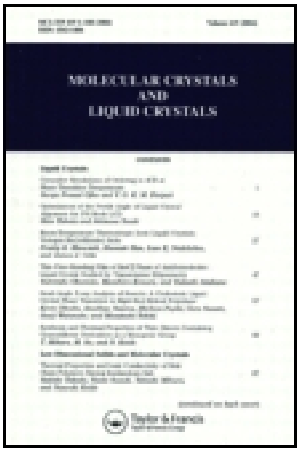

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Instability of a Nematic Lyophase

M. Laurent [a] , A. Hochapfel [a] , M. Boidart [a] & R. Viovy [a]
[a] Laboratoire de Physico-Chimie des Pigments Végétaux et Substances Modèles, de l'Ecole Normale Supérieure de Saint-Cloud, Grille d'Honneur-Parc de, Saint-Cloud 92211, Saint-Cloud, France

Version of record first published: 20 Apr 2011.

To cite this article: M. Laurent , A. Hochapfel , M. Boidart & R. Viovy (1984): Instability of a Nematic Lyophase, Molecular Crystals and Liquid Crystals, 109:2-4, 189-201

To link to this article: http://dx.doi.org/10.1080/00268948408078706

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 189–201
0026-8941/84/1094–0189/$18.50/0

Printed in the United States of America

Instability of a Nematic Lyophase

M. LAURENT, A. HOCHAPFEL, M. BOIDART and R. VIOVY

Laboratoire de Physico-Chimie des Pigments Végétaux et Substances Modèles, de l'Ecole Normale Supérieure de Saint-Cloud, Grille d'Honneur-Parc de Saint-Cloud 92211 Saint-Cloud France

(*Received May 12, 1983; in final form March 12, 1984*)

We have observed that a ternary nematic solution from sodium decyl sulphate, decanol and heavy water separated into layers of different phases during storage. The separation was favoured when the sample had been previously heated above room temperature up to 50 ° C. The time needed for the demixing to occur varied from several hours to weeks. The solution ended up as a three-phase system: lamellar at the top, nematic in the middle, and isotropic at the bottom. The initial homogeneous nematic solution was restored when the layers were stirred. The nematic solution prepared with ordinary water was far more resistant to demixing. The similarity to emulsions is discussed.

INTRODUCTION

Nematic phases in lyotropic solutions are now well recognized, largely due to Reeves and coworkers,[1-3] Saupe,[4,5] Long[6] and Charvolin.[7,8] These systems make useful membrane models, because their micellar aggregates can be oriented either by surface treatments or by magnetic fields. Guest molecules oriented within the micelles lead to effects such as linear dichroism which has been studied by our group.[9]

We have used the nematic solution (initially proposed by Reeves[1]) of the following composition: 35.9% sodium decyl sulphate, 7.2% decanol, 56.9% deuterium oxide. Hendrikx[10] determined the phase diagram of the ternary system at 22 °C and showed that the nematic area is limited to within a few percent variation of each compound. It is surrounded by poly-phasic regions. The phase diagram for similar compositions given by Yu[5] shows that the nematic domain shrinks with increasing temperatures up to 45 ° C.

The above described composition, chosen from the middle of the nematic domain, has characteristic textures and reversible transition temperatures.[9]

Nevertheless, we have observed that the initially homogeneous nematic solution separated into several phases under certain conditions. The demixing was greatly favoured when the solution was brought back to room temperature after moderate heating. It was first observed as a coincidence when we studied the temperature effect on the dichroism in a magnetic field of a nematic dye solution up to slightly above 50 °C. We checked that no loss of compounds had occurred and no hydrolysis of the sodium decyl sulphate had taken place during the experiment. The homogeneous nematic phase was easily restored by stirring. The separation and remixing have been observed at least twenty times in samples from various preparations of the nematic stock solution. In another study,[11] we have shown that the behaviour is concentration dependent. Under the same conditions, some nematic mixtures chosen from the phase diagram did demix, while others remained stable.

A much greater stability against phase separation was observed in preparations made from water instead of deuterium oxide.

EXPERIMENTAL

Phase preparation was carried out as described in the literature.[2] The samples were stored in a Memmert RO8 incubator at 24 °C. Thermal conditioning at various temperatures was performed in the following manner: spectroscopic cells of path 1 mm were filled with nematic solution and placed into tight fitting cavities evenly spaced in a copper bar between two sources of heat providing a suitable temperature gradient (23–52 °C).

Samples from the various layers were withdrawn using a hypodermic syringe while viewing the cell between crossed polaroid films.

The textures were observed and photographed in polarized light using samples placed on the hot stage of a Leitz Dialux Pol microscope in flat cells of path 10 μ.

The dye kindly given to us by Dr. M. G. Pellatt of BDH Chemicals Ltd, 1-(4′-butoxyanilino)-4-hydroxyanthraquinone (D 11), was used as a guest molecule. It was dissolved at a concentration of 10^{-3} M kg^{-1} in the lyotropic solution through alternate sonication and moderate heating up to 50 °C.

The absorption spectra were measured with a Beckmann Acta CIII spectrophotometer. Densities were measured in a glass pychometer (1 cm^3) at room temperature.

Analysis of the concentration of sodium decyl sulphate was made through titration of the acidity with 0.1 M sodium hydroxide solution after complete sample hydrolysis in sealed tubes at 135 °C for 5 hours. The method was checked with test samples to give results with an accuracy of ±0.5%. The concentration of decanol was determined by a chromatographic method published elsewhere.[12]

RESULTS

Figure 1 shows the layer separation in a cell; Figure 1*a* shows the situation as it was seen after about three weeks, and Figure 1*b* after two months. The first picture shows various diffuse zones that end up in a three-phase separation having distinct interfaces, as seen in the second picture. The amount of each layer varied from one experiment to another, but most of the time, the observed volume ratios were close to those given in Table I.

In order to investigate the influence of the thermal history of the sample, we have compared nematic solutions stored at 24°C after preparation with solutions preheated up to 50 °C at 6 °C per hour, non critical conditions close to those of the experiment on dichroism where the demixing was first observed.

We further wished to examine if there were some effects from phase transitions and viscosity variations.[13] This was done by thermal conditioning of both normally stored and preheated samples, and ten cells of each were heated at regular intervals between 23 and 52 ± 1°C for six days and then stored at room temperature overnight before observation. We could definitely see much more pronounced effects in the preheated cells. The best layer separation had taken place around 27 and 45 °C which are transition temperatures for the nematic solution. To avoid temperature gradients during thermal conditioning, fresh samples were heated at 26.85 ± 0.01°C and 45.25 ± 0.01°C, again for six days, and then stored for two days. Figure 2 shows pictures of these cells. The lower temperature conditioning resulted in a three layer separation for the preheated sample. The bottom layer had not yet become isotropic, but this was also the case for the samples shown in Figure 1 at the beginning of storage. The normally stored sample showed a less clear separation. Only two layers could be seen in the higher temperature conditioned sample.

The exact conditions for demixing are difficult to determine because of its slow kinetics. This might be explained by the presence of large aggregates in the solution and related to the high viscosity (300–600

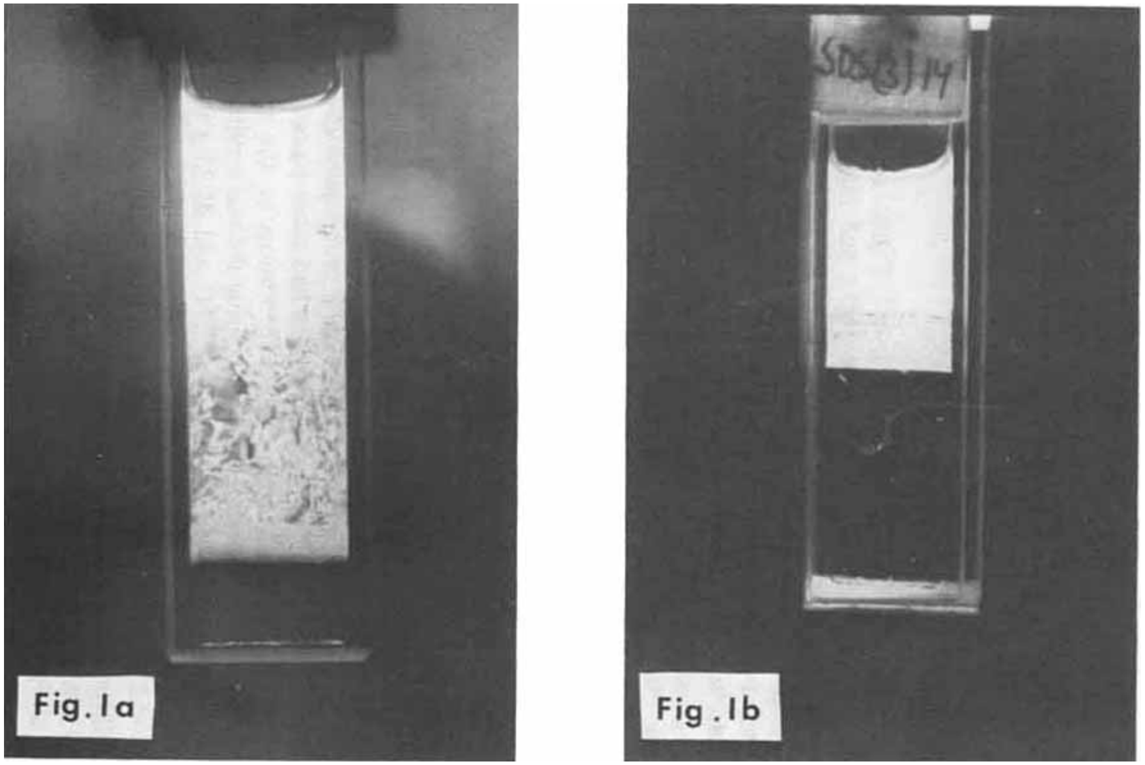

FIGURE 1 Demixing observed at 22° C of the nematic solution from 35.9% sodium decyl sulphate, 7.2% decanol, 56.9% deuterium oxide: *a*) during the demixing period, *b*) when no further change could be seen.

TABLE I

Experimental results for the analysis of the demixed layers compared with those for the initial solution
(Lam = lamellar; N = nematic; Iso = isotropic)

Sample	Relative volume	Texture 22 °C → 40 °C	Sodium decyl sulphate % (by weight)	Decanol—Relative weight ratio	Specific gravity
Top layer 1.	2	Lam(+N)	37.1	1.3	1.105 ± 0.01
Middle layer 2.	1	N	35.2	1.0	—
Bottom layer 3.	3	Iso	33.9	0.8	1.115 ± 0.01
Initial homogeneous phase		N	35.9		1.113 ± 0.001

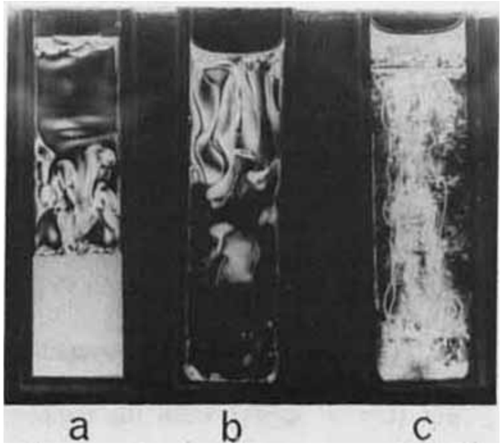

FIGURE 2 Demixing observed at 22 °C of the nematic solution from 35.9% sodium decyl sulphate, 7.2% decanol, 56.9% deuterium oxide after thermal conditioning of samples at the temperatures indicated below for six days, followed by storage at 24 °C for two days. *a*) Preheated sample conditioned at 26.85 ± 0.01 °C; *b*) Normally stored sample conditioned at 26.85 ± 0.01 °C; *c*) Preheated sample conditioned at 45.25 °C.

cP).[11] The thermal effect is clear but complex and reproducible results are hard to obtain. Ultracentrifugation up to 160,000 G for 65 hours was found insufficient in order to start demixing.

The nematic solution prepared with water instead of deuterium oxide and with the same molar ratios separated in layers only after a few months' storage even in preheated cells.

Sample control

We have observed our samples in tightly stoppered cells and checked that the loss of weight did not exceed 0.1% during heating.

The pH inside the cells under study remained neutral, showing that no hydrolysis of the sodium decyl sulphate had taken place.[12]

We observed that the textures and transition temperatures of the initial nematic solution were restored when the layered samples were mixed with a magnetic stirrer.

Phase studies

We have made investigations of the three phases which separated as in Figure 1b; we have named these layers 1, 2 and 3 from top to bottom. The textures of each layer and their variations with temperature are shown in Figure 3, together with the texture sequence of the initial homogeneous solution.

Layer 1, Figure 3*a*, *b*, *c*: at room temperature the preparation is mainly black, homeotropic, containing drops of nematic *schlieren* texture (*a*). At 33 °C, numerous positive and negative units develop in the black areas and slowly grow into a fine mosaic (*b*). This is a characteristic of the lamellar texture.[14] At 45 °C there is a transition of the entire sample into large areas of fan-like texture separated by some isotropic liquid (*c*).

Layer 2, Figure 3*d*, *e*, *f*: at 23 °C, the texture is of the planar nematic type (*d*). No significant modification is seen at 27 °C. At 47 °C the sample becomes dotted with *bâtonnets* (*e*), and at 53 °C it turns into a fan-like texture (*f*).

Layer 3, Figure 3g, *h*: the sample shows overall extinction from room temperature up to 45 °C, remaining black in convergent light. Focal-conic groups start to appear when the temperature is raised further.

The phases in the separated layers, as identified through their textures, are thus found to be the following (as indicated in Table I): lamellar in coexistence with small quantities of nematic, possibly due to incomplete demixing at the top; nematic, somewhat modified through changes in composition in the middle; isotropic at the bottom.

The measured densities are given in Table I. Compared with the initial phase, the upper layer was of lower and the bottom layer of higher density.

The layer composition was analysed on the one hand with respect to sodium decyl sulphate content and on the other hand to decanol content. The results are given in Table I and show a decrease of both

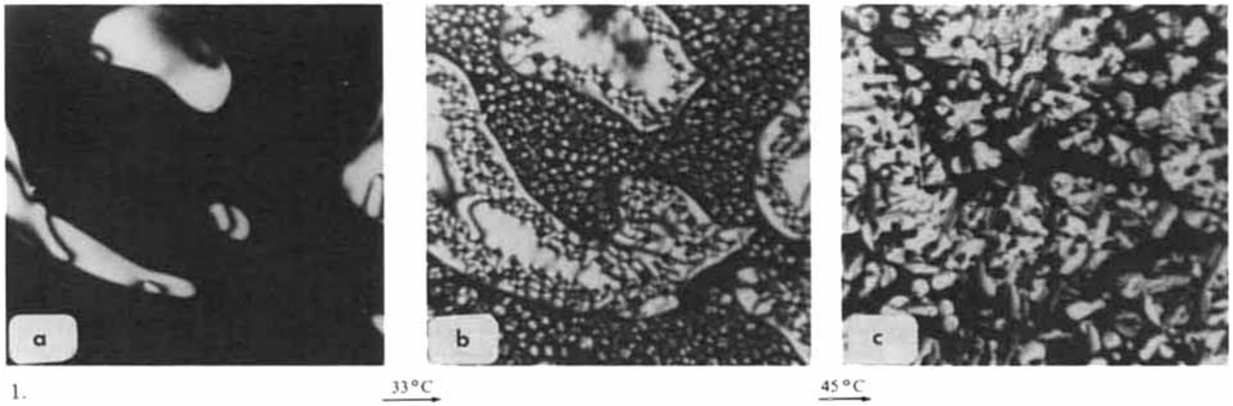

FIGURE 3 Sequence of textures and transition temperatures of the layers of the nematic solution from 35.9% sodium decyl sulphate, 7.2% decanol, 56.9% deuterium oxide at the end of the demixing. Layer 1. *a*, *b*, *c*, layer 2. *d*, *e*, *f*, and layer 3. *g*, *h*. Sequence of textures and transition temperatures of the initial homogeneous solution:[9]

$$\text{Cryst.} \xrightarrow{18\,°\text{C}} \text{Homeotropic } N_D \xrightarrow{27\,°\text{C}} \text{Planar or schlieren } N_C \xrightarrow{42\,°\text{C}} \text{Iso} \xrightarrow{45\,°\text{C}} \text{Fanlike}$$

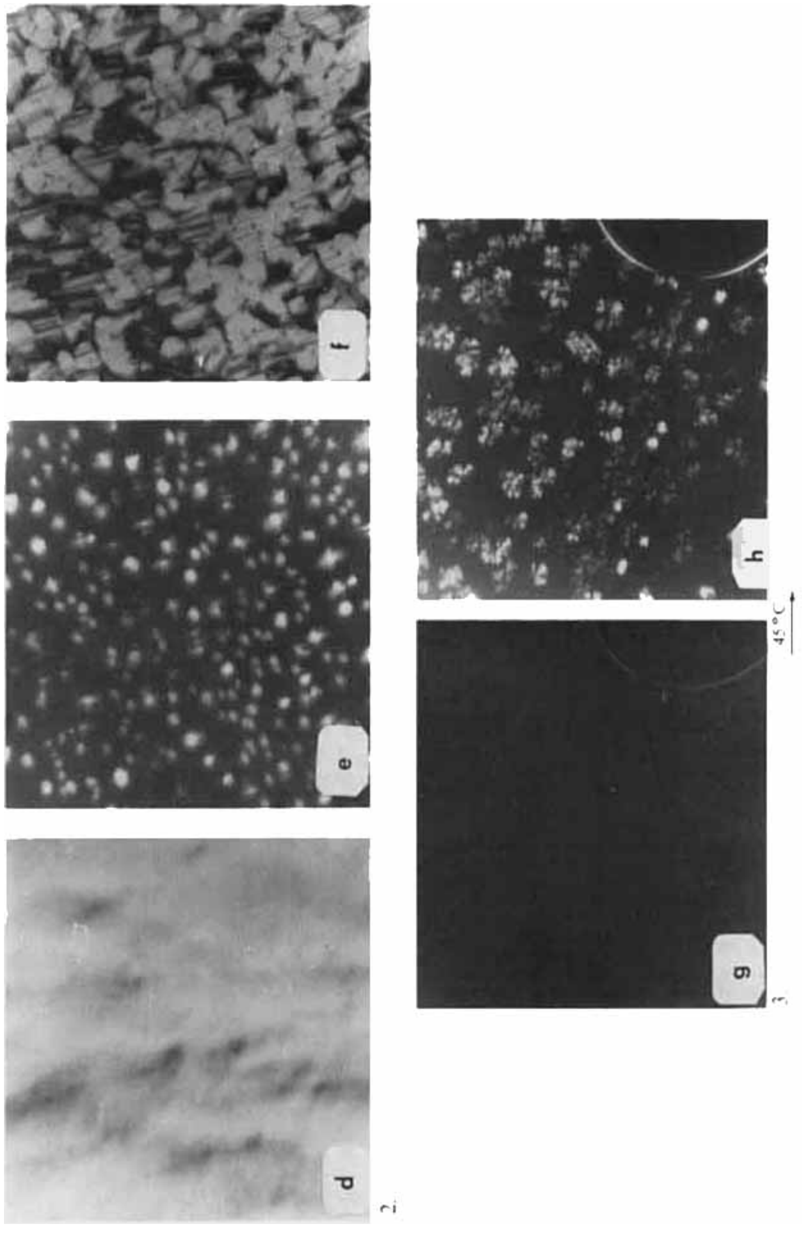

FIGURE 3 (*Continued*)

components when moving downwards from the top. The decanol content varied to a much greater extent than that for sodium decyl sulphate. Because of the small quantity available of the middle layer, analysis revealed no significant difference from the initial solution.

We have prepared two solutions according to the top and bottom layer concentrations given in Table I. The "top" solution was of the following composition: 37.9% sodium decyl sulphate, 9.4% decanol, 52.7% deuterium oxide and had a lamellar texture which remained up to higher temperatures. The "bottom" solution had the following composition: 34.6% sodium decyl sulphate, 5.8% decanol, 59.6% deuterium oxide and was isotropic at room temperature and up to 30 °C. We mixed the two solutions through magnetic stirring in the following proportions 2 of "top" : 3 of "bottom". This resulted in a nematic solution at room temperature with the following textures and transition temperatures

$$\text{Homeotropic} \xrightarrow{25\,^\circ\text{C}} \text{Planar} \xrightarrow{40\,^\circ\text{C}} \text{Isotropic} \xrightarrow{45\,^\circ\text{C}} \text{Fan-like}$$

The similarity to the initial solution shows the self consistency of the experiment.

Distribution of a solute

When nematic-dye solutions of 1-(4′-butoxyanilino)-4-hydroxyanthraquinone demixed, we observed unequal distribution of the dye between the layers. The ratio of the optical densities of the top and bottom layers was about 1.3.

DISCUSSION

We have found that a ternary nematic solution of sodium decyl sulphate, decanol and heavy water separates into several layers, and after sufficient time gives a final situation with a less dense lamellar phase at the top and a more dense isotropic phase at the bottom. The differences in densities were established and the nature of the phases were identified by their textures. The phase assignment agrees with comments made on relative phase densities.[15] The behaviour is close to the phase separation from poly-phasic solutions as described by Mandell,[16] and the phase sequence with varying water content is in agreement with Winsor's R-theory.[17] The three types of phases are found to coexist in the poly-phasic region surrounding the nematic domain.[10] In the phase diagram, we find the expected phases for the measured layer composition. Chemical analysis shows the highest amphiphile concentration at the top, decreasing towards the bottom, and this confirms the phase separation. The unequal solubility of the water insoluble dye is related to the concentration of amphiphilic micelles.

Separation of the nematic phase into layers is enhanced when the temperature is raised. This can be explained by the phase diagram of Yu and Saupe. With increasing temperature, the sample first goes through the transition $N_D \rightarrow N_C$ where there is a certain instability. This transition region is referred to as "biaxial".[18] Our results provide good evidence that the "biaxial" phase may be a Nc/Nd emulsion.

At higher transition $N_C \rightarrow \text{Iso} + (M) \rightarrow M$, the sample reaches another situation of instability.[13] We assume that a certain "nucleation" then takes place, probably through local rearrangements of micellar fields which result in concentration gradients.

From the available phase diagrams, one can reasonably suppose that the nematic phase exists in a cone-shaped volume when the

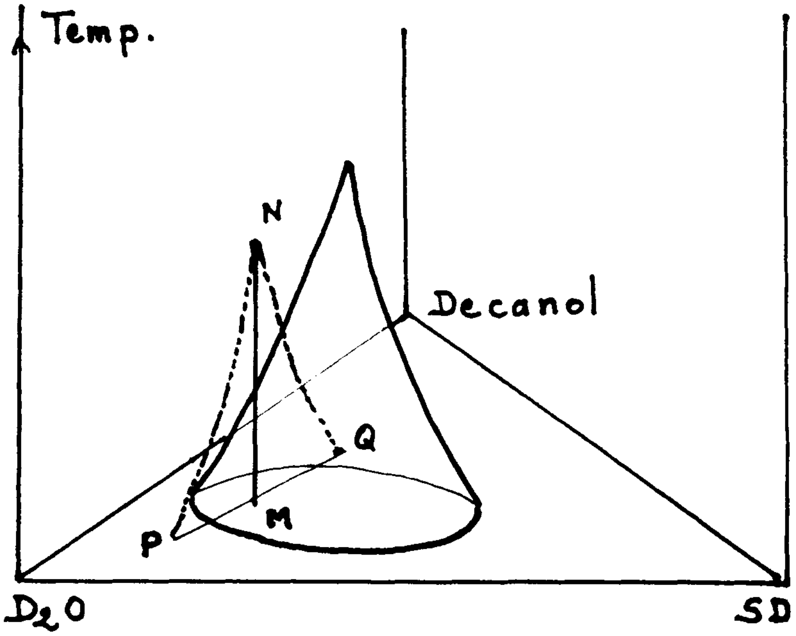

FIGURE 4 Schematic diagram explaining the expected mechanism of demixing. Demixing appears outside the cone at high temperatures (Point N). Cooling takes place along both lines NP and NQ. The compositions remain altered at low temperatures (Points P and Q).

temperature is raised, as shown by the drawing in Figure 4. The temperature increase and the concentration gradients might move the sample from inside the cone into poly-phasic regions as shown in the phase diagram of Hendrikx and Charvolin. The drawing shows the supposed variation of a point M representing the composition of the solution studied.

The fact that ultracentrifugation had little effect must mean that the separation is related to some process of formation governed by slow kinetics. The phase separation cannot be explained by density differences alone. It needs the thermal initiation described above. The demixing of the nematic solution seems, according to the experimental evidence, to reach an equilibrium, because some nematic phase (slightly modified) remains in the middle layer. This reminds us of the Winsor III system of microemulsions recently discussed by Biais.[19] The "final" situation where we have observed three phases is not contradictory to the phase rule for a ternary system at constant temperature and pressure.[20]

We have examined a series of samples with constant heavy water concentration, but with a varying ratio of sodium decyl sulphate to decanol.[11] The compositions were situated on a line crossing the middle of the nematic area in the phase diagram. On one part of this line, the samples were stable under the given conditions. For a difference of 0.26% decanol, the sample moved to another part of the line where progressive demixing took place as the decanol content increased.

We can presume that the nematic layer 2 belongs to a stable concentration area, reached through small variations in the composition.

The fact that the nematic phase behaves as a homogeneous and thermally reversible solution on the microscope hot stage and in nmr studies must partly be due to the slow kinetics of demixing and partly to wall effects and sample mixing.

The greater stability of nematic phases prepared with water than those prepared with deuterium oxide is in agreement with results found in the literature. Eicke[21] observed similar properties of micellar aggregates in micro-emulsions. The faster phase separation in deuterium oxide than in water is probably the result of the layer density difference between phases of different water content.

Tamamushi[22] has more recently taken up the discussion of Ostwald at the beginning of the 1930's on the relations between colloids and mesomorphic systems, and Friberg[23] has shown how mesomorphic order interferes to stabilize emulsions. This is the case for microemulsions where two insoluble liquids are brought into a homogeneous dispersion when separated by an ordered membrane of surfactant and cosurfactant. Friberg[23] shows an example of a liquid two phase system leading to a lamellar mesophase when mixed, but which separates again with time, when left to itself.

The influence of slight modifications of temperature or concentration demonstrates that the nematic compositions have phase boundaries that are hard to define, because of small free energy differences between neighbouring and nematic phases. This explains why a sample behaves like a stable monophase in a region that is multi-phase at equilibrium.

There are thus relations between emulsions and lyomesophases which lead us to believe that the nematic solution we have studied behaves like an emulsion of lamellar and isotropic solutions. We need similar observations on other nematic lyophases to determine whether or not the demixing is general in such systems.

References

1. K. Radley and L. W. Reeves, *Can. J. Chem.*, **53**, 2998 (1975).
2. K. Radley, L. W. Reeves and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
3. B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981).
4. A. Saupe, *J. Coll. Interf. Sci.*, **58**, 549 (1977).
5. L. J. Yu and A. Saupe, *J. Amer. Chem. Soc.*, **102**, 4879 (1980).
6. R. C. Long and J. H. Goldstein, "Liquid Crystals and Ordered Fluids" (Eds. J. F. Johnson and R. S. Porter) Plenum Press, New York and London (1974), Vol. 2, p. 147.
7. J. Charvolin and Y. Hendrikx, *J. Phys. (Paris) Lett.*, **41**, L-597 (1980).
8. J. Charvolin and Y. Hendrikx, "Liquid Crystals of One- and Two-Dimensional Order" (Eds. W. Helfrich and G. Heppke), Springer Verlag, Berlin, Heidelberg, and New York (1980), p. 265.
9. M. Laurent, A. Hochapfel, and R. Viovy, "Liquid Crystals of One- and Two-Dimensional Order" (Eds. W. Helfrich and G. Heppke), Springer-Verlag, Berlin, Heidelberg and New York (1980), p. 282.
10. Y. Hendrikx and J. Charvolin, *J. Phys. (Paris)*, **42**, 1427 (1981).
11. M. Laurent, M. Boidart, A. Hochapfel and R. Viovy, To be presented at the 4th European Winter Conference on Liquid Crystals of Low Dimensional Order and their Applications (1984).
12. A. Hochapfel, M. Boidart and M. Laurent, *Mol. Cryst. Liq. Cryst.*, **75**, 201 (1981).
13. A. Hochapfel, M. Boidart and R. Viovy, *C.R. Acad. Sci., Paris, Série II*, **293**, 353 (1981).
14. F. B. Rosevear, *J. Amer. Oil Chem. Soc.*, **31**, 628 (1954).
15. F. Y. Fujiwara and L. W. Reeves, *J. Phys. Chem.*, **84**, 653 (1980).
16. L. Mandell, K. Fontell and P. Ekwall, "Ordered Fluids and Liquid Crystals" (Eds. R. S. Porter and J. F. Johnson) Amer. Chem. Soc. Publication, Washington (1967), p. 89.
17. P. A. Winsor, "Liquid Crystals and Plastic Crystals" (Eds. G. W. Gray and P. A. Winsor) Ellis Horwood Ltd, Chichester (1974), Vol. 1, p. 199.
18. L. J. Yu and A. Saupe, *Phys. Rev. Lett.*, **45**, 1000 (1980).

19. J. Biais, B. Clin and P. Lalanne, *C.R. Acad. Sci. (Paris), Série II*, **294**, 497 (1982).
20. A. Skoulios, *Ann. Phys.*, **3**, 421 (1978).
21. H.-F. Eicke, "Microemulsions" (Ed. I. D. Robb), Plenum Publishing Corporation (1982), p. 17.
22. B.-I. Tamamushi, *Pure Appl. Chem.*, **48**, 441 (1976).
23. S. Friberg and K. Larsson, "Advances in Liquid Crystals" (Ed. G. H. Brown), Academic Press, New York, San Francisco, and London (1976), Vol. 2, p. 173.