

## **NMR Study on Phase Transitions in Lyotropic Liquid Crystals Caused by Hydrophobic Additives**

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### SUMMARY

Broad line NMR spectra have been measured at room temperature of the binary system Arkopal ( $C_9H_{19}C_6H_4O(CH_2CH_2O)_{15}H$ ) - heavy water (40 % to 60 % by weight) and of the ternary systems Arkopal - heavy water - paraffin at different paraffin concentrations at constant Arkopal - heavy water ratio. It has been established how the additives change the lyotropic phases.

In the lyotropic phases the hydrophilic heads of the mesogenic molecules lie on fixed surfaces, in which they perform translational diffusion. The hydrophobic parts of these molecules, following the heads in their lateral diffusion, possess a strict orientational order and are usually normal on average to the above mentioned surfaces. In the case of lamellar lyotropic phase, where the curvature of the layers is negligible, these surfaces can be considered to be planes. This means that the longitudinal molecular axis will keep its orientation in space. Of course, this simple picture is slightly distorted by the temperature induced orientational fluctuations of the separate segments of the hydrophobic parts of the molecules, especially at their ends. Nevertheless, the hexagonal lyotropic phase is quite different. In this case, the surfaces at which the hydrophilic molecular heads diffuse are cylinders. Upon diffusion of the molecule around the cylinder, the molecular axis changes direction. This change may occur with considerable speed. The greater orientational molecular fluctuations in the hexagonal phase result in a narrow-

ing of the broad line NMR spectrum in comparison with the corresponding spectrum of the lamellar phase. This gives the possibility of broad line NMR spectroscopy to be used for the indication of different phases. In the cubic phase, in which every lateral shift of the molecule is connected to a change of the molecular orientation, the narrowing of the spectrum is still greater.

That the stability of one lyotropic phase or another depends on the molecular structure of the mesogenic compound and on the percentage proportion of the mesogenic ingredients (in our case amphiphilic molecules) has been subject of a number of investigations: CHARVOLIN and MELY (1978), DERZHANSKI and BIVAS (1979), ISRAELACHVILI et al. (1976). Although different sides of this phenomenon are treated in these papers, their results can be summarized generally as follows: the lamellar phase is stable when the cross-section of the hydrophilic part and the hydrophobic part of one molecule are approximately equal. When increasing the cross-section of the hydrophilic heads in comparison to the hydrophobic chains a transition occurs to a hexagonal phase and after that to a micellar phase going eventually through intermediate isotropic liquid crystal phases.

If in the opposite case the hydrophobic part is more developed and its cross-section per molecule exceeds the cross-section of the hydrophilic head, the system passes by analogy through reverse hexagonal and reverse micellar phases.

In addition to modifying the structure of the mesogenic molecules, changes of the lyotropic phases can be caused also by introducing nonmesogenic admixtures - for example normal paraffins. Such an experiment was successfully done with water solutions of sodium dodecyl benzene sulphate, CHERNEVA (1976).

The present study considers the influence of the normal decane admixtures and normal octane admixtures on the polymorphism of the solutions of the non-ionic surface acti-

ve material  $C_9H_{19}C_6H_4O(CH_2CH_2O)_{15}H$  (Arkopal 15) in heavy water.

The binary system (Arkopal 15)- $D_2O$  displays a hexagonal lyotropic phase at proportions 40 % (Arkopal 15) to 60 %  $D_2O$  by weight at room temperature.

Using a homemade NMR spectrometer, we recorded broad line NMR spectra of the binary system (Arkopal 15)- $D_2O$  in the above mentioned proportion and of the ternary systems (Arkopal 15)- $D_2O$ -octane and (Arkopal 15)- $D_2O$ -decane for different concentrations of the paraffins keeping the same proportion between (Arkopal 15) and  $D_2O$ .

The second moments  $\Delta H^2$  characterizing the widths of the spectra recorded by us are given in Table 1. The data show that the increase of the concentrations up to about 5 % of both paraffins, which is connected to the effective increase of the hydrophobic chain cross-sections, leads to a broadening of the spectrum. This can be explained by passing of the system to a lamellar phase.

The above-mentioned transition from a hexagonal to a lamellar phase is confirmed also by the polarizing microscope textures presented in GRAY and WINSOR (1974) of the respective samples (figure 1).

A further increase of the content of the octane or decane of 10 % - 15 % results in a narrowing of the spectrum, table 1. This could mean a transition to a reverse hexagonal phase. But since at these concentrations the samples observed in the polarizing microscope are optically isotropic, it is more likely that another isotropic phase between the lamellar and reverse hexagonal phases occurs. The jellylike consistency of these samples also testifies to this.

ratio A15 to D <sub>2</sub> O to paraffin	kind of paraffin	$\overline{\Delta H^2}$ OCTANE	$\overline{\Delta H^2}$ DECANE
40:60: 0		1,87	1,87
40:60: 2,5		2,21	2,47
40:60: 5		4,10	4,81
40:60:10		3,63	3,88
40:60:15		2,91	3,75

TABLE 1

Values of the second moments of the spectra for the  
different mixtures

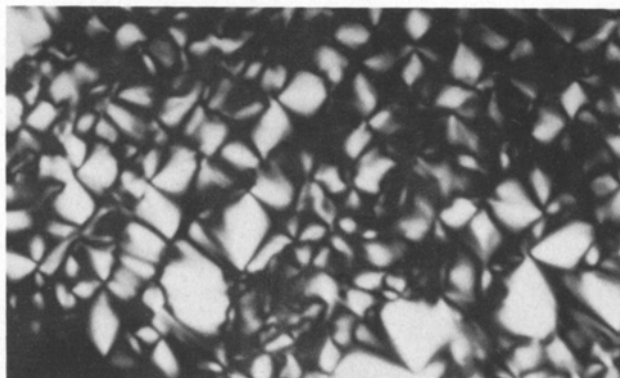


FIGURE 1a

Hexagonal phase of the water solution of Arkopal 15  
40 % to D<sub>2</sub>O 40%



FIGURE 1b

Lamellar phase of the water solution of  
Arkopal 15 40% to  $D_2O$  60% to 2,5% octane



FIGURE 1c

Lamellar phase of the water solution of  
Arkopal 15 40 to  $D_2O$  60% to 2,5% decane

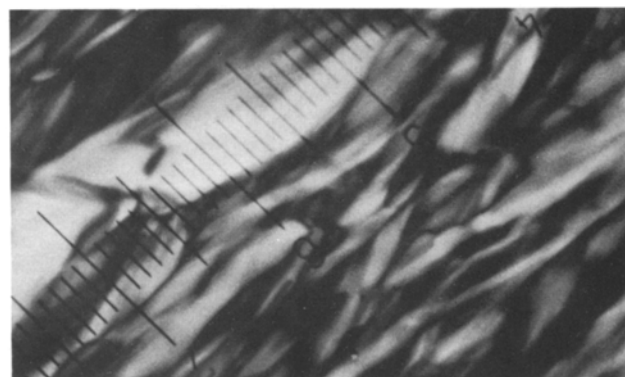


FIGURE 1d

Lamellar phase of the water solution of  
Arkopal 15 40% to  $D_2O$  60% to 5% octane

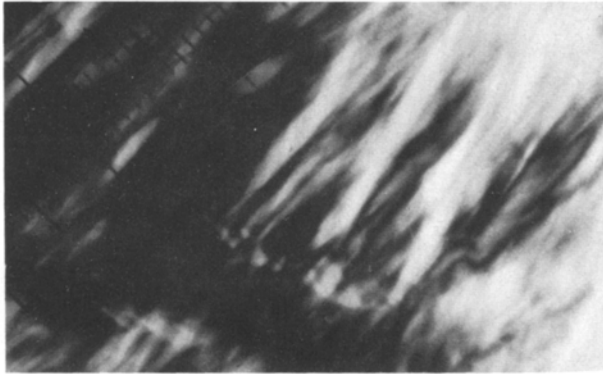


FIGURE 1e  
Lamellar phase of the water solution of  
Arkopal 15 40% to D<sub>2</sub>O 60% to 5% decane.

### References

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