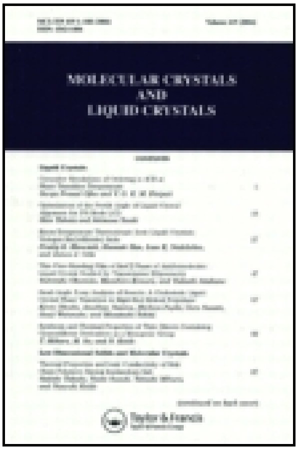

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The Structure of Lyotropic Nematic Decylammoniumchloride and Bromide Systems by PMR of Monomethyltin Complexes and by Microscopic Studies†

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The pmr spectrum of methyltintrichloride in aqueous micellar solutions of decylammoniumchloride and KCl, and of decylammoniumbromide and KBr was investigated. The large scalar SnH couplings of 134.0 Hz and 130.2 Hz respectively indicate the formation of six coordination complexes $CH_3SnCl_5^{-\,-}$ and $CH_3SnBr_5^{-\,-}$ in the micellar solutions, but the geometrical structure of the CH_3Sn moiety is little affected by the complex formation. The complexes orient with their symmetry axis preferably parallel to the nematic axis.

In microscopic studies on selected mixtures a reversible first order phase transition was observed between nematic and isotropic micellar solution at about 45°C and a reversible transition between a lamellar smectic phase and the nematic phase at about 30°C that appears to be of second order. The optical observations and the orientation of the methyltin complex indicate that the nematic solutions have micelles of a bilayer structure.

1 INTRODUCTION

The molecular structure of nematic phases formed in aqueous solutions of amphiphiles has not been satisfactorily established. Their classification as nematics is based on microscopic textures which imply an absence of long-range correlations in the density distribution. It follows that these phases are micellar solutions with long-range orientational order only. The structure of the micelles themselves is uncertain. There are two structural models that are presently discussed.

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In the first model, which is usually adopted, micelles of a rod-like shape are assumed with a molecular structure similar to the cylindrical aggregates of amphiphiles in the hexagonal smectic phase or middle soap, but the average length of the aggregates is much shorter than in the hexagonal phase. The nematic state is due to a long-range orientational order of the micelles so that the cylinders are preferably parallel to the main symmetry axis of the liquid crystal.

In the second model, the micelles are disc-shaped and of a molecular structure similar to the bilayers in a lamellar smectic phase or neat soap. The nematic state results from the orientational order of the disc-shaped micelles so that the micelles orient preferably perpendicular to the main symmetry axis of the liquid crystal.

There is evidence for the existence of two types of amphiphilic nematics[1] so that both models may be applicable to real systems. They can be differentiated by nmr studies on dissolved molecules provided that a qualitative theoretical statement is accepted about the preferred orientation of the solute molecule. It is also possible to distinguish the two types by microscopic studies when transitions to other liquid crystalline phases of known structures can be observed.

In this paper we study nematic phases with decylammoniumchloride (DACl), or decylammoniumbromide (DABr), as amphiphiles. We use methyltintrichloride as solute for the pmr studies. It forms a six coordination complexes in the micellar solution that have a high symmetry and give a simple spectrum. The sign of the degree of order can be experimentally determined from the SnH couplings. The orientation of the complexes in the nematic solutions will be mainly due to interactions with the micellar surfaces which have the properties of electric double layers. It seems reasonable to assume that the complex aligns preferably parallel to the surface normal. There are two such orientations, the methyl group can point inward or outward. Both correspond to energy extremes, but the inward orientation will be preferred because of the hydrophobic nature of the methyl group.

With a preferred orientation of the complex parallel to the surface normal, the degree of order of its symmetry axis with respect to the nematic axis is negative for nematics with cylindrical micelles and positive for nematics with lamellar micelles. It is, of course, irrelevant for this sign whether the methyl group points inward or outward.

Microscopic observations on thin films are also reported. The textures are used for the classification of the phases formed by our systems. The study of phase transitions induced by heating or cooling proves to be particularly useful for the characterization of the molecular structure of the nematic phase.

II EXPERIMENTAL

DACl and DABr were prepared by neutralizing a chilled diethyl ether solution of decylamine with the appropriate hydrohalic acid. Impure surfactants precipitated from the neutralized solutions on rechilling. They were recrystallized twice from ethanol/pet. ether (60°–90°). Methyltintrichloride was purchased from Alpha Chemicals and was used without purification. The pmr spectra of our samples showed some additional lines due to dimethyltin and some other unidentified compounds. They were probably due to some decomposition during storage of the methyltintrichloride. Some measurements were repeated with freshly obtained methyltintrichloride. No additional lines were observed in these spectra.

The compositions that gave suitable nematic solutions had to be found by trial and error. They are listed in Tables I and II. The pmr spectra were taken with a Varian XL-100 spectrometer.† The HOD proton signal was used for locking. It was downfield from the methyltin spectrum. The probe temperature was 40°C.

III ANALYSIS OF THE PMR SPECTRUM

The dominant part of the proton resonance spectrum of monomethyltin is a 1 : 2 : 1 triplet with a line separation equal to $3D_{\mathrm{HH}}$ where

$$D_{\mathrm{HH}} = \frac{\hbar\gamma_{\mathrm{H}}^2}{8\pi r_{\mathrm{HH}}^3} S_{\mathrm{C}_3} \tag{1}$$

Here S_{C_3} is the degree of order of the SnC-axis with respect to the magnetic field and r_{HH} the distance between the methyl-protons. The other symbols have their usual meaning.

There are, in addition, four satellite triplets due to the isotopes Sn^{117} and Sn^{119} which have spin $\frac{1}{2}$ and a natural abundance of 7.65% and 8.68%. The centers of the satellite triplets are at the frequencies $\nu_0 \pm A/2$, where ν_0 is the center of the main triplet and

$$A = |J_{\mathrm{SnH}} + 2D_{\mathrm{SnH}}|. \tag{2}$$

The values of J_{SnH} and D_{SnH} are different for the two isotopes because they have different magnetic moments. For the direct coupling we have

$$D_{\mathrm{SnH}} = -\frac{\hbar\gamma_{\mathrm{Sn}}\gamma_{\mathrm{H}}}{8\pi r_{\mathrm{SnH}}^3}(3\cos^2\beta - 1)S_{\mathrm{C}_3}. \tag{3}$$

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† Funds for the equipment were obtained partly from the National Science Foundation under Grant No. GP-10481.

Here r_{SnH} is the distance between tin and the methylprotons and β the angle between an axis through Sn and H and the molecular symmetry axis. By combination of (1) and (3) we obtain with $r_{\mathrm{HH}} = \sqrt{3}\, r_{\mathrm{SnH}} \sin \beta$

$$\frac{D_{\mathrm{SnH}}}{D_{\mathrm{HH}}} = -3^{3/2} \sin^3 \beta (2 - 3 \sin^2 \beta) \frac{\gamma_{\mathrm{Sn}}}{\gamma_{\mathrm{H}}}. \tag{4}$$

The right hand side of (4) is positive since β is near 20° and $\gamma_{\mathrm{Sn}}/\gamma_{\mathrm{H}} < 0$, accordingly D_{SnH} and D_{HH} have the same sign.

The analysis gives only the absolute value of D_{HH} and A. There are, therefore, two absolute values possible for D_{SnH}, namely $\frac{1}{2}|J_{\mathrm{SnH}} \mp A|$. The right value was found by measuring a sequence of samples with varying solute orientation. The ratio $D_{\mathrm{HH}}/(J_{\mathrm{SnH}} \mp A)$ remains constant only for the proper sign combinations and the proper value for J_{SnH}. We used for J_{SnH} the value measured in the isotropic micellar solution. It agrees within error limits with the best fit value of the nematic phase.

IV SPECTROSCOPIC RESULTS

The experimental data and deducted results are summarized in Tables I and II. The coupling constants $\bar{D}_{\mathrm{SnH}}$ are equal to the arithmetic means of the Sn^{117} and Sn^{119} couplings. We give the mean values because the satellite lines were not resolved in the chloride solutions. The J-couplings measured

TABLE I

Nematic solution with chlorine counterions
Composition by Weight

Sample	DACl	KCl	CH_3SnCl_3	D_2O
(1)	0.80	0.08	0.120	1.15
(2)	0.80	0.08	0.120	1.20
(3)	0.80	0.08	1.126	1.23

TABLE II

Nematic solutions with predominantly bromine counterions
Composition by Weight

Sample	DABr	KBr	CH_3SnCl_3	D_2O
(1)	1.20	0.15	0.127	1.30
(2)	1.20	0.20	0.106	1.40
(3)	1.20	0.15	0.1275	1.35

in the isotropic micellar solutions are

$$\left.\begin{aligned} J_{\mathrm{Sn}^{119}\mathrm{H}} &= 131.0 \pm 0.2\ \mathrm{Hz} \\ J_{\mathrm{Sn}^{119}\mathrm{H}} &= 137.0 \pm 0.2\ \mathrm{Hz} \end{aligned}\right\}\text{for chloride}$$

$$\left.\begin{aligned} J_{\mathrm{Sn}^{117}\mathrm{H}} &= 127.2 \pm 0.2\ \mathrm{Hz} \\ J_{\mathrm{Sn}^{119}\mathrm{H}} &= 133.2 \pm 0.2\ \mathrm{Hz} \end{aligned}\right\}\text{for bromide}$$

These coupling constants are about 40 Hz larger than for methyltinbromide in benzene.[2] We assume therefore that the six coordination complexes $CH_3SnCl_5^{--}$ and $CH_3SnBr_5^{--}$ are formed in the solutions. The sign of J_{SnH} for CH_3SnBr_3 is positive[3] ($J_{\mathrm{SnH}} = +89.4$ Hz). The same sign will be valid for the complexes. We find experimentally that the direct couplings have the opposite sign of J_{SnH} and it follows that the degree of order with respect to the nematic axis is positive. The values given in Tables III and IV were obtained from D_{HH} assuming a distance of 1.80 Å between the methylprotons. For the chloride systems S varies between 0.104 and 0.067. It is much smaller in the bromide systems where it varies from 0.030 to 0.023. The decrease in order is presumably due to the shielding of the CH_3-group by the larger bromine atoms.

The structural angle β is practically the same as for the dimethyltin complexes.[4,5] We find that β for the bromide complex is slightly larger than for the chloride complex. The direction of the change is opposite to what one

TABLE III

PMR data for $CH_3SnCl_5^{--}$ in the chloride systems of Table I. D_{HH} and D_{SnH} direct coupling constants in Hz, S degree of order of molecular symmetry axis relative to nematic axis, β angle between Sn–H axis and molecular symmetry axis.

Sample	D_{HH}	D_{SnH}	$D_{\mathrm{SnH}}/D_{\mathrm{HH}}$	S	β
(1)	−537.53	−95.55	0.1776	0.1044	23.21°
(2)	−425.43	−75.60	0.1770	0.0827	23.20°
(3)	−347.40	−61.75	0.1775	0.0675	23.20°

TABLE IV

PMR data for $CH_3SnBr_5^{--}$ in the bromide systems of Table II. Notations as in Table III.

Sample	D_{HH}	D_{SnH}	$D_{\mathrm{SnH}}/D_{\mathrm{HH}}$	S	β
(1)	−152.80	−27.50	0.1800	0.0297	23.34°
(2)	−134.68	−24.55	0.1823	0.0262	23.47°
(3)	−120.97	−22.00	0.1819	0.0235	23.44°

expects for steric reasons. The larger bromines should repulse the protons more strongly than the chlorines, and thus should tend to decrease β. Obviously some other effects compensate for this repulsion. There may also be a systematic error in our data because we use the *J*-couplings from the isotropic solutions, but a change of *J* in the order of 1 Hz would be required to explain the difference.

V MICROSCOPIC STUDIES

Microscopic studies were made on the chloride sample (2) and the bromide sample (2). The observations were made on films of 0.1 mm thickness in flat capillaries which were sealed to avoid evaporation. A Mettler hot stage was used for heating. Both samples showed similar textures under the polarizing microscope and had nearly the same transition temperatures.

Upon cooling the nematic phase formed near 45°C. It nucleated in spherical drops as shown in Figure 1. All simple drops have a structure of $D_{\propto h}$ symmetry. The structure is characterized by two poles formed by radial singular points located diammetrically on the surface or very close to the surface. In cooling further a nematic Schlieren texture is obtained (Figure 2).

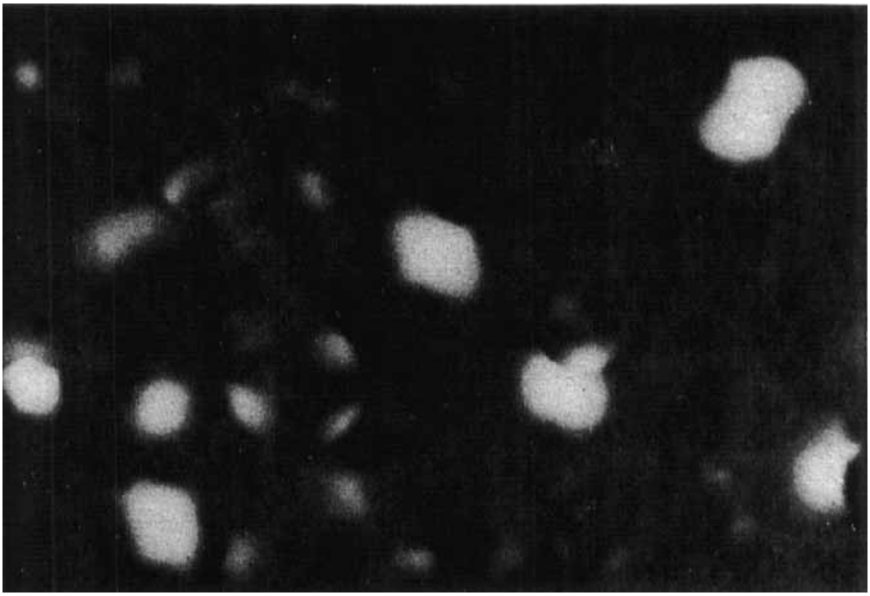

FIGURE 1 Isotropic-nematic transition. Bromide sample (2), 46.8°C, 160 ×, crossed polarizers.

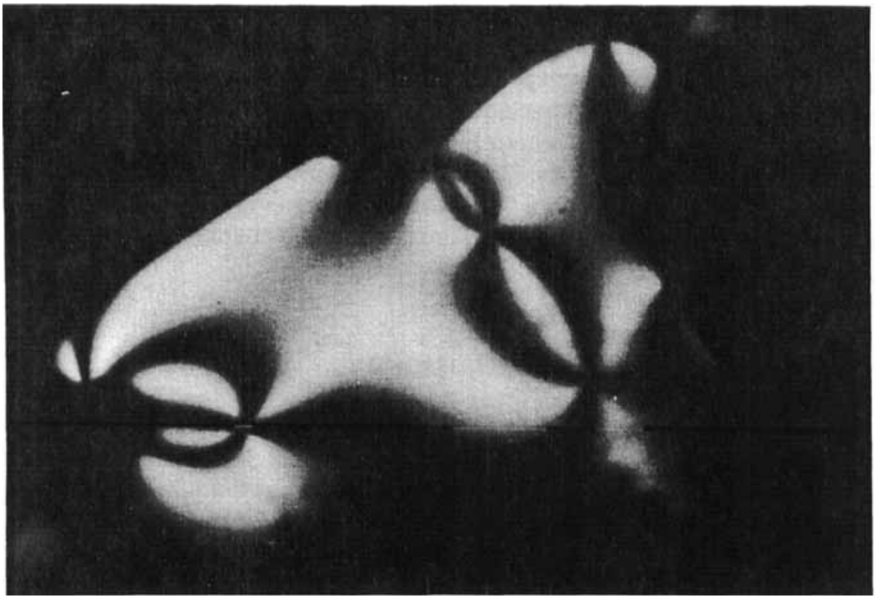

FIGURE 2 Nematic Schlieren texture and pseudoisotropic areas. Bromide sample (2), 34°C, 160 ×, crossed polarizers.

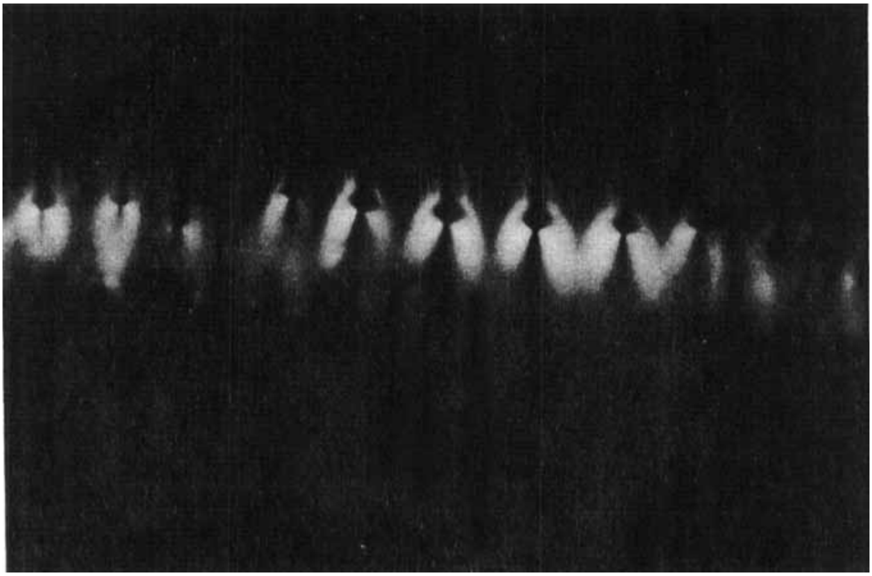

FIGURE 3 Smectic focal conix texture at edge of capillary. Bromide sample (2), 25°C, 160 ×, crossed polarizers.

It changes in time slowly to a pseudoisotropic texture. At about 30° a transition to a lamellar smectic phase occurs. This transition may be second order. There was no two-phase mixture with defined interfaces observable and the transition cannot be recognized in areas with an undisturbed pseudoisotropic texture. In areas where the pseudoisotropic texture is disturbed, as along the boundaries of the film, the birefringent smooth nematic texture changes at the transition to a focal conic texture (Figure 3). Both phases are optically positive uniaxial and there is no strong change in birefringence at the transition.

VI DISCUSSION AND CONCLUSIONS

The microscopic textures established the nematic properties of the higher temperature liquid crystalline phase. Splay and bend deformation constants have the same order of magnitude except probably at temperatures that are close to the nematic–smectic transition where the bend constant may diverge. No twist deformations were observed, but we suppose that they occur also readily and do not require higher energies. The smectic phase has a lamellar structure as indicated by the existence of focal conic textures and of pseudoisotropic textures with "oily" streaks.

The observation that the nematic-smectic transition appears optically to be of second order or nearly so, is well compatible with the second model where the nematic phase has micelles of a bilayer structure. The micelles in the pseudoisotropic texture of the nematic phase are preferably parallel to the plane of the film. At the transition the disc-shaped micelles will merge forming continuous bilayers. This transformation can proceed without a disturbance of the pseudoisotropic texture, and without strong effects on the optical properties of the material.

The transition to a lamellar smectic phase is more complex when the nematic phase has cylindrical micelles. The cylinders are preferably vertical to the film in the pseudoisotropic texture. The formation of bilayers at the transition could best be accomplished by a lateral merging of the parallel cylinders which leads to vertically aligned bilayers and therefore a birefringent smectic texture. Even if we assumed some mechanism which allows a direct transition to a smectic-pseudoisotropic texture, difficulties would still remain. There should be a strong change in optical properties and in general also a change of the optical sign since the preferred alignment of the amphiphiles in the nematic phase is perpendicular to the optical axis while it is parallel in the smectic phase. The optical observations indicate, therefore, in agreement with the nmr data that the nematic liquid crystals of the studied systems have micelles of a bilayer structure.

It has been found in nmr studies that amphiphilic nematics can have positive or negative diamagnetic anisotropics and a division has been made on this basis in nematic I and II.[1,6] It seems likely that most phases with negative diamagnetic anisotropy have bilayer micelles as the systems studied in this paper, while cylindrical micelles are most likely to give diamagnetically positive phases. However, it is clear that exceptions to these rules will exist because the molecular diamagnetic properties change with the molecular structure. For instance, a diamagnetically positive nematic phase where the nmr data indicate bilayer micelles has been reported recently by Diehl and Tracey.[7] A reversal of the above rules can, in general, be expected when a sufficiently large fraction of aromatic molecules are incorporated in the micelles.

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