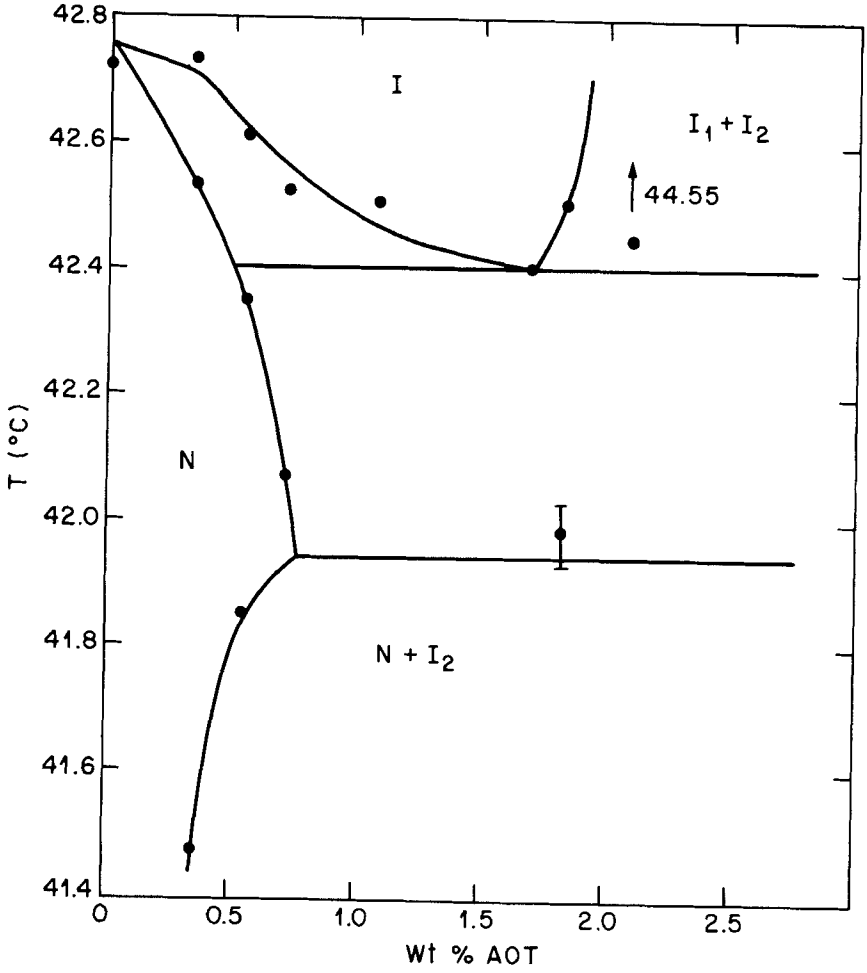

FIGURE 2. Detail of 8CB-rich end of 8CB-AOT phase diagram.

The cholesterol derivatives present a very different picture. As shown in Fig. 4, there is no two-liquid region when the solvent is cholesterol butyrate (CB), and the solubility of AOT in CB is much larger than in 8CB. As the AOT concentration increases, the high-temperature blue phase (BPII) drops out, followed by the BPI, until only the cholesteric is left. This behavior is typical of cholesterics mixed with achiral additives. What is very atypical is that the blue phases are suppressed by only 5% AOT. It would take 30% or more of a typical nematogen to do the same job[3]. Also, suppression of the blue phases is almost always accompanied by a lengthening of the pitch. A long pitch is known to be incompatible with the formation of blue phases.

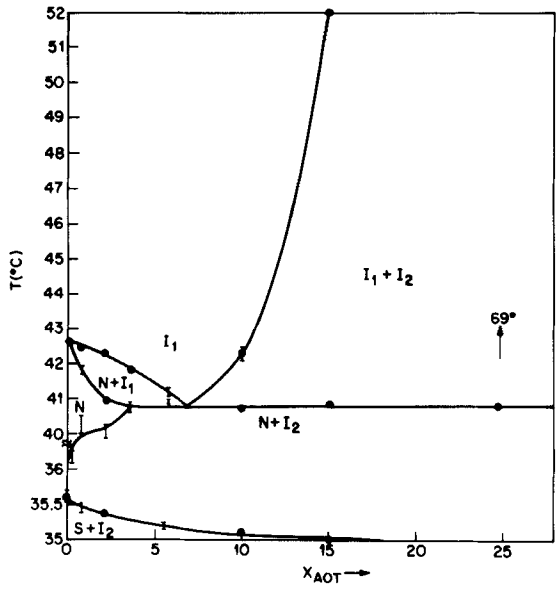

FIGURE 3. Phase diagram for 8CB-wet AOT system.

The blue phases make the phase diagram of the cholesterol butyrate - AOT system rather complex, and the short pitch of the ester makes it hard to measure the pitch of a mixture without the use of a Cano wedge. Such a wedge works best if the alignment is homogeneous, but the presence of AOT in the mixture probably induces homeotropic alignment. In nematics, the alignment is definitely homeotropic. Thus, I decided to use as a reference system a cholesterol derivative with a long pitch, hence no blue phases. Among the dozens of pure cholesterol derivatives I looked at, there were none with an enantiotropic cholesteric-isotropic transition and a pitch long enough to suppress the blue phase. Hence, it was necessary to use a mixture of cholesterogens of opposing twists. Such a mixture was 42.29 w/o cholesteryl chloride in cholesterol proprionate. I call this mixture "LPC", which stands for "Long-Pitch Cholesteric". LPC is nearly an ideal mixture, with a two-phase region .27° wide. At the top of its one-phase cholesteric region, it has a pitch of $1.9 \pm .07\mu$, which is long enough to measure accurately with the "fingerprint" method.

The phase diagram for LPC-AOT is shown in Fig. 5. As advertised, all the complexities of the blue phases have disappeared, leaving only cholesteric, isotropic, and two-phase regions. AOT is far more soluble in the cholesteric phases than in the nematic phase of 8CB. However, this difference is not evidence that there is something "magic" about cholesteric mesophases as opposed to nematics. Rather, it is more likely that the cholesterol derivatives are chemically more compatible with AOT than is 8CB. Note that there is no miscibility gap in the isotropic phases of the cholesterol compounds as there is with 8CB.

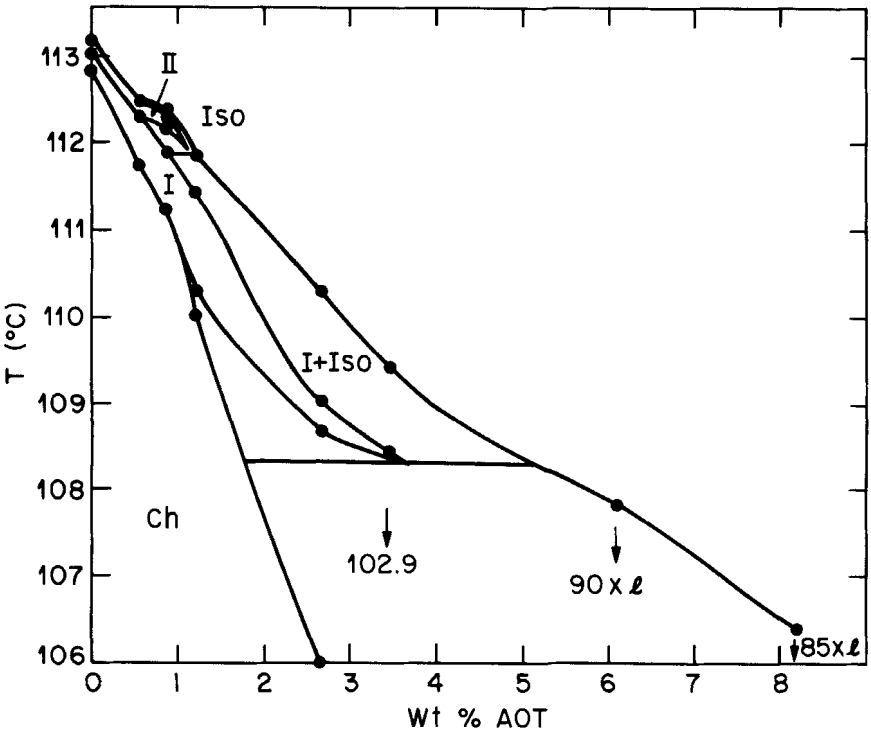

FIGURE 4. The cholesterol butyrate - AOT phase diagram. The roman numerals refer to blue phases, as identified by microscopy.

4. DISCUSSION

What can we learn from the foregoing phase diagrams about the interaction of micelles with mesophases? The above comparison of 8CB and cholesterol derivatives makes it clear that the molecular structure of the solute is important in determining what happens in both isotropic and meso- phases.

Consider the elastic energy cost of putting a micelle into a nematic. The director will have some preferred orientation at the micelle surface. This orientation will differ from the orientation far from the micelle, so there will be an elastic energy cost involved in this distortion. Suppose, just to get a rough number, that the micelle is long and cylindrical, with perpendicular boundary condition, and perpendicular to the unperturbed director. Then, if all elastic constants are equal, the energy cost of the distortion around the cylinder is given by $.072KL$, where K is a Frank constant, and L the length of the cylinder. Actually, the micelles of AOT are usually considered to be nearly spherical, so the effective length of the cylinder becomes equal to some multiple of its diameter, so the free energy cost assuming $L=2R$ is $.15KR$. Now let us plug in some numbers. For R we use the figure cited by Wong, et. al. for AOT in heptane[4], which is 13 Å For K

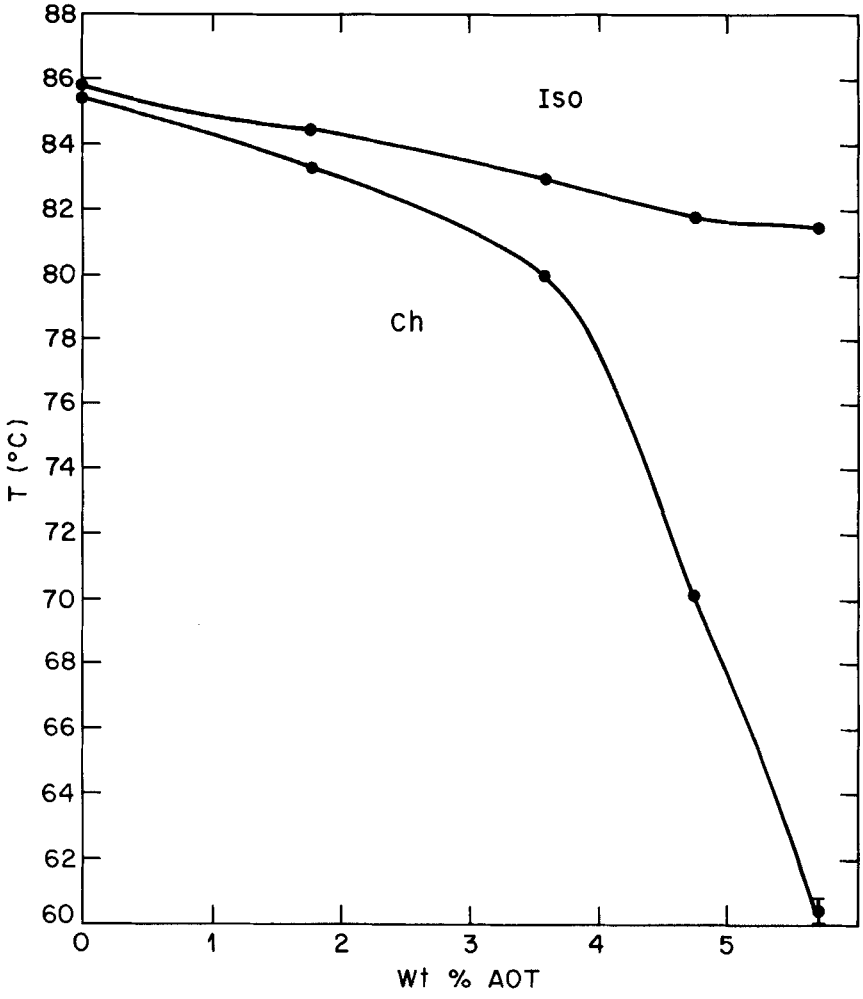

FIGURE 5. The LPC - AOT pseudobinary phase diagram.

we use the value for K_{11} for 8CB obtained by Madhusudana, et. al., which is 4×10^{-7}dynes[5]. The energy we get is 8×10^{-15}ergs. Now compare this to kT at 300°K, which is 40×10^{-15}ergs. We see that the two energies are within a factor of 5 of each other. Of course, many approximations went into this figure, not the least of which is the use of Frank theory on a scale smaller than a molecular length. Still, the point I want to stress is that the elastic cost of putting in micelles is comparable to kT, and may be the cause of the insolubility of the AOT in 8CB.

Perhaps the differences between the systems based on 8CB and cholesterol derivatives may be explained in terms of differences in elastic constants or effective

micelle sizes. The elastic constants for cholesterol derivative are not known, and the uncertainties mentioned above make micelle size more of a fitting parameter than a physical quantity.

Another point of interest is the drastic effect of small amounts of AOT on the blue phases of cholesterol butyrate. As shown above, it is not likely that the suppression of the blue phases can be explained by an increase of pitch with AOT content. Rather, it seems likely that the AOT affects the elastic constants or the surface-energy terms important to the formation of blue phases. A resolution of this question will have to wait for a means of measuring elastic constants of tight-pitch cholesterics.

5. CONCLUSIONS

We have seen that the addition of AOT to mesogens produces a variety of effects, which are not yet well-understood. There are many possibilities yet unexplored in micelle-former - mesogen systems.

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