Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A new soap/detergent/water lyotropic liquid crystal with a biaxial nematic phase

E. A. Oliveira[a]; L. Liebert[ab]; A. M. Figueiredo Neto[a]
[a] Institute de Fisica, Universidade de São Paulo, São Paulo, SP, Brazil [b] Laboratoire de Physique des Solides, Université de Paris-Sud, Orsay, Cedex, France

To cite this Article Oliveira, E. A. , Liebert, L. and Neto, A. M. Figueiredo(1989) 'A new soap/detergent/water lyotropic liquid crystal with a biaxial nematic phase', Liquid Crystals, 5: 6, 1669 — 1675
To link to this Article: DOI: 10.1080/02678298908045677
URL: http://dx.doi.org/10.1080/02678298908045677

LIQUID CRYSTALS, 1989, VOL. 5, NO. 6, 1669–1675

A new soap/detergent/water lyotropic liquid crystal with a biaxial nematic phase

by E. A. OLIVEIRA, L. LIEBERT† and A. M. FIGUEIREDO NETO
Instituto de Física, Universidade de São Paulo, CP: 20516, CEP: 01498,
São Paulo SP, Brazil

A new lyotropic liquid crystal, potassium laurate, decylammonium chloride and water, which has two uniaxial phases and a biaxial nematic phase, is reported. A surface of the phase diagram and X-ray diffraction studies are presented. The chemical stability of this mixture is compared with the potassium laurate/decanol/water mixture. Optical measurements of the birefringence and X-ray studies indicate that this new mixture is more stable than the usual mixtures with alcohol.

1. Introduction

To date, biaxial nematic phases have been observed only in lyotropic mixtures containing alcohol and soap [1–3]. Indeed, it has been proposed [4] that in lyotropic mixtures the alcohol is important for stabilizing the nematic phases. On the other hand, many lyotropic mixtures [5] containing only one amphiphile and water (with or without a salt) present uniaxial nematic phases. Usually, the uniaxial nematic phase domain is surrounded [6, 7] by highly ordered phases (hexagonal, lamellar, rectangular), gel or coagel and isotropic regions. The existence of a biaxial nematic phase in lyotropic mixtures has been investigated by optical [1, 8, 9] and X-ray diffraction [10, 11] techniques. Interest in investigating this phase has increased in the last few years and many fundamental concepts [12] involving its physics and physico-chemistry are not yet completely understood. In addition, topological studies concerning the existence of unusual defects [13] in the texture of the biaxial phase, under proper boundary conditions, are of great interest.

One of the most puzzling questions concerning lyotropics (uniaxial and biaxial phases) is the chemical stability of these mixtures. It is well known that a hydrolysis reaction can occur in lyotropic mixtures with an alcohol and a soap [14]. Saupe and co-workers [15] suggested that a slow esterification reaction takes place between the alcohol and the soap.

At present there is a growing interest in preparing nematic phases without alcohol or salt, and this has recently been achieved. Uniaxial nematic phases have been observed in a binary mixture of soap and water [16, 17].

In this paper a new lyotropic liquid crystal composed of a mixture of a soap, a detergent and water is reported. This mixture presents two uniaxial (calamitic, N_C; discotic, N_D) phases and a biaxial (N_{BX}) nematic phase. Optical and X-ray diffraction techniques are used in this study. A surface of the phase diagram of this mixture is presented. The chemical stability is investigated and a comparison is made with the usual lyotropic mixtures with alcohol.

---

† Laboratoire de Physique des Solides, Université de Paris-Sud, Bât. 510, 91405 Orsay, Cedex, France.

0267-8292/89 $3.00 © 1989 Taylor & Francis Ltd

2. Experiment

2.1. *Mixture*

The potassium laurate (KL) and the decylammonium chloride (DaCl) are synthesized and recrystallized in the laboratory and kept in a dry atmosphere. The decanol (DeOH) was obtained from Merck. The compounds were weighed with 0·05 mg accuracy and placed together in clean glass tubes. The mixtures were shaken and centrifuged for some time, until they were homogeneous. The tubes were sealed to avoid water loss, and kept at 23 ± 2°C.

2.2. *Optical microscopy*

The samples were sealed in flat microslides from Vitro Dynamics Inc., of 200 μm thickness and 2 mm width, and then placed in a temperature-controlled stage (0·2°C accuracy). The transition temperatures were determined by observing the texture of the samples in a microscope with polarized light. Thin films of sample in the N_D phase are homeotropically oriented by wall effects, presenting a homogeneous texture. In the transition to the N_{BX} phase the appearance of defects is clearly observed owing to random orientation of the secondary optical axis. The texture of the N_C and N_{BX} phases are similar, and the transition from N_C to N_{BX} cannot be identified by this technique.

2.3. *Conoscopy* [8, 9]

The samples were doped with ferrofluids [18] and sealed in a glass cell (1·5 mm thickness). The cell was placed in a servocontrolled thermostat, with 0·01°C accuracy, and a horizontal magnetic field of 1·5 kg was applied. The samples, initially in the N_D phase, were oriented by repeated rotations around a vertical axis. The director, in the uniaxial phases, align parallel (N_C) or perpendicular (N_D) to the magnetic field. In the biaxial phase there are three directors to be aligned [8, 9].

A polarized convergent He–Ne laser beam was used to illuminate the sample, and the interference pattern was observed through an analyser. It is not possible to determine the N_{BX} to N_C transition temperature from observation of the interference patterns only.

The positions of the interference fringes were measured at the equilibrium temperature along the direction of the magnetic field and perpendicular to it. This was performed for two orthogonal directions of the incident polarized light, in order to measure the position of the integer and half-integer interference order. These values, with the average refractive index of the sample and its thickness, were introduced into a least-squares fit to calculate the birefringences. In the uniaxial nematic phases one of the birefringences vanishes, while in the biaxial phase both have non-zero values. With this technique, it is possible to determine the transition temperature from the N_{BX} to the N_C phase with good precision.

2.4. *X-ray diffraction* [10, 11]

The samples were sealed in glass capillaries of 1·5 mm diameter and placed vertically in a temperature controlled stage (0·2°C accuracy). The Laue geometry in the transmission set-up was used to identify the microscopical symmetry of each phase. The diffraction pattern was recorded on photographic plates.

The laboratory frame is defined with the 3-axis vertical. In the horizontal plane, the 2-axis is defined parallel to the incident X-ray beam direction, and the 1-axis perpendicular to it.

The repeating distances d are defined as $d = \lambda/2\sin\theta$, where λ is the wavelength of the X-rays and 2θ is the scattering angle.

With samples in the N_D phase, the director is vertically oriented, with the bilayers perpendicular to the 3-axis. From the diffraction pattern, one can determine the repetition distance from micelle to micelle along the director, d_3, and perpendicular to it, d_{12}.

To obtain a surface in the reciprocal space of the N_{BX} phase, the sample was sealed in a flat glass capillary, about 200 μm thick. The orientation of the N_{BX} phase was achieved by combining the surface effect and a magnetic field; one of the directors (perpendicular to the amphiphilic bilayer) was oriented perpendicular to the glass surface and another (along the biggest micellar dimension [10]) was oriented parallel to **H**. In this condition, the 3-axis of the laboratory frame was positioned perpendicular to the flat capillary surface; the 1-axis was parallel to **H**. The X-ray beam could be directed along the 3- or the 2-axis.

3. Results and discussion

3.1. *The surface of the phase diagram*

Figure 1 shows particular surface of the phase diagram of the mixture DaCl/KL/H_2O. In this surface the ratio

$$\frac{[\mathrm{DaCl}] + [\mathrm{KL}]}{[\mathrm{H_2O}]}$$

is kept constant, equal to 5×10^{-2}, and the ratio

$$R = \frac{[\mathrm{DaCl}]}{[\mathrm{KL}]}$$

varies in the range $0{\cdot}14 \leqslant R \leqslant 0{\cdot}20$ ([ ] represents the molar concentration).

The transition temperatures between the hexagonal phase (H_α) and the calamitic uniaxial nematic phase (N_C), between the biaxial nematic phase (N_{BX}) and the

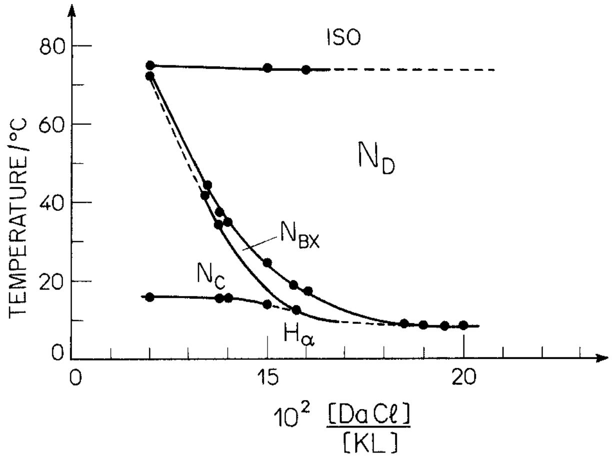

Figure 1. Surface of the phase diagram of the mixture DaCl/KL/water. T is the temperature. $[\mathrm{DaCl}] + [\mathrm{KL}]/[\mathrm{H_2O}] = 5 \times 10^{-2}$; [ ] represents the molar concentration. H_α is a hexagonal phase; N_C, N_D and N_{BX} are the uniaxial calamitic, uniaxial discotic and biaxial nematic phases respectively; ISO is an isotropic phase.

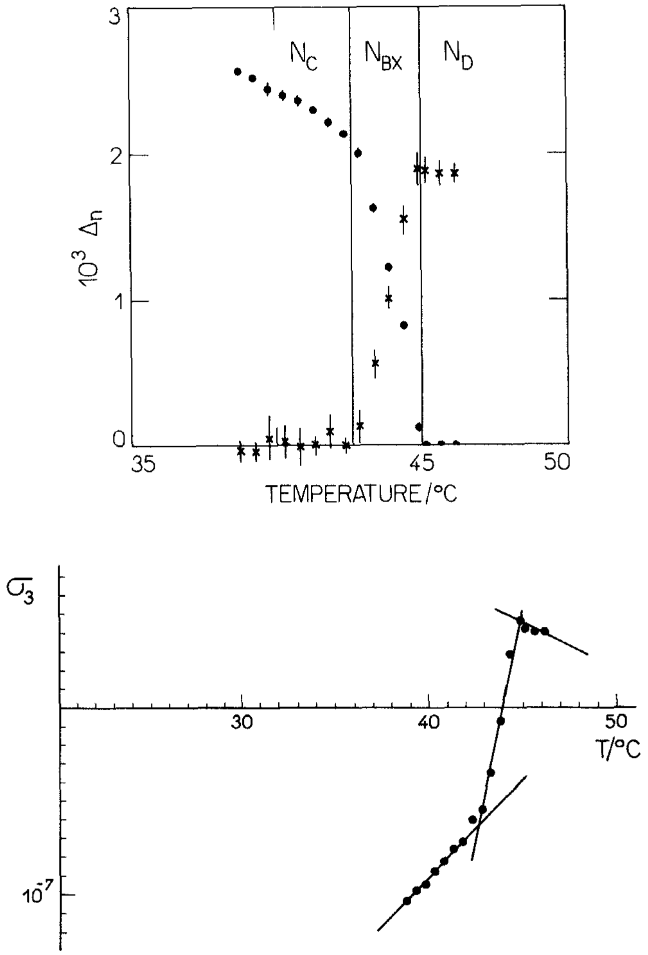

Figure 2. (*a*) Birefringences Δn as functions of the temperature T: ○, $n_1 - n_2$; ×, $n_2 - n_3$; DaCl/KL/H_2O mixture, $R = 0{\cdot}148$. (*b*) ***Invariant*** of the order-parameter optical susceptibility σ_3 as a function of the temperature; DaCl/KL/H_2O mixture, $R = 0{\cdot}148$.

discotic uniaxial nematic phase (N_D), and between the N_D phase and the isotropic phase (ISO) were determined by optical microscopic observations of the typical textures. The transition-temperature line between the N_C and the N_{BX} phases was determined by laser conoscopy. This technique is necessary for determining the transition temperatures between the uniaxial and the biaxial phase since the textures of oriented N_C and N_{BX} phases are very similar. Figure 2(*a*) shows typical measurements of the birefringences Δn as functions of the temperature T. In this line of the phase diagram the two uniaxial (N_C and N_D) phases and the biaxial phase (N_{BX}) are observed. In lyotropic liquid crystals the optical susceptibility (ε) can be chosen [8, 9] as a good order parameter. In this picture Δn is proportional to the order parameter. Figure 2(*b*) shows the invariant of the order parameter σ_3 defined [9] as

$$\sigma_3 = 4\varepsilon a_1 \varepsilon a_2 \varepsilon a_3$$

where εa_i ($i = 1, 2, 3$) are the diagonal elements of the traceless tensor ε. Mean-field theory (Landau-type) predicts [9] a linear behaviour of σ_3 with T near the uniaxial-to-biaxial phase transition (a second-order phase transition). This behaviour is observed in figure 2(*b*) and can be a very precise way to determine the transition temperatures.

It is interesting to compare the topology of this phase diagram with the one observed [3] in the mixture KL/decanol/water: the phase sequence is inverted as a function of T. In the alcohol-free mixture the discotic N_D phase appears at higher temperatures than the N_C phase. This fact could be related to the shape anisotropy of the micelles in this mixture and the orientational fluctuations [11] of the biaxial correlation volumes as a function of T. We shall return to this point later. From figure 1, it can be seen that on increasing the DaCl concentration, the N_D phase domain increases.

3.2. *Local order and microscopic structure*

The X-ray diffraction patterns of the DaCl/KL/water mixture of the oriented nematic phases present typical first-order and second-order bands [10] in the direction perpendicular to the amphiphilic bilayer. This indicates that the pseudo-lamellar ordering observed in other lyotropic mixtures [11] also exists in this new system. The typical repeating distances obtained in oriented nematic phases along the 1-, 2- and 3-axes of the laboratory frame are given in table 1: sample 1, N_{BX} phase; sample 2, N_D phase. The parameters d_i ($i = 1, 2, 3$) measure essentially the available volume per micelle [11] in each phase. The nematic samples are oriented with the amphiphilic bilayer perpendicular to the 3-axis. Comparing these values with the repeating distances obtained in the KL/decanol/water mixture [11], we observe that d_3 measured along the axis perpendicular to the amphiphilic bilayer is smaller in the DaCl mixture than in the decanol system. We expect that the introduction of the DaCl or decanol molecules does not drastically modify the potassium laurate bilayer. On the other hand, the microscopic shape anisotropy of the available volume per micelle is 30 per cent smaller in the DaCl mixture compared with the decanol mixture [11] (table 1). Assuming that the water covers the flat and the curved parts of the micelles equally, this shape anisotropy of the available volume gives an estimate of the micellar shape anisotropy. This difference between the DaCl and the decanol systems could be responsible for the inversion of the phase sequence as a function of temperature. Neutron-scattering experiments [19] show that the alcohol concentrates at the flat core of the micelles rather than at the high-curvature rim. As the DaCl and decanol molecules have the same paraffinic chain length, we propose that the DaCl molecules concentrate preferentially at the flat core of the micelles. The repulsion between the KL^- ions is reduced by the $DaCl^+$ ions, which reduces the local curvature. The same result is achieved by the OH heads of decanol. Another fact that justifies this assumption is that on increasing the DaCl (or the decanol) concentration in a lyotropic mixture, the discotic N_D phase domain increases (figure 1 and [3]). In this

Table 1. Repeating distances d_1, d_2 and d_3 along the 1-, 2- and 3-axes for $DaCl/KL/H_2O$ samples and shape anisotropy of the available volume per micelle. 1-N_{BX} phase ($T = 36°C$); 2-N_D phase ($T = 20°C$).

Sample	R	$d_1/Å$	$d_2/Å$	$d_3/Å$	Shape anisotropy
N_{BX} phase, $T = 36°C$	0·145	65	58	43	1·5/1·4/1
N_D phase, $T = 20°C$	0·166	70	70	42	1·7/1

picture, on increasing the DaCl molar concentration, we expect an increasing in the microscopic shape anisotropy of the micelles. This is because the KL amphiphilic bilayer is kept constant and the dimensions of the micelles along the 1- and 2-axes increase. This can be verified by comparing the spacing distances of two samples with different values of *R* (table 1): sample 2 has a higher value of *R* and a higher micellar shape anisotropy.

3.3. *Physico-chemical stability*

In this experiment two samples were prepared: one with potassium laurate/decanol/water and the other with potassium laurate/decylammonium chloride/water. They are sealed and stored together under the same conditions. The transition temperatures were determined by optical microscopy, as described above. Table 2 shows the transition temperatures determined for each sample. The measurements were performed periodically at one-month intervals.

In addition, the average birefringence was measured for non-oriented samples, using an Abbé refractometer. These measurements were repeated after each month. The results are shown in table 3 for each samples.

From these results it is clear that in the mixture with alcohol the changes in transition temperatures are soon observed, and after some time a re-entrant N_D phase appears. The birefringence also changes with time. Changes in the microscopic structure and local order have been reported previously [10, 11]; they cannot be

Table 2. (*a*) Transition temperatures between the different phases in the DaCl and DeOH mixtures; measured as functions of time. The measurements were performed periodically at one-month intervals.

Sample	Transition temperatures/°C	
[DaCl]/[KL] = 0·14	H 15·1 N_C, N_{BX} 31 N_D ~ 70 ISO	Time ↓
$\frac{[\mathrm{DaCl}]+[\mathrm{KL}]}{[\mathrm{H_2O}]} = 5{\cdot}5\times10^{-2}$	H 15·1 N_C, N_{BX} 31·8 N_D ~ 70 ISO	
	H 14·9 N_C, N_{BX} 36·6 N_D ~ 70 ISO	
	H 19·0 N_C, N_{BX} 35·4 N_D ~ 70 ISO	
	H 18·5 N_C, N_{BX} 33·3 N_D ~ 70 ISO	
[DeOH]/[KL] = 0·38	ISO 9·5 N_D 18·8 N_{BX}, N_C 37·2 ISO	Time ↓
$\frac{[\mathrm{DeOH}]/[\mathrm{KL}]}{[\mathrm{H_2O}]} = 4{\cdot}6\times10^{-2}$	ISO 10 N_D 15·3 N_{BX}, N_C 34·2 ISO	
	POL 9·6 N_D 19·6 N_{BX}, N_C 37·8 N_D 42·5 POL	
	POL 9·4 N_D 19·3 N_{BX}, N_C 31·5 N_D 41·7 POL	
	POL 8·6 N_D 19·3 N_{BX}, N_C 31·6 N_D 41·5 POL	

Table 3. Birefringences Δn of the DaCl and DeOH mixtures as functions of the time (one-month interval each). The Δn measurements were made at the temperatures listed at the last column.

Sample	Δn	Temperature	
KL/DaCl/water	$(1{\cdot}51 \pm 0{\cdot}08)\times10^{-3}$	41°C (N_D)	Time ↑
	$(1{\cdot}5 \pm 0{\cdot}5)\times10^{-3}$	22°C (N_C)	
	$(1{\cdot}0 \pm 0{\cdot}5)\times10^{-3}$	18°C (N_C)	
KL/DeOH/water	$(1{\cdot}56 \pm 0{\cdot}06)\times10^{-3}$	17°C (N_D)	Time ↑
	$(2{\cdot}5 \pm 0{\cdot}5)\times10^{-3}$	22°C	
	$(3{\cdot}0 \pm 0{\cdot}5)\times10^{-3}$	18°C	

explained only by water loss. X-ray diffraction studies of the DaCl/KL/water mixture in the nematic phase have shown that the spacing distances remain unchanged over a period of three months. The width at half-height of the first-order diffraction band also remains the same, within our experimental resolution. These results indicate that the microscopic structure (i.e. the pseudo-lamellar ordering) remains the same—at least over a three-month period. It has previously been reported [11] that the KL/DeOH/water mixture shows an ageing effect in the typical X-ray diffraction patterns: with time, the first-order band becomes more sharp.

Samples of alcohol-free mixtures, when allowed to lose water, showed a shift in the transition temperature, increasing the range of the H_α and N_D phases. This may explain the results reported in table 2 for the sample with DaCl.

4. Conclusions

A biaxial nematic phase has been seen in a lyotropic mixture composed of soap, detergent and water. When the alcohol is replaced by the detergent DaCl an inversion in the phase diagram is observed, although the amphiphilic concentration in both systems is very similar, about 5 per cent.

It has also been observed that less DaCl than DeOH is necessary to produce a biaxial phase: [KL]/[DeOH] = 3 and [KL]/[DaCl] = 6. This may be due to the inverse polarity of the DaCl molecule head with respect to the KL one. It would be easier for a DaCl than a DeOH molecule to go into the micelle.

The DaCl molecule in this new lyotropic liquid crystal must play the same role as the alcohol. This permits the growth of anisotropic aggregates.

With respect to the stability of the system, one can only say that it is more stable than the one with alcohol, and that the changes may be explained by water loss.

References

[1] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
[2] Bartolino, R., Chiaranza, T., Meuti, M., and Compagnoni, R., 1982, *Phys. Rev.* A, **26**, 1116.
[3] Figueiredo Neto, A. M., Liebert, L., and Galerne, Y., 1985, *J. phys. Chem.*, **89**, 3737.
[4] Gelbart, M. W., McMuller, E. W., Masters, A., and Ben-Shaul, A., 1985, *Langmuir*, **1**, 101.
[5] Boidart, M., Hochapfel, A., and Laurent, M., 1988, *Molec. Crystals liq. Crystals*, **154**, 61.
[6] Ekwall, P., 1975, *Advances in Liquid Crystals*, Vol. 1, edited by G. H. Brown (Academic Press), p. 1.
[7] Figueiredo Neto, A. M., and Amaral, L. Q., *Molec. Crystals liq. Crystals*, **95**, 129.
[8] Galerne, Y., and Marcerou, J. P., 1983, *Phys. Rev. Lett.*, **51**, 2109.
[9] Galerne, Y., and Marcerou, J. P., 1985, *J. Phys., Paris*, **46**, 81.
[10] Figueiredo Neto, A. M., Galerne, Y., Levelut, A. M., and Liebert, L., 1985, *J. Phys., Paris, Lett.*, **46**, L-499.
[11] Galerne, Y., Figueiredo Neto, A. M., and Liebert, L., 1987, *J. chem. Phys.*, **87**, 1851.
[12] Boonbrahm, P., and Saupe, A., 1984, *J. chem. Phys.*, **81**, 2076. Melnik, G., Photinos, P., and Saupe, A., 1989, *Phys. Rev.* A, **39**, 1597.
[13] Galerne, Y., and Liebert, L., 1985. *Phys. Rev. Lett.*, **55**, 2449.
[14] Hochapfel, A., Boidart, M., and Laurent, M., 1981, *Molec. Crystals liq. Crystals*, **75**, 201.
[15] Melnik, G., and Saupe, A., 1987, *Molec. Crystals liq. Crystals*, **145**, 95.
[16] Holmes, M. C., Reynolds, D. J., and Boden, N., 1987, *J. phys. Chem.*, **91**, 5257.
[17] Boden, N., Bushby, R. J., Jolley, K. W., Holmes, M. C., and Sixl, F., 1987, *Molec. Crystals liq. Crystals*, **152**, 37.
[18] Liebert, L., and Martinet, A., 1979, *J. Phys., Paris, Lett.*, **40**, L-363.
[19] Hendrikx, Y., Charvolin, J., and Rawiso, M., 1984, *J. Colloid Interface Sci.*, **100**, 597.