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P. Boonbrahm<sup>a</sup> & A. Saupe<sup>a</sup>

<sup>a</sup> Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio, 44242

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## Nematic States in Micellar Systems of Mixed Composition

P. BOONBRAHM and A. SAUPE

*Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242*

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The correlation between the molecular composition of micelles and the temperature stability of micellar nematic states is investigated on mixtures of cetyltrimethylammonium bromide (CTAB) or decyltrimethylammonium bromide (DTAB) with decylammoniumchloride (DACl) or potassium laurate (KL), 1-decanol, and NaBr. The phases were identified using a polarizing microscope. Replacing, in a CTAB/1-decanol system with a nematic phase, CTAB mole by mole with KL increases the temperature stability of the lamellar smectic state but the width of the nematic range is reduced. Similarly, replacing CTAB with decanol increases the stability of the smectic state and reduces the width of the nematic range. In contrast, replacement of CTAB by DACl has little effect on the width of the nematic range up to 35% replacement and no enhancement of the temperature stability of a latent smectic state is observed. The results are qualitatively interpreted in terms of the electrostatic interactions of the ionic surfactants and of the surface areas per headgroup.

### I. INTRODUCTION

It is known that a micellar nematic liquid can form in a mixture of surfactants and water<sup>1,2</sup>; the surfactant can be either a cationic or anionic amphiphile. The electrostatic repulsion between the head groups of ionic surfactants plays an important role in the formation of the micelles (see, for example, Israelachvili, *et al.*<sup>3</sup>). One expects that it will also influence the formation of nematic states, but recent studies<sup>4,5</sup> show that nematic states can be obtained for all ratios of cationic to anionic amphiphilic  $N_L$  phases. The studies on systems with mixed cationic and anionic surfactants seem to indicate that the electrostatic repulsion has surprisingly little effect.

In an effort to clarify the role of the electrostatic repulsion between surfactants, we studied the formation of nematic and lamellar smectic states in systems of a mixed composition, specifically, mixtures of cationic and anionic surfactants, of cationic and cationic surfactants and of cationic surfactant and co-surfactants. The phases formed by these systems were identified by microscopic observation.

## II. SAMPLE PREPARATION

The cationic surfactant cetyltrimethylammonium bromide [CTAB, certified grade from Fisher Scientific Co.] and decyltrimethylammonium bromide, from Eastman Kodak Co.] were used without further purification. Decylammoniumchloride [DACl,  $\text{CH}_3(\text{CH}_2)_9\text{NH}_2\text{Cl}$ ] was made and purified according to procedures described in Ref. 6.

The anionic surfactant potassium laurate [KL,  $\text{CH}_3(\text{CH}_2)_{10}\text{COOK}$ ] was synthesized by neutralizing an ethanol solution of excess potassium hydroxide (pellets, 85 + % from Aldrich Chemical Co.) with the appropriate amount of lauric acid (99.5 + % from Aldrich Chemical Co.). The KL was purified by recrystallization from absolute ethanol twice, then dried in a vacuum desiccator for several days. The melting point was 262°C.

Deuterated water ( $\text{D}_2\text{O}$ , 98.8 atom%D) and 1-decanol [decyl alcohol,  $\text{CH}_3(\text{CH}_2)_9\text{OH}$ , 99%] from Aldrich Chemical Co. were used without further treatment.

The exact amounts of the components were carefully mixed using a magnetic stirrer until a clear homogeneous texture was observed. The mixing was done above room temperature since some of the samples freeze at 21–22°C. The samples were left in an oven at  $\approx 32^\circ\text{C}$  for a few days before use.

The microscopic observations were made on thin films sealed in flat capillaries of 0.3 mm thickness (microslide from Vitro Dynamics, In.) using a Leitz polarizing microscope equipped with a Mettler FP2 heating stage.

## III. RESULTS

Many of the studied mixtures had a lamellar smectic phase at lower temperatures which upon heating transformed continuously into a nematic phase. Both phases tend to give a pseudoisotropic texture. The smectic phase was identified by defects in the texture, e.g. "oily

streaks." At the transition to the nematic phase the defects smooth out and disappear. In some nematic films a Schlieren texture could be observed before the pseudo-isotropic texture gradually appeared. Nematic and lamellar smectic phases of all studied mixtures were uniaxially positive.

The observed properties indicate that the micellar aggregates of the nematic phases were disc-shaped with a structure similar to the aggregates in the lamellar smectic phases. Usually this type of a micellar nematic is denoted as  $N_L$  or  $N_d$ .

The transition to the isotropic phase from the nematic or smectic phase is first order with a two phase region where nematic and isotropic phase or smectic and isotropic phase co-exist. The beginning of these regions is recognizable by the appearance of isotropic droplets. In specific parts of the phase diagram three phase regions could be observed with co-existent smectic, nematic and isotropic phases.

Table I summarizes results obtained with mixtures of the cationic surfactant CTAB or DTAB and the anionic surfactant KL. Similar mixtures were studied by Reeves *et al.*<sup>4,5</sup> using nmr spectroscopy. Following their example the total number of surfactant molecules were kept constant ( $\sim 3.18$  mmol per 100 mmol  $D_2O$ ) while the ratio of anionic to cationic surfactant is varied. An exception is sample 5 that contains three surfactants with a total of 3.01 mmol. Several samples were made for each surfactant ratio with different amounts of decanol.

TABLE I

Sample	Amount in mmol <sup>c</sup>			Transition Temperatures in °C			
	KL	DTAB	CTAB	1-dec	$N_L^a$ (°C)	$2\phi^b$	Iso (°C)
1	—	—	31.73	5.75	22.1	60.8	63.0
2	3.20	—	28.53	3.56	22.0	60.5	63.0
3	4.80	—	27.04	2.38	22.0	56.0	59.0
4	9.55	—	22.20	—	19.0	65.5	69.0
5	12.67	6.75	10.64	1.82	8.0	54.7	61.3
6	12.67	19.07	—	5.20	5.0	44.8	54.7
7	15.96	15.96	—	2.53	5.0	50.1	56.7
8	22.22	9.60	—	—	5.0	45.0	47.1
9	28.64	3.18	—	2.64	5.0	—	25.5
10	32.05	—	—	4.82	25.5	37.2	43.2

<sup>a</sup> Transition from solid phase except for sample 10 where it is from a two-phase smectic–isotropic region.

<sup>b</sup> Transition to two-phase nematic–isotropic region.

<sup>c</sup> Per mole  $D_2O$  plus 15.9 mmol NaBr.

Starting from a relatively high concentration, decanol was decreased in steps of 1 mmol until the smectic phase disappeared. The mixtures listed in Table I contain the amount of decanol determined by this procedure. It is an approximate upper limit of the range that has no smectic phase.

The upper part of Table I, sample 1–4, contains the results of the CTAB, KL mixtures. The data show that the amount of decanol must be decreased, to prevent the formation of a smectic state, when CTAB is replaced by KL. A smectic phase forms without decanol when the ratio CTAB/KL becomes smaller than 2. DTAB has to be substituted for CTAB when the ratio of cationic to anionic surfactant is further decreased.

The sequence 6 to 8 is similar to the sequence 1 to 4 insofar as the increase of KL requires a decrease of decanol but in sample 9 and 10 the trend is reversed. It is remarkable that the two-phase range at the nematic isotropic transition practically disappears for sample 9. This transition appears to be continuous under the polarizing microscope.

In the phase diagram represented in Figure 1, the amount of decanol is constant while the ratio KL/CTAB varies. The temperature

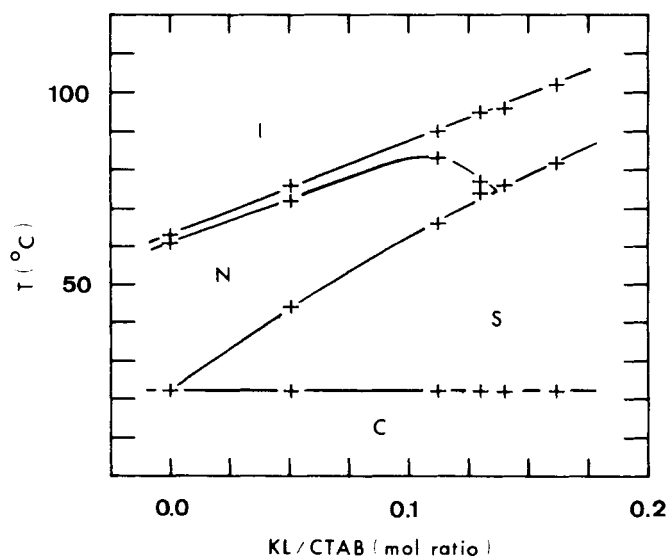


FIGURE 1 Phase diagram of cationic-anionic system (KL + CTAB/NaBr/1-decanol/D<sub>2</sub>O = 3.173/1.59/0.575/100 mol. ratio).

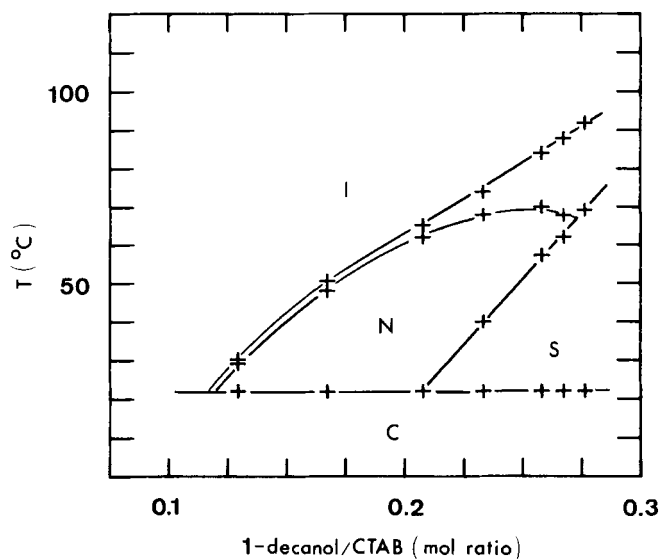


FIGURE 2 Phase diagram of CTAB and 1-decanol system (CTAB + 1-decanol/NaBr/D<sub>2</sub>O = 3.173/1.59/100 mol. ratio).

stability of the smectic phase increases with the molar ratio KL/CTAB but the nematic range shrinks and reduces to zero when KL/CTAB > 0.14. The two-phase nematic-isotropic region which is only three degrees wide at low ratios, enlarges to 20 $^{\circ}\text{C}$  at the point where the nematic phase disappears. A three-phase region occurs near this point where smectic, nematic, and isotropic phase co-exist.

Figure 2 shows the influence of the 1-decanol substitution. Here the ratio decanol/CTAB is varied while other components are kept constant. A nematic range can be observed only when the molar ratio is > 0.12. With increasing decanol concentration the nematic range increases to a width of 40 $^{\circ}\text{C}$ . Then a smectic phase appears and the nematic range decreases until it disappears. The phase diagram has the same characteristics as the one shown in Figure 1, including the existence of a three-phase region.

Figure 3 shows the phase diagram that results when CTAB is replaced by the equally cationic surfactant DACl. The replacement has little effect on the nematic range up to 35% and there is no formation of a smectic-smectic state. Only when the substitution approaches 50% the nematic range disappears and is replaced by a

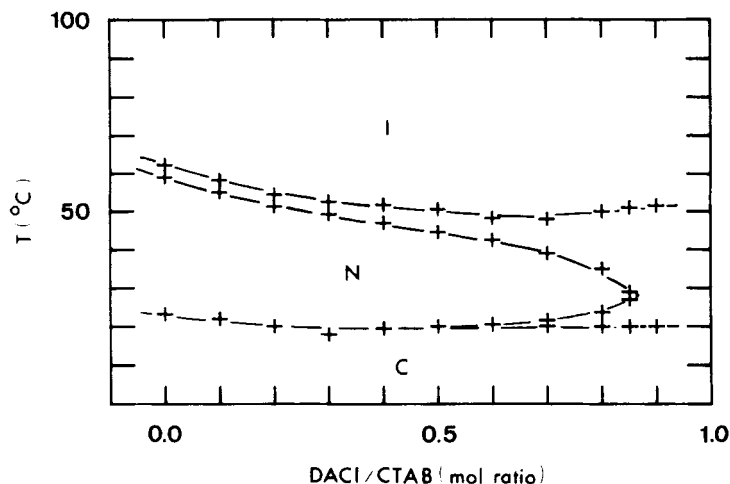


FIGURE 3 Phase diagram of cationic-cationic system (CTAB + DACl/1-decanol/NaBr/D<sub>2</sub>O = 3.17/.575/1.59/100 mol. ratio).

nematic-isotropic two-phase region. The material appears to be strongly turbid in this range.

#### IV. DISCUSSION

The aggregates in the nematic ranges are disc-shaped and of a finite size. In the neighboring smectic regions they may remain finite but as one advances deeper into the smectic range their size will increase and, eventually, they will fuse to continuous bilayers. The "mesogenic" character of the aggregates is determined by the ratio diameter to thickness ( $d/h$ ). It increases with  $d/h$ . The thickness  $h$  is about twice the length of the surfactant molecules and probably fairly constant, but  $d$  may vary sensitively with the composition. An addition of decanol, for instance, increases the volume occupied by the hydrophobic alkyl chains without adding much to the surface area of the aggregates. The shapes of the aggregates adapt accordingly so that the ratio surface area to the number of alkyl chains is smaller. It will result in aggregates with a larger  $d/h$ .

KL has a significantly larger polar head group than decanol. The head group is of course not as bulky as that of CTAB or DTAB but, disregarding electrostatic interactions, we would expect that it has less influence on  $d/h$  than decanol. The attractive interaction between  $L^-$  and  $CTA^+$ , on the other hand, allows a denser packing of the head

groups and the net effect may become comparable to that of decanol.

The cationic  $\text{DA}^+$  is, as far as geometrical shape and the size of the head group is concerned, not much different from  $\text{L}^-$ , but the repulsive interaction between  $\text{DA}^+$  and  $\text{CTA}^+$  does not allow a significant reduction of the average surface area. One will expect that substitution by DACl does not have very strong effects on the phase boundaries.

The experimental results are qualitatively in agreement with these deductions. The substitution of CTAB by KL or decanol lead to an enhancement of the temperature stability of the lamellar smectic phase and, at least in the beginning, also of the temperature stability of the nematic phase. The latter, however, is finally replaced by an extended two phase region. The nematic-smectic transition temperatures are approximately a linear function of the ratios  $\text{KL}/\text{CTAB}$  or  $\text{decanol}/\text{CTAB}$ . Decanol seems to be about 1.7 times more effective than KL in shifting the smectic-nematic transition. The data in Table I also demonstrate that the co-surfactant decanol can be replaced by an ionic surfactant which has a charge opposite to that of the main surfactant component. As expected, the substitution of CTAB by the equally cationic DACl does not have much effect on the nematic and smectic ranges up to the relatively high substitution of about 35%.

In replacing CTAB mole by mole with significantly smaller molecules, the volume fraction occupied by the surfactant aggregates decreases. The decrease should result in a lowering of the transition temperatures, but apparently this effect is more than compensated (see Figures 1 and 2) by the increase of  $d/h$ , i.e. the size of the aggregates.

The increase in particle size is probably also the cause for the disappearance of the nematic phase. In the smectic isotropic two-phase region that replaces the nematic phase, the smectic phase may have continuous bilayers or very large bilayer aggregates while the surfactant concentration in the isotropic domains is relatively low so that there are too few aggregates to give a nematic phase. The formation of a nematic phase requires disc-shape aggregates in a high concentration so that the interaction between the aggregates leads to orientational order but the size of the aggregates must remain small enough to prevent the formation of a lamellar smectic phase. In other words the balance of conditions has to be such that the proper finite ratio of  $d/h$  is maintained in spite of a relatively high surfactant concentration.

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**References**

1. K. D. Lawson and T. J. Flautt, *J. Am. Chem. Soc.*, **89**, 5489 (1967).
2. B. J. Forrest and L. W. Reeves, *Chem. Rev.* **81**, 1 (1981).
3. J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc. Faraday Trans. II*, **72**, 1525 (1976).
4. Y. Lee, L. W. Reeves and A. S. Tracey, *Can. J. Chem.*, **58**, 110 (1980).
5. L. Hecker, L. W. Reeves and A. S. Tracey, *Mol. Cryst. Liq. Cryst.*, **53**, 77 (1979).
6. K. Radley and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **44**, 227 (1977).