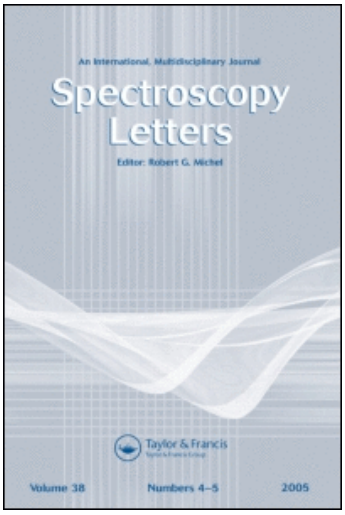

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POLARIZING MICROSCOPIC AND ^{31}P NMR STUDIES OF DECYL-AMMONIUM CHLORIDE/POTASSIUM CHLORIDE/WATER SYSTEM. CONTAINING PHOSPHORIC ACID MONODECYL ESTER AND H_3PO_4

Key words: Phase transitions in lyotropics, polarizing microscopy, ^{31}P NMR spectra.

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ABSTRACT

The decylammonium chloride (DACl), KCl and D_2O system forms two phases(N_c+N_d) in the nematic range. The N_d phase was ca. 15% by volume and exhibited extinct appearance. From conoscopic measurements it was inferred that the optical axis of the N_d phase was tilted. The lamellar phase of the DACl-KCl-D_2O system as well as the lamellar phase obtained by adding phosphoric acid

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decylester/phosphoric acid (PDE/H_3PO_4) showed the following phase sequence:

$$L_\alpha + N_d \xrightarrow{35\,^\circ C} H_\alpha + N_d \xrightarrow{40\,^\circ C} N_c + N_d \xrightarrow{45\,^\circ C} N_c \xrightarrow{50\,^\circ C} \text{isotropic}$$

The line shapes of ^{31}P NMR of PDE/H_3PO_4 were found to be sensitive to micelle size and dynamics occuring in the lyotropic system, but they do not differentiate between different micelle shapes.

INTRODUCTION

In a previous paper we have reported on ^{31}P NMR spectra of a lyotropic mesophase composed of decylammonium chloride (DACl), phosphoric acid decylester/phosphoric acid (PDE/H_3PO_4) and heavy water[1]. This system exhibited the phase sequence,

Lamellar → nematic → nematic + isotropic → isotropic,

as the temperature was raised. The results obtained showed that the nematic phase consisted of oblate(disc) shaped micelles with negative diamagnetic anisotropy (N_d).[1,2,3]

The dynamics and changes in the DACl -PDE/H_3PO_4 -D_2O system on going from lamellar phase (large fragmented micelles)[4] to smaller oblate shaped micelles (N_d) were reflected in the line shapes of ^{31}P NMR spectra.[1] Consequently, one is tempted to assume that the line shapes of ^{31}P NMR spectra obtained from the DACl-PDE/H_3PO_4-D_2O system were affected mainly by micelle size and micelle shape. In order to test this assumption it would be of interest to develop from the same amphiphile (DACl) a lyotropic mesophase with different shaped micelles, e.g. a lamellar phase (L_α), a hexagonal phase (H_α) and a nematic phase of cylindrical micelles (N_c).

Using KCl as electrolyte we have developed a mesophase of DACl with and without PDE/H_3PO_4 exhibiting a peculiar phase sequence. Therefore, in the current study we present polarizing microscopic and ^{31}P NMR results on the phase sequence,

$L_\alpha + N_d \rightarrow H_\alpha + N_d \rightarrow N_c + N_d \rightarrow N_c \rightarrow$ isotropic,

observed in the DACl-KCl -D_2O system with and without PDE/H_3PO_4.

EXPERIMENTAL

DACl and PDE have been synthesized and purified as given previously.[5,6] A typical composition for the mesophase in weight per cent was 33.95 (DACl), 3.16 (KCl), 3.06 (PDE/H_3PO_4) and 59.83 (D_2O). The total concentration of H_3PO_4 in the mesophase was approximately 0.4 percent.

The optical textures were examined by a polarizing microscope, using a hot stage (Unkam) with 0.1 K resolution. A small amount of the liquid crystalline sample is transferred into flat capillaries of various thickness (0.1 mm-0.3 mm, CAMLAB, UK) by capillary force. Both ends of the capillaries were fused carefully by flame.

^{31}P NMR and ^{2}H NMR spectra were recorded on a Bruker NMR spectrometer with a magnetic field of 9.4 T at 161.977 MHz and 61.423 MHz, respectively. In order to determine any changes by temperature effect the ^{31}P NMR spectra were measured with the same number of transients.

RESULTS AND DISCUSSION

Knowing that some electrolytes may affect the diamagnetic anisotropy ($\Delta\chi$) of a lyotropic mesophase, we have found that the replacement of NH_4Cl by

KCl in the thoroughly investigated DACl-NH_4Cl-H_2O system[4] reverses the diamagnetic anisotropy from negative ($\Delta\chi<0$) to positive ($\Delta\chi>0$). The system developed (DACl-KCl-D_2O) with the composition in weight percent, 38.55, 3.61 and 57.83, respectively,contained two nematic phases N_c and N_d at room temperature. The amount of the N_d phase, however, was small, approximately 15 % by volume as estimated visually by polarizing microscopy. The appearance of the nematic phase (N_c) with $\Delta\chi>0$ was a cotton-like but that of the N_d phase was always black, Fig.1a. As we have analysed the extinct area in Fig.1a by conoscopy, we obtained interference figure indicating sections lying obliquely to the optic axis,i.e. the director of the mesophase is tilted.[9] If the microscope stage was rotated by ca. 50°, the interference figure went apart,indicating some biaxiality[9,10], Fig. 1b. As the temperature was raised slowly, the cotton-like appearance (left side of Fig. 1a) and the extinct area (the right side of Fig. 1a) passed over at ca. 38°C to an N_c phase of a schlieren texture. Fig. 1c.

The existence of the N_d phase could not be removed by increasing the amount of the electrolyte approximately by 1%. As the amount of KCl increased to ca. 1% by keeping the other ingredients constant, the liquid crystalline system obtained was lamellar and contained nearly the same amount of the N_d phase as the first sample. The lamellar phase was also investigated by polarizing microscopy and the following phase sequence in dependence of temperature was observed:

$$L_\alpha + N_d \xrightarrow{35\,^\circ C} H_\alpha + N_d \xrightarrow{40\,^\circ C} N_c + N_d \xrightarrow{45\,^\circ C} N_c \xrightarrow{50\,^\circ C} \text{isotropic}$$

We have recognised that the liquid crystalline system (DACL-KCl-H_2O) together with methyltintrichloride (CH_3SnCl_3) was used first by Radley and Saupe to investigate its structure in the nematic range by ^1H NMR.[11] The

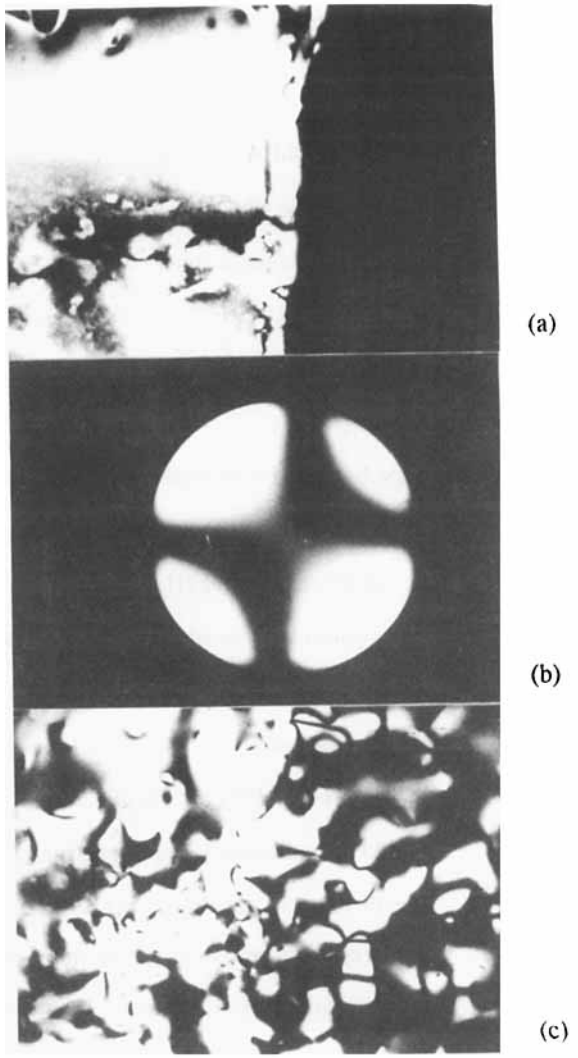

Fig.1. Polarizing microscopic results of the DACl-KCl-D_2O lyotropic system in the nematic region. (a) The cotton-like texture of the nematic phase N_C (left) and the extinct appearance of the N_d phase (right) at room temperature. (b) Interference figure of the N_d phase, indicating some biaxiality. (c) The change of Fig.1(a) (the N_c+N_d nematic region) to N_c phase at ca. 38 °C.

authors inferred from ^1H NMR of CH_3SnCl_3 that the liquid crystalline system in nematic range possessed a negative diamagnetic anisotropy, $\Delta\chi<0$ i.e. the optical axis of the mesophase aligned perpendicular to the magnetic field direction. This result contradicts what we have found where the DACl-KCl-D_2O system in nematic range contains mainly an N_C phase with $\Delta\chi>0$. Nevertheless, the CH_3SnCl_3 may have changed the diamagnetic anisotropy since these authors did not give any information on the DACl-KCl-H_2O system without CH_3SnCl_3.

The phase sequence in the lamellar phase of the DACl-KCl-D_2O system offered a good opportunity to analyse the ^{31}P NMR line shapes in dependence of micelle size and micelle shape.In order to measure ^{31}P NMR spectra, we have added PDE/H_3PO_4 to the DACl-KCl-D_2O system as the composition is given in experimental section. The addition of PDE/H_3PO_4 did not change the diamagnetic anisotropy of the system and the phase sequence remained almost the same as the one of the lamellar phase obtained from DACl-KCl-D_2O mixture.

The ^{31}P NMR spectra measured are summarized in Fig.2. The sharp lines on the left side stem from the free H_3PO_4 and the broad lines from PDE.[1] The broad spectrum of PDE at 23 °C indicates a non-aligned lamellar phase, i.e. a random distribution of the director of the liquid crystalline system in the L_α+N_d range. As the temperature was raised to 35 °C, the shape of the spectrum of PDE was narrower and sharper compared to the one of the lamellar phase. At 40 °C the spectrum of PDE remained in height nearly the same but was broader than the one at 35 °C.

These results may be interpreted as a definite alignment of the director of the phase as well as a change in micelle size. Since the N_d phase remains until the temperature reaches 45 °C, the ^{31}P NMR spectra do not appear to be

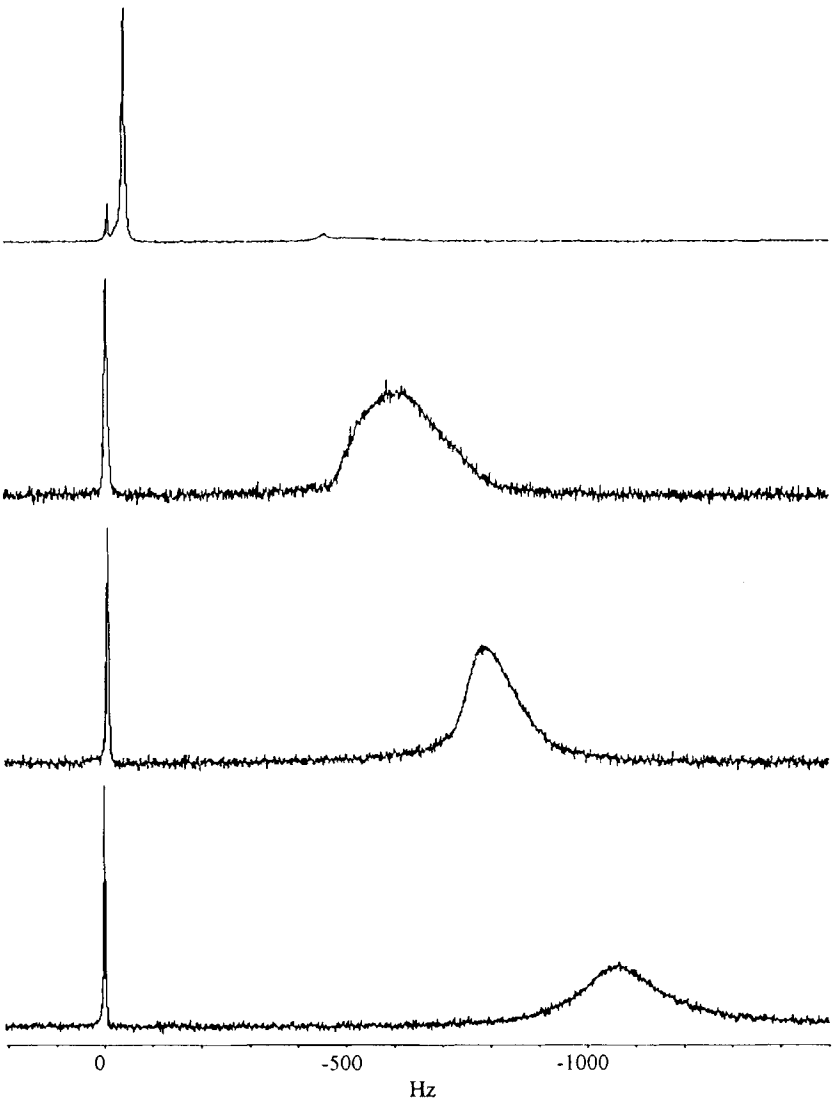

Fig.2. ^{31}P NMR spectra of PDE/H_3PO_4 in the DACl-KCl-PDE/H_3PO_4-D_2O lyotropic mesophase from lamellar region to isotropic phase. Further explanations are given in the text.

sensitive to micelle shape. Otherwise, we had to expect different lines in the range (H_α+N_d) phases for H_α and N_d or in the range (N_c+N_d) phases for N_c and N_d. Nevertheless, the ^{31}P NMR spectra of PDE give a good indication of the change in micelle size on going from (L_α+N_d) range to N_c phase since there are successive changes in the line shapes. Therefore, the ^{31}P NMR spectrum at 35 °C can be associated with a hexagonal phase (H_α) and that at 40 °C with an N_c phase where the PDE molecules tumble slowly between different micelles. Finally, the spectrum at 45 °C which consists nearly of two isotropic lines, indicates very fast motion of PDE molecules in the N_c phase. This is in accordance with the phase transition from (N_c+N_d) range to the single N_c phase as observed by polarizing microscopy. The arrow in the ^{31}P NMR spectrum at 45 °C, however, shows that the system was not completely changed to the N_c phase.

The liquid crystalline system (DACl-KCl-D_2O) with or without PDE/H_3PO_4 was studied also by ^2H-NMR of D_2O in the temperature range from 23 °C to 50 °C. In the temperature range from 23 °C to 45 °C a doublet but at 50 °C a single line were obtained, indicating a liquid crystalline system and an isotropic phase, respectively.

CONCLUSIONS

The line shapes of ^{31}P NMR spectroscopy using PDE/H_3PO_4 with support of polarizing light microscopy can give satisfactory information on the orientation of the director of the mesophase, changes in micelle size and dynamics. However, it does not appear to differentiate between different micelle shapes existing in the lyotropic liquid crystalline system.

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