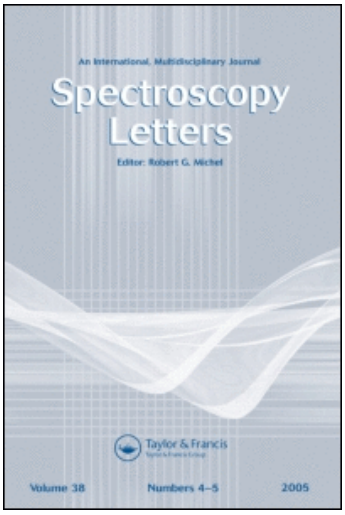

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THE FT-IR AND RAMAN SPECTROSCOPIC STUDIES OF SOME LIQUID CRYSTALS

Key words: Lyotropic liquid crystals, IR and Raman spectra.

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ABSTRACT

Room temperature FT-IR and Raman spectra of some lyotropic liquid crystals in anionic and cationic mesophases composed of sodium dodecylsulphate/ orthophosphoric acid monodecyl ester/H_2O and decylammonium chloride/ orthophosphoric acid monodecylester/H_2O have been studied together with polarizing microscopy. All the vibrational bands observed are assigned. Intramolecular order is found to decrease upon dilution. Hydrogen bonding type interaction between the head groups of sodium dodecylsulphate or decylammonium chloride and orthophosphoric acid monodecylester is detected.

INTRODUCTION

Lyotropic nematic phases lie between the optically isotropic micellar phase and the boundary of the lamellar phase,L_α or the hexagonal phase H_α. These lyomesophases can align spontaneously between two glass plates with their director (optical axis) either parallel or perpendicular to the surface of these plates or to the direction of the magnetic field. In the first case ,they possess a positive diamagnetic anisotropy ($\Delta x > 0$), in the second , however, a negative diamagnetic anisotropy ($\Delta x < 0$) (1).

Recently, we have shown that aqueous orthophosphoric acid,H_3PO_4, can be used as a solvent in forming lyotropic liquid crystalline phases (2). The ^{31}P chemical shift of H_3PO_4 consisted of an anisotropic peak, e.g. a symmetrical singlet. A natural question which then was associated with this work was to investigate the effect of the bound phosphoric acid in these systems. Therefore we have developed anionic and cationic mesophases, formed by the anionic surfactant; sodium dodecylsulphate (SDDS), orthophosphoric acid monodecylester (PDE), heavy water (D_2O) and cationic surfactant; decylammonium chloride (DACl), PDE and D_2O.To understand the effect of PDE in the anionic and cationic mesophases, these systems were investigated by NMR (3).

Although NMR investigations (measurements of ^{31}P chemical shift of PDE and deuterium quadrupolar splitting of D_2O in these systems) gave valuable information on the behaviour and dynamics of the phases, the effect of PDE in the anionic and cationic mesophases could not be understood well. In order to follow such questions, measurements of quadrupolar splittings of the hydrocarbon segments of the amphiphiles are required. This type of work, however, needs specifically deuterated hydrocarbon chains and is, therefore, very time consuming (4,5). In contrast, IR and Raman spectroscopy can be applied directly and easily to investigate the overall motions of the head groups and hydrocarbon chains which result from the interactions of the amphiphiles with each other and the solvent in these systems and the solvent.Hence, the present work is directed toward the measurement of FT-IR and Raman spectra of a series of anionic and cationic lyomesophases to extract some information on the interactions of PDE with SDDS and DACl and to deliver the phase type by polarising light microscopy.

EXPERIMENTAL

n-Decylammonium chloride, DACl and orthophosphoric acid monodecylester, PDE, have been synthesized, using published procedures (2,6), respectively.

Sodium n-dodecylsulphate, SDDS, was purchased from Merck with a high purity.

The samples were prepared by weighting approximately 1g of the ingredients in test tubes which were then sealed off. Homogenizing of the samples was achieved by keeping the test tubes in a water bath ($40-50^0C$) and centrifuging occasionally.

The textures as well as the optical axes of the mesophases were investigated by an Olympus polarizing light microscope, using orthoscopic and conoscopic measurements. All textures were determined between two glass plates at room temperature and with 40x10 magnification.

The FT-IR spectra were recorded on a Nicolet MX-IE spectrometer at ambient temperature ($\simeq 18^0C$). The spectrometer was calibrated using CO_2 bands. The samples were placed in a 15μm pathlenght cell of AgCl. The water absorption bands were subtracted by computation based on the 2150 cm^{-1} association band of H_2O.

Raman spectra of the samples were excited using the 514.5 nm line of an Ar ion laser recorded on a Carry 81 spectrometer with a slit width of 6.4 cm^{-1}. Laser power at the sample was approximately 100 mW.

RESULTS AND DISCUSSION

A. POLARIZING MICROSCOPY

The anionic mesophases composed of SDDS, PDE and H_2O, have been prepared varying the SDDS concentration from 12 % to 15 % and the water concentration from 68 % to 59 %, respectively. In the cationic mesophases composed of DACl, PDE and H_2O, the concentrations of the ingredients could also be varied and it was found that suitable phases were obtained as the concentrations of DACl were changed between 33 % and 40 %, the PDE concentrations between 8 % and 10 % and the H_2O concentrations between 58 % and 50 %, respectively.

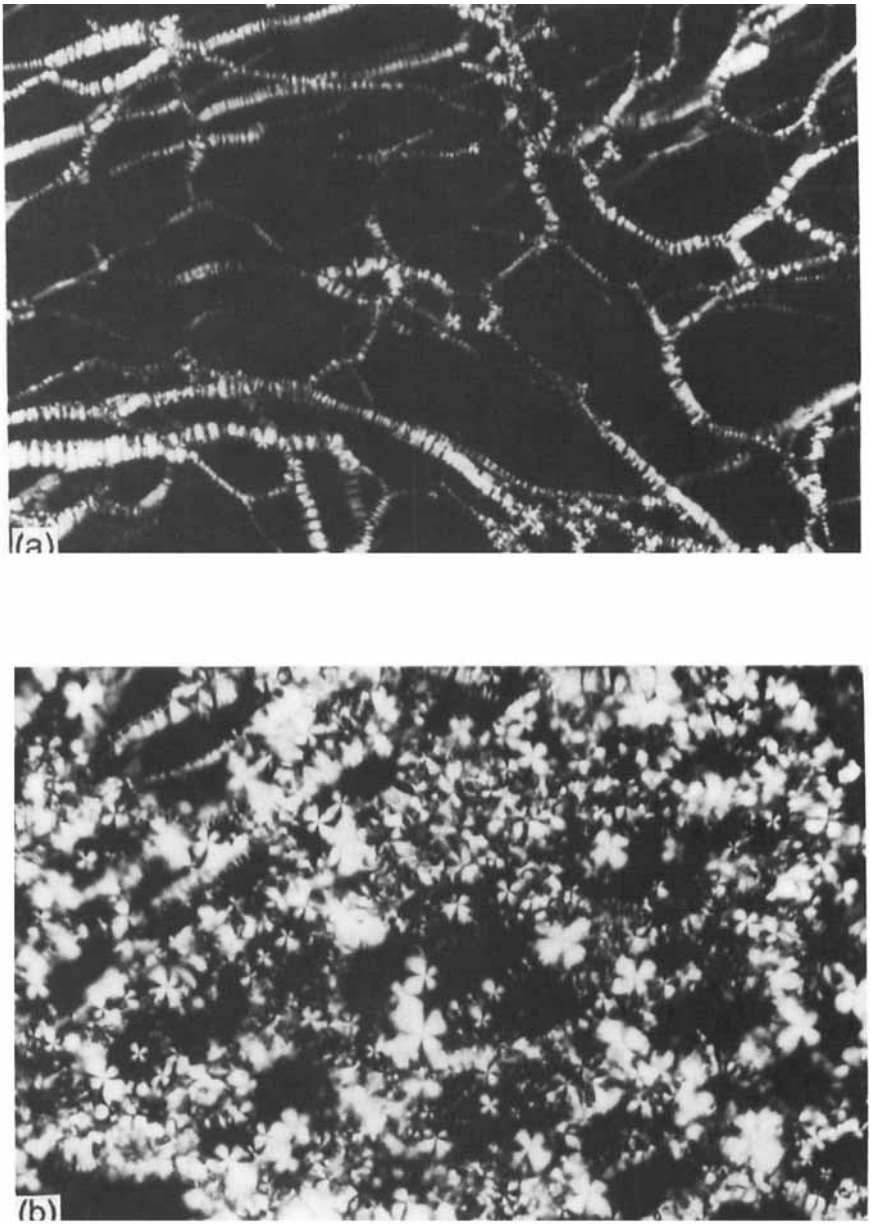

Fig.1. Optical textures of the mesophases formed by DAC1/PDE/H_2O, composed of (a) 33.90 % DAC1, 8.47 % PDE and 57.63 % H_2O (sample C1),(b) 40.00 % DAC1, 10.00 % PDE and 50.00 % H_2O (sample C2).

Fig.2. A nematic lyotropic mesophase formed by SDDS/PDE/H_2O, composed of 20.02% SDDS, 12.02% PDE and 67.96 % H_2O (sample A1).

All the mesophases of higher water content were fluid and those of lower water content were slightly viscous and transparent. Centrifuging of these mesophases did not cause any phase separation indicating that they consist of one phase.

A cationic mesophase (C1) composed of 33.90 % DACl, 8.47 % PDE and 57.63 % H_2O was within the boundary of the lamellar phase, figure 1a. Another sample (C2) composed of 40.00 % DACl, 10.00 %PDE and 50.00 % H_2O gave, however, a lamellar phase of a coarse mosaic texture, figure 1b, which is similar to plate 1 in a previous study (7). All the textures of the samples of the cationic mesophases within these concentrations disappeared with time, i.e. as viewed by the polarising microscope a dark field is observed. Conoscopic measurements gave a cross, indicating that the optical axis of these liquid crystalline phases align perpendicular to the surface of the microscope slide (2)

An anionic lyotropic mesophase (A1) composed of 20.02 % SDDS, 12.02 % PDE and 67.96 % H_2O showed a peculiar nematic texture, figure 2. As the mesophase was placed between the slide and cover glass, it appeared of low birefringence. After equilibrating the microscope sample at room temperature sufficiently long (ca. 1 hour) some areas of the mesophase appeared dark which gave only a few areas a well developed cross. This result suggests that the director of the phase is tilted in respect to the normal of the microscope slide. As the concentration of SDDS is increased, a lamellar phase of similar texture as fig. 1b is obtained. IR and Raman spectroscopic measurements have been recorded in these ranges of the phases.

B. IR AND RAMAN SPECTROSCOPIC STUDIES

The FT-IR and Raman wavenumbers obtained for the liquid crystals at ambient temperature are given in tables 1 and 2 and the corresponding spectra in figures 3 and 4 respectively.

The posphate group vibrational modes of PDE are expected to occur in the 1000-1300 cm^{-1} region of the IR spectrum. We observed two strong bands at 1195 and 1073 cm^{-1} in the IR spectrum of PDE, and assigned them to ν(P=O) and ν(P-O) stretching vibrational modes by comparing to those of inorganic phosphate and phosphatidic acid (8). In the case of anionic mesophase although, the former band (ν(P=O)) is screened with ν_a(S=O) mode, the latter is clearly distinguished in the IR spectra of A1 and A2 samples as shown in Figure 3. This mode (ν(P-O)) is found to shift to lower frequency in the anionic and cationic mesophases (Δ=5-12 cm^{-1}). The observed shift is hydrogen bonding characteristics. On the other hand, we also observed shifts to lower frequency in the ν_a(S=O) and ν_s(S=O) vibrational modes of the anionic mesophases, in comparison to those of pure SDDS. In the IR spectra of SDDS/PDE/H_2O systems the frequency shifts of ν(P-O) and ν(S=O) vibrations with respect to those of pure PDE and SDDS, respectively, are found to increase by decreasing the water content, i.e., on going from sample A1 to A2. Therefore depending on the spectroscopic features, a hydrogen bonding type interaction between the hydrogen of the OH group of PDE and one of oxygens

TABLE 1
The FT-IR wavenumbers of liquid crystals[a].

Tentative Assignments	*PDE*	*SDDS*	*DAC1*	*A1*	*A2*	*C1*	*C2*
$\nu_a(CH_3)$	2958s	2960s	2958s	2961m	2960m	2961w	2960m
$\nu_a(CH_2)$	2924vs	2925vs	2920s	2925vs	2923vs	2926vs	2925vs
$\nu_s(CH_3)$	-	-	-	2875vw	2875vw	-	2875w
$\nu_s(CH_2)$	2853s	2855s	2850s	2855s	2854s	2855s	2855s
$\delta_a(NH_3^+)$	-	-	1600s	-	-	1642s	1641s
$\delta_s(NH_3^+)$	-	-	1513vs	-	-	1523s	1521ms
CH_2scissoring $\delta(CH_2)_n$	1468m	1468s	1468s	1468m	1468ms	1468s	1468s
$\delta_a(CH_3)$	-	-	-	1458sh	1459sh	1458sh	1458sh
$\nu(P=0)$	1195s	-	-	-	-	1189s	1191s
$\nu_a(S=0)$	-	1235vs	-	1211vs	1208vs	-	-
$\nu(CC)+\nu(CN^+)$	-	-	1148m	-	-	1167s	1165s
$\nu(P-0)$	1073s	-	-	1063s	1061s	1068s	1066s
$\nu_s(S=0)$	-	1042s	-	1027s	1024s	-	-
	-	1015vs					
$\nu(CC)$	-	995vs	1010m	1020sh	1020sh	1020s	1019s
$\nu(CC)$	960s	970m	950m	977m	980m	975m	975m

[a] A1 and A2 are SDDS/PDE/H_2O systems composed of, 20.02 % SDDS, 12.02 % PDE and 67.96 % H_2O and 25.74 % SDDS, 14.85 % PDE, 59.41 % H_2O respectively; C1 and C2 are DAC1/PDE/H_2O systems composed, 33.90 % DAC1, 8.47 % PDE and 57.63 % H_2O, and 40.00 % DACl, 10.00 % PDE, 50.00 % H_2O respectively.
vs=very strong, s=strong, m=medium, w=weak and sh=shoulder.

TABLE 2
Raman vibrational wavenumbers of liquid crystals[a]

Tentative Assignments	*A1*	*A2*	*C1*	*C2*
$\nu_a(CH_3)$	2928sh	2928sh	nm	nm
$\nu_a(CH_2)$	2880vs	2880vs	nm	nm
$\nu_s(CH_2)$	2854s	2854s	nm	nm
$\delta(CH_2)$	1459vs	ca.1457vs	1459m	1459s
$\delta(CH_2)$	1441vs	ca.1441vs	1445s	1445s
$\rho(CH_2)$	1304s	1305s	1303s	1302s
$\nu(CC)$	1128m	1128m	1125m	1125m
$\nu(CC)$	1068vs	1063s	1070m	1066m

[a] See the foot notes of Table 1.
nm=not measured.

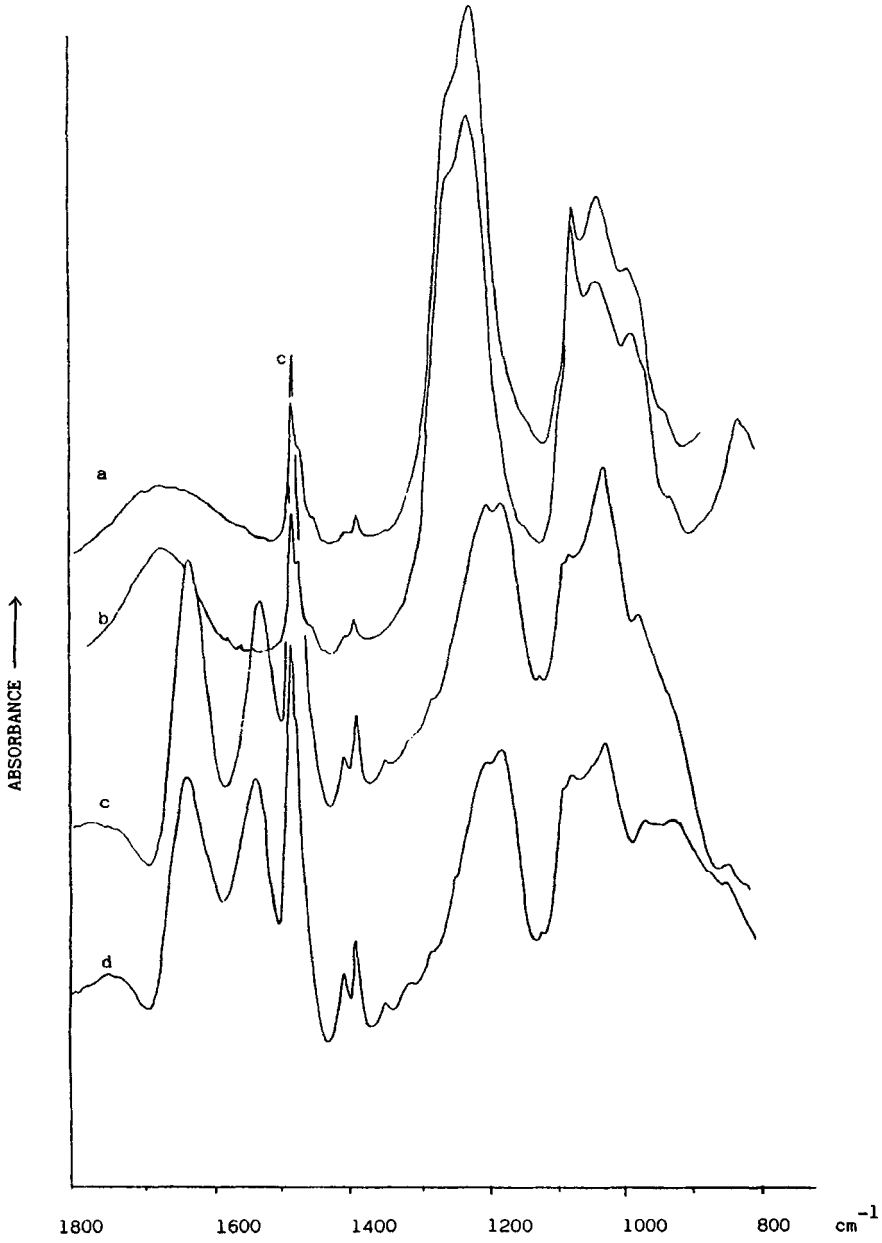

Fig.3. FT-IR spectra of: (a) sample A2, (b) sample A1, (c) sample C2 and (d) sample C1, after subtraction of water bands.

of the sulphate group of SDDS is proposed in addition to the hydrogen bonding interaction between the water molecules and the head group of SDDS or PDE, since upon dilution the interaction between PDE and SDDS groups will be weakened and the shifts of ν(P−O) and ν(S=O) vibrational wavenumbers are decreased. This is what we observed.

Asymmetric and symmetric NH_3^+ bending vibrations are observed at 1600 and 1513 cm^{-1}, respectively, in the IR spectrum of pure DAC1.These modes are observed ca.1640 and 1520 cm^{-1} in the IR spectra of the DAC1/PDE/H_2O systems, after water bands are subtracted. It will not be safe to analyse the frequency shift of $\delta_a(NH_3^+)$ mode, due to being overlapped with $\delta(H_2O)$ mode, although we analyse the subtracted spectra. But, when symmetric bending vibration of NH_3^+ head group of DCA/PDE/H_2O systems are compared to that of pure DAC1 it is clearly that this mode show an upward shift upon the formation of cationic phase. This upward shift in bending mode is characteristics of H bonding interaction (9), probably between NH_3^+ group of DAC1 and water molecules because it slightly increases upon dilution. Nevertheless we must also bear in mind presence of H bonding type interaction between NH_3^+ group of DAC1 molecules and PO_2^- groups of PDE molecules, since as we mentioned before the ν (P=O) and ν (P-O) vibrational wave numbers also showed H bounding, characteristics (see table 1).

The Raman spectra of the sample A2 and A1 are given in figure 4a and b, respectively. The C-C stretching region is known to be more sensitive to changes in lattice packing than the 2900 cm^{-1}CH stretching region (10,11). In the C-C stretching mode region of the Raman spectra of sample A2, we observed two bands at 1128 and 1063 cm^{-1}. The second band is observed at 1068 cm^{-1} in the Raman spectra of sample A1. A similar shift (1062 $\rightarrow$1079 cm^{-1}) is observed in the Raman spectra of phospholipid multilayers(10) as the mobility of the hydrocarbon chains increases. For the phospholipid multilayer systems the intensity ratio of the ν (CC) bands, I_{1128} / $I_{1062\ or\ 1079}$ is taken as a spectral index of intrachain disorder (8,10). A dramatic decrease in this ratio is observed as the intrachain disorder increases (8,10) Investigation of the Raman spectra of lyotrophic crystals indicated that the disorder of the hydrocarbon

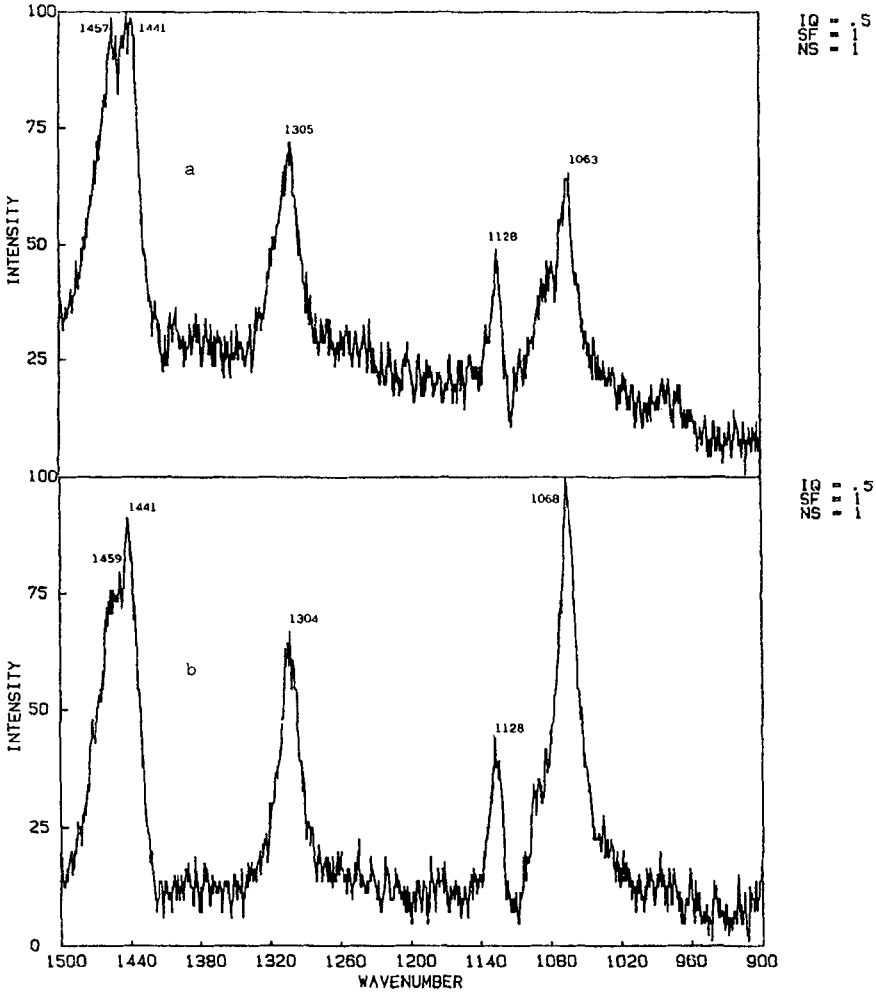

Fig.4. Laser-Raman spectra of: (a) sample A2 and (b) sample A1.

chains increase as the water content increases (see Fig.4), which is consistent with our IR spectroscopic results: We observe a slight increase of the full width at 0.75 peak height of CH_2 stretching modes of both anionic and cationic mesophases upon dilution. The increase in the band width demonstrates an increase in the mobility of the hydrocarbon chains. This result is also consistent with deuterium quadrupolar splitting results of lytropic liquid crystals(12)

CONCLUSIONS

We have investigated FT-IR and Raman-spectra of some lytropic liquid crystals in anionic and cationic mesophases. It was concluded that hydrogen bonding type interaction is present between the head groups os SDDS or DAC1 and PDE in addition to hydrogen bonding to water molecules. On the other hand the mobility of the hydrocarbon chains are found to increase by increasing the water content.

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