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DEMIXING OF NEMATIC LYOPHASES

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Abstract We are studying the conditions for the demixing of nematic lyomesophases from decanol, heavy water and sodium decylsulphate or potassium laurate.

INTRODUCTION

Nematic lyophases provide good biological membrane models. The phase of this kind most frequently encountered was initially studied by Radley and Reeves[1].

We have shown in a recent work[2] that the usual nematic solution separates in layers after having been submitted to a raise in temperature. This was neither due to evaporation nor to hydrolysis of the sodium decylsulphate[3]. The demixing of the solution depended on the thermal pretreatment. It usually started after a couple of days but needed sometimes several weeks to be accomplished.

The present work is a complementary study of the lyophase evolution. It discloses the influence of the surfactant cosurfactant ratio on the layer separation. The effect from a previous raise in temperature is shown. We also report that demixing occured in a parent nematic lyophase initially studied by Yu and Saupe[4].

EXPERIMENTAL PART

Hendrikx and Charvolin have determined the phase diagram of the mixture sodium decylsulphate (SdS), decanol (dOH) and deuteriumoxide[5].

In order to study the influence of small concentration variations on the demixing, we have prepared a series of 12 solutions for which the ratio (in weight) amphiphile (SdS + dOH) to deuteriumoxide was kept constant but the ratio SdS to dOH varied (figure 1).

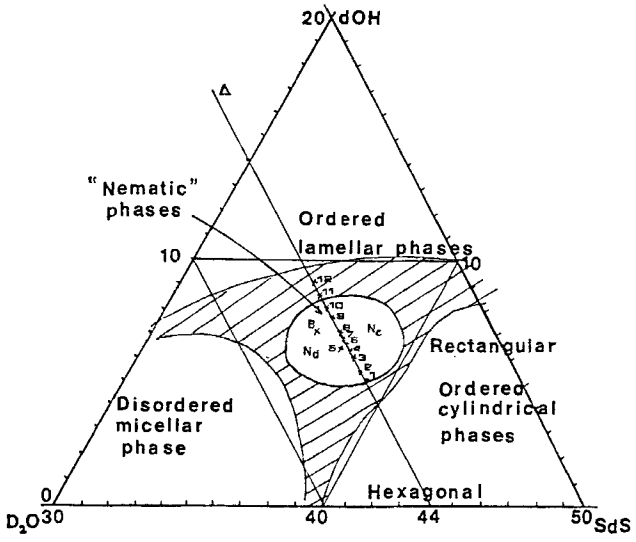


FIGURE 1. The phase diagram of the solution SdS-dOH-D_2O after Hendrikx and Charvolin. The compositions 1 to 12 are situated near the straight line Δ. Point B represents the composition : 35.9% SdS, 7.2% dOH, 56.9% D_2O

We have determined the upper limits of the nematic domain as the temperature was raised above 22°C. This was done through texture observations of the 12 solutions. The transition temperatures were plotted against the alcohol concentrations (figure 2).

According to the previously described method[2] we have preheated the samples at 6°C per hour up to 60°C. They were

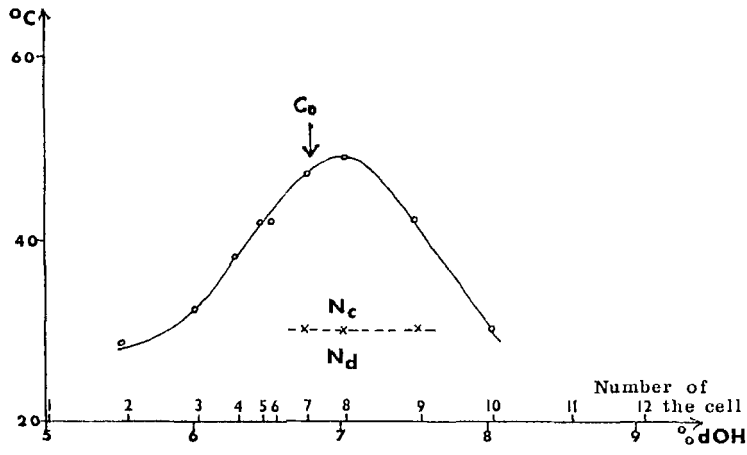


FIGURE 2. Transition temperatures plotted aginst the alcohol concentrations.

then brought back to room temperature at the same rate. This pretreatment introduced no appearent change. The samples were then maintened at 27.00 ± 0.05°C for six days.

The nematic phase of Yu and Saupe[4] was prepared from potassium laurate (KL) according to literature (26.10% KL, 6.24% dOH, 67.66% D_2O).

A series of samples of the laurate phase was placed in a thermostate at temperatures varying between 10 ans 50°C with a temperature difference of 3 to 4°C between each cell. It was maintained for six days.

The experiences were performed in spectroscopic cells of path 1 mm. The texture observations were done with a "Leitz Dialux Pol" hot stage microscope.

The cells were observed and photographed in crossed polarized light at room temperature after the described thermal treatments.

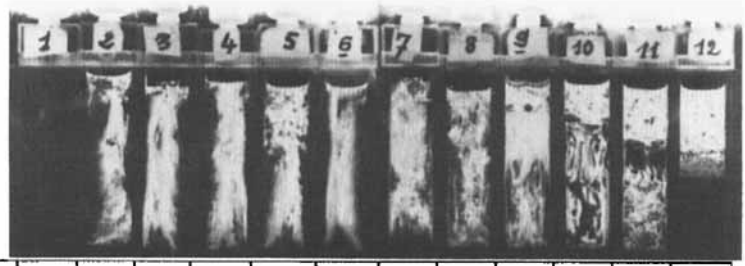
The demixing of the various nematic compositions has

been observed qualitatively. A more complete investigation of the well separated layers has been done previously for composition B^2. In this case the upper layer was found to be lamellar the middle layer nematic and the bottom layer isotropic.

RESULTS AND DISCUSSION.

Figure 2 shows that the nematic domain shrinks in the SdS-solutions when the temperature is raised. This is in agreement with the result given by Yu and Saupe for a series of varying concentrations where the percentage of dOH was kept constant[6]. Transitions N_D (discotic nematic) to N_C (calamitic nematic) were observed only for the samples n°7, 8 and 9. The solutions n°1, 11 and 12, situated close to the border of the nematic domain, appear polyphasic or isotropic at room temperature.

Figure 3 shows the SdS-samples photographed at room temperature after the thermal treatment described above.



% dOH	5.02	5.54	6.02	6.28	6.43	6.55	6.77	7.03	7.52	8.02	8.54	9.03
Ratio SdS/dOH	7.8	7.0	6.3	6.0	5.8	5.7	5.5	5.3	4.9	4.5	4.2	3.9

FIGURE 3. Samples 1 to 12 between crossed polarizers.

Demixing appeared in the solutions above a critical concen-

tration C_o (6.77%). The aspects of the samples close to the borders are, however, related to initial polyphasic mixtures.

The samples n° 2 to 7 have remained monophasic. The layer separation appeared from n° 8 onwards with a regular increase of the upper layer.

Nematic solutions along Δ close to C_o have the highest upper transition temperatures for the nematic phase with a maximum for sample n° 8 as seen in figure 2. This explains a more or less rapid escape from the nematic domain for the various compositions as the temperature was raised.

We believe that the demixing is caused by rearrangement of the molecular aggregates resulting from nucleation during preheating. Above C_o the return is irreversible and layer separation appears in the sample. At concentration lower than C_o the solutions remain stable in spite of similar passages into non nematic phase domains.

The effect of thermal pretreatment is shown in figure 4. The three samples were of the same composition B.

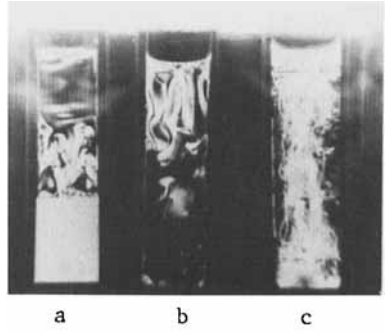


FIGURE 4. Evidence of necessary preheating.

We have here compared the preheated cells a and c with the non preheated cell b. Demixing appeared clearly in a (after six days at 27°C) and less pronounced in c (after six days

at 45°C). Cell b (after six days at 27°C) showed no distinct layers.

The qualitative result of temperature effect on demixing of the KL-solution is shown in figure 5.

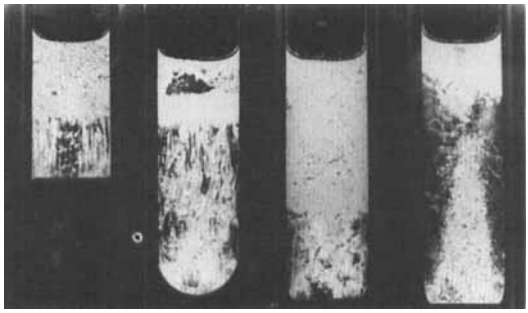


FIGURE 5. Demixing of the potassium laurate solution.

We are only showing pictures of the cells where layers had formed. This was the case for the following temperatures 11°C, 34°C, 37°C and 48°C. The first and the last are close to the known transition temperatures while the intermediate temperatures are not. For the initial sample, we have observed in accordance with literature [7].

$$\text{Iso} \xrightarrow{13^\circ C} N_D \xrightarrow{20^\circ C} N_C \xrightarrow{42^\circ C} \text{Biph.} \xrightarrow{45^\circ C} \text{Iso}$$

Thus, thermal conditioning close to a transition temperature does not seem to be the only decisive factor on the demixing proceedure.

Visual observations in crossed polarized light showed that the demixing looked like that of the previously studied solution B. We have not done any microscopic texture determinations of the various layers here described.

The similarity in the behaviour of the two nematic solutions, one from SdS and the other from KL, shows that the observed phenomenon is general and not related to specific

properties of the amphiphile.

The practical conclusions of our studies are that when such nematic solutions undergo raises in temperature, more or less stable domains with respect to demixing appear in the phase diagram.They are limited by critical decanol concentrations as seen from C_o in the present investigation.

Also, as mentioned previously [2] water solutions are much more stable than solutions prepared with deuterium-oxide.

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