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Formation of micellar nematic phases from surfactants and aqueous orthophosphoric acid

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It is shown that aqueous orthophosphoric acid can be used as a solvent for cationic surfactants to form micellar nematics which align spontaneously in magnetic fields. The cationic surfactants investigated were decylammonium chloride (DACl) and decylammonium dihydrogen phosphate ($DAPH_2$). The percentage of pure H_3PO_4 in the nematic phases of DACl could be varied from 10 to 70 per cent while $DAPH_2$ gave a nematic phase in a narrow range with 60 per cent H_3PO_4. As the percentage of pure H_3PO_4 in the DACl nematic phase increased, the ^{23}Na quadrupolar splitting decreased; this was attributed to an alteration in the binding sites of these systems. ^{31}P N.M.R. of H_3PO_4 in DACl and $DAPH_2$ nematic phases gave a symmetric singlet indicating that the chemical shift of H_3PO_4 in these systems is isotropic. A mixture of the anionic surfactants, sodium decylsulphate (SDS) with 10 per cent H_3PO_4 gave a micellar nematic phase as a result of a replacement reaction in which orthophosphoric acid monodecylester (PDE) was produced. The director of the nematic phases of the DACl, $DAPH_2$ and SDS systems aligned perpendicular to the magnetic field direction (negative diamagnetic anisotropy, $\Delta\chi < 0$). The ^{31}P N.M.R. spectrum of PDE in the SDS nematic phase gave an asymmetric singlet which is assumed to result from the ^{31}P chemical shift anisotropy. Solutions of *n*-decanol and 85 per cent H_3PO_4 gave viscous birefringent phases which contained an isotropic phase and a lamellar phase.

1. Introduction

As far as we are aware micellar nematic phases which spontaneously align in nematic fields are only formed by using water as a solvent [1, 2]. Some polypeptides in polar organic solvents also form alignable lyotropic liquid-crystalline phases [3, 4], these, however, are not related to the aqueous bilayer micellar structures [5, 6]. To find another solvent rather than water which may be used in forming micellar nematic phases, we have been attracted by aqueous orthophosphoric acid, H_3PO_4, since most important biological molecules contain phosphate groups. Our first attempt to understand the effect of this solvent was the treatment of the surfactants, *l*-serine hydrochloride decylester, *l*-SDE, and its racemic mixture, *dl*-SDE, with 43 per cent H_3PO_4 [7]. It was found that an isotropic solution composed of *l*-SDE or *dl*-SDE and H_3PO_4 formed a birefringent solution as time proceeded [7]. Further studies with amphiphilic esters derived from amino acids and long chain alkanols in H_3PO_4 show that these always give this phenomenon, and this results because the so-called acidolysis reaction takes place where the head group of the ester, the amino acid group, is replaced by the phosphate group. A detailed account on these systems will be given elsewhere [8]. In the present work, we extend our investigations to cationic, anionic and neutral surfactants to understand the actual role and effect of aqueous H_3PO_4 in micellar

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liquid-crystalline systems. We are particularly interested in those systems which align spontaneously in magnetic fields and so can be used for N.M.R. [2] and optical experiments [9].

Consequently, it will be possible to compare our results with those described in the literature. Therefore, thoroughly the investigated surfactants, *n*-decylammonium chloride (cationic) [10] and *n*-decylsulphate [1] (anionic), among others, have been studied and as neutral surfactants, *n*-alkanols, were chosen. Since our systems contained H_3PO_4 as a solvent and sodium ions as counter or co-ions, we have studied the micellar nematic phases by ^{31}P and ^{23}Na N.M.R, as well as by polarized light microscopy.

2. Experimental

2.1. *Chemical*

Decylammonium chloride (DACl) was prepared by neutralizing decylamine with dilute hydrochloric acid and was purified by recrystallizing it from petroleum ether (30–70°C) and a minute amount of ethanol. Decylammonium dihydrogenphosphate ($DAPH_2$) was prepared with following procedure. To a 0·4 M aqueous solution of H_3PO_4, 0·13 moles decylamine was added while stirring vigorously. The solution was heated approximately to 70°C, and as it was cooled to room temperature, $DAPH_2$ crystallized. The crystals were filtered and recrystallized twice from ethanol and then dried under vacuum. Sodium decanoate ($C_{10}Na$) was prepared by neutralizing decanoic acid by an alcoholic solution of sodium hydroxide. The crude material was recrystallized twice from ethanol. Sodium decylsulphate (SDS) was prepared and was purified by the procedures described in [11, 12]. Sodium dodecylsulphate (SDDS) was purchased from Merck and its purity was indicated to be greater than 99 per cent. *n*-Decanol, dec, was purchased from Janssen Chemical/Belgium and was of 99 per cent purity. The solvent orthophosphoric acid, H_3PO_4, was purchased from Riedel de Haen, and according to the manufacturer, it was an 85 per cent aqueous solution. Lower concentrations of it were prepared by dilution with water.

2.2. *Preparation of the micellar liquid-crystalline phases*

Samples were prepared by weighing the appropriate amounts of materials (approximately 2 g) into test tubes which were then scaled. The compositions and the approximate temperature ranges of the micellar nematic phases are given in the table.

2.3. *N.M.R. measurements*

^{23}Na quadrupolar splittings and ^{31}P N.M.R. spectra were recorded with a WP 200 Bruker spectrometer having a superconducting magnet of 4·7 T. The resonance frequencies were 52·911 MHz and 81·015 MHz, respectively. Since the spectrometer had an internal D_2O lock, capillary tube containing water was always immersed in the N.M.R. tube (10 mm in diameter) where the liquid crystalline sample was placed. Before the measurement the samples were left in the magnet for at least 30 min but in some cases 2–3 h; all measurements were carried out without sample spinning. The experimental temperature was 21°C, and approximately 1–2000 transients were required.

2.4. *Polarized light microscopy*

A Leitz (orthoplan) polarizing microscope was used to investigate the optical texture of the micellar liquid-crystalline phases. The microscope samples were

Approximate temperature ranges determined in sealed tubes, and compositions in percent by weight of the micellar nematics formed by the surfactants, DACl, $DAPH_2$ and SDS. H_3PO_4 gives the percentages of the solvent in the corresponding mesophase whereas % H_3PO_4 indicates the percentage of the pure H_3PO_4 in the solvent.

Decylammonium chloride systems						
Composition	DACl	Na_2SO_4	Dec	H_3PO_4	% H_3PO_4	Temperature ranges
wt %	31·85	0·85	3·50	63·80	10	(2°–42°C)
wt %	28·96	3·18	2·42	63·43	30	(10°–44°C)
wt %	30·85	3·70	2·96	62·50	50	(14°–55°C)
wt %	36·07	0·98	4·90	58·03	70	(6°–43°C)
Decylammonium dihydrogenphosphate system						
Comp	$DAPH_2$	Na_2SO_4	Dec	H_3PO_4	% H_3PO_4	
wt %	33·60	3·50	9·64	53·26	60	(−5°–102°C)
Sodium decylsulphate system						
Composition	SDS	H_3PO_4	% H_3PO_4			
wt %	50·20	49·80	10			(12°–35°C)

prepared using a 0·05 mm thick teflon spacer between the microscope slide and the cover slip. All measurements were carried out between crossed polars and with a magnification of × 40 at room temperature, if not otherwise indicated.

3. Results and discussions

3.1. *The solvent, aqueous orthophosphoric acid*

Orthophosphoric acid is a tribasic acid and, is moderately strong. In the anhydrous form, H_3PO_4 is crystalline and melts at 42·35°C. According to an X-ray structure study of the aqueous orthophosphoric acid solutions (55 to 86 per cent), at least a single hydrogen bond exists between two phosphate ions. In the more dilute solutions (below 54 per cent H_3PO_4), the phosphate ions are bound to water by hydrogen bonds [13]. From Raman spectroscopic studies, it is also inferred that the H_3PO_4 is a five-atom molecule, XY_4, and has a tetrahedral symmetry [13]. Such basic information is important to understand the role of H_3PO_4 in the formation of micellar liquid-crystalline phases.

3.2. *General features of the mixtures composed of surfactants and aqueous orthophosphoric acid*

The surfactant, decylammonium chloride, decanol and aqueous orthophosphoric acid form micellar liquid-crystalline phases which align spontaneously in applied magnetic fields. These systems can incorporate some sodium sulphate and the concentration of H_3PO_4 in the solvent can vary from 10 to 70 per cent (see the table). The micellar phases of 10 and 70 per cent H_3PO_4 incorporate approximately 1 per cent whereas the phases of 30 and 50 per cent H_3PO_4 take up as much as 3 per cent Na_2SO_4. If the phases are prepared without Na_2SO_4, it must be replaced by DACl and decanol. For example, a composition of micellar liquid crystalline phase prepared in 50 per cent H_3PO_4 free of Na_2SO_4 is DACl: 33·8 per cent, Dec: 3·60 per cent, H_3PO_4: 62·51 per cent. Mixtures of DACl, dec and the solvent containing more than 70 per cent H_3PO_4 gave viscous phases, but also mixtures composed of only DACl/H_3PO_4 with and without Na_2SO_4 were either viscous or simply liquid-crystalline at higher temperatures.

In contrast the surfactant, decylammonium dihydrogenphosphate ($DAPH_2$) was less soluble in water, but it is soluble in 85 per cent H_3PO_4. The mixtures of only $DAPH_2/H_3PO_4$ were also viscous, and combination of one of these mixtures with decanol and Na_2SO_4 gave a micellar liquid-crystalline phase (table) which aligned spontaneously in the magnetic field. The existence of this phase was found to be sensitive to the concentration of H_3PO_4. If the ratio of $DAPH_2/Na_2SO_4$/dec was kept constant, and the concentration of H_3PO_4 was varied 5 per cent below or above the actual content (60 per cent) in the mesophase, two birefringent phases or a viscous phase were obtained, respectively.

Mixtures composed of sodium decanoate and H_3PO_4 did not form any mesophase due to hydrolysis of $C_{10}Na$ to produce decanoic acid and NaH_2PO_4. Here, mixtures of decanoic acid and H_3PO_4 did not form any liquid-crystalline phase. Sodium decylsulphate gave viscous isotropic phases with H_3PO_4 of percentages higher than 20. These phases could not take up decanol or Na_2SO_4 and crystallized at about room temperature. However, a transition from an isotropic to a birefringent phase can be observed if SDS is dissolved in 10 per cent H_3PO_4 in a sealed tube at about 40°C. A viscous isotropic phase was obtained initially which then passed to a birefringent and fluid phase as this was heated to approximately 70°C. This phenomenon is similar to the acidolysis reaction [7, 8] and is only possible if the sulphate group in SDS are replaced by a phosphate group. Repeating the same experiment with sodium dodecylsulphate (SDDS) 37·20 per cent in 10 per cent H_3PO_4 showed the same phenomenon, nevertheless, the birefringent phase obtained solidified at about room temperature.

n-Alkanols containing (C_8–C_{12}) and 85 per cent H_3PO_4 also form micellar liquid-crystalline phases which, however, did not align spontaneously in the magnetic field. As an example, the *n*-decanol/H_3PO_4 system has been investigated. The neutral amphiphile, decanol, formed viscous birefringent phases with 85 per cent H_3PO_4 in the mol ratio from 1 : 1 to 1 : 5. All of these mixtures separated into two phases (isotropic and birefringent) when they were centrifuged. If the solvent was diluted from 85 to 80 per cent H_3PO_4, the solubility of decanol decreased and the main part of the system formed was isotropic and viscous. In order to measure the ^{23}Na quadrupolar splitting, a small amount of Na_2SO_4 was added to a phase composed of decanol and 85 per cent H_3PO_4 in the mol ratio 1 : 5.

To understand the formation of the micellar liquid-crystalline phases the surfactant PDE has been synthesized, which would have been produced in the dec/H_3PO_4 mixtures if a reaction between decanol and H_3PO_4 had taken place. PDE, however, does not form any mesophase either with water or with H_3PO_4, we have concluded therefore that no reaction takes place between decanol and H_3PO_4. Consequently, the formation of the mesophases in the dec/H_3PO_4 mixtures must result from electrostatic attractive forces which may be enhanced by partial protonation. As a result of partial protonation, the 85 per cent H_3PO_4 is even able to hydrolyse long chain amphiphilic esters [8].

3.3. *Polarizing microscopy*

Except for the decanol/H_3PO_4 system, all liquid-crystalline phases with the compositions presented in the table have a micellar nematic character. The nematic phases of DACl with less than 70 per cent H_3PO_4 were quite fluid, and exhibited a threadlike texture, while the phase in 70 per cent H_3PO_4 was somewhat viscous, but was still nematic, see figures 1 and 2. The optical appearance of the liquid-crystalline phases of the $DAPH_2/H_3PO_4$ and SDS/H_3PO_4 systems were similar to that in figure 2. The

Figure 1. A typical nematic texture of DACl systems up to 50 per cent H_3PO_4. The photomicrograph was taken after equilibrating the sample for *c.* 15 min.

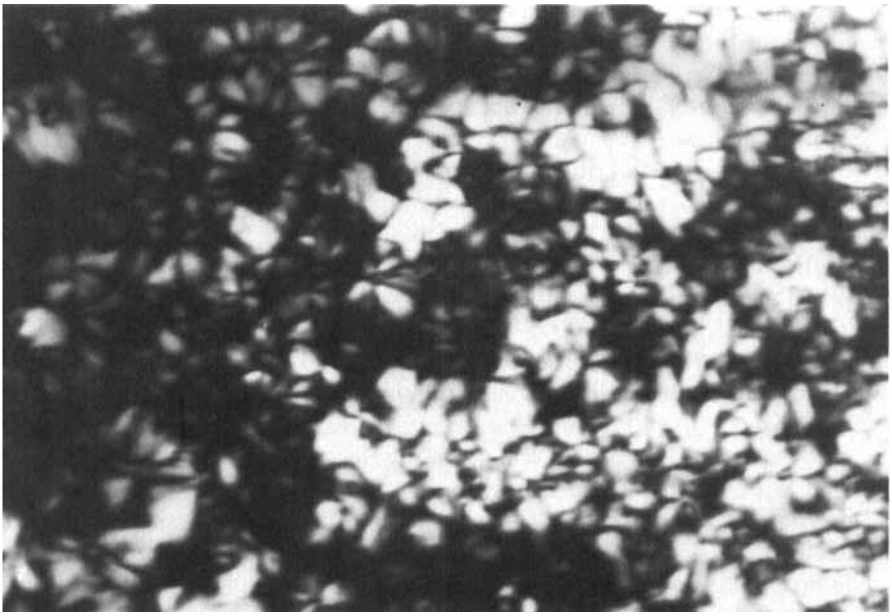

Figure 2. The nematic texture of DACl/70 per cent H_3PO_4 system obtained after equilibrating the sample for *c.* 2 h.

textures in figures 1 and 2 disappeared with time, i.e. a total extinction occurred indicating that the director of each mesophase was aligned perpendicular to the surface of the microscope slide (cf. figure 5) [14]. The complete alignment of the director shown in figure 1 took approximately one hour but that of figure 2 took four

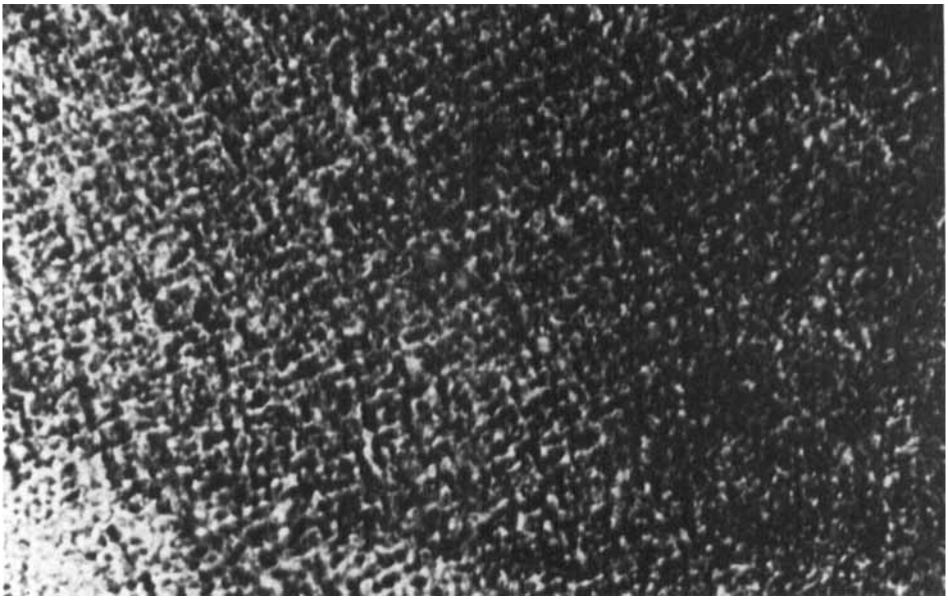

Figure 3. A typical appearance of the lamellar phase of low birefringence observed in the decanol/H_3PO_4 system. The photomicrograph was taken after equilibriating the sample *c*. 3 h, mag. 40 × 10.

hours. Investigation of the liquid crystalline phase formed by decanol/H_3PO_4 system in the mol ratio 1 : 5 showed a lamellar texture with a low birefringence which did not align in the microscope sample, see figure 3. Addition of Na_2SO_4 does not change markedly the texture of the phase, but it appears to increase somewhat the amount of the isotropic phase.

If the micellar nematics obtained from surfactants in H_3PO_4 are compared with those obtained from surfactants in pure water, then similar structures could be recognized. DACl with H_3PO_4 as well as with pure water [10] forms micellar nematics with negative diamagnetic anisotropy ($\Delta\chi < 0$). The surfactant SDS however forms two types of micellar nematics with water, one with ($\Delta\chi < 0$) (SDS/Na_2SO_4/dec/H_2O) and the other with ($\Delta\chi > 0$) (SDS/dec/H_2O) [15].

Since SDS with H_3PO_4 forms only one type of nematic phase ($\Delta\chi < 0$), its overall interactions with H_3PO_4 are completely different from those with water. Although DACl/H_3PO_4 and DACl/H_2O micellar nematics possess the same diamagnetic anisotropy ($\Delta\chi < 0$), this does not, of course, imply that the overall interactions between DACl and H_3PO_4 are the same as between DACl and water. The difference between the two systems may be studied if the quadrupolar splittings of a common nucleus in the aqueous layers as well as the order parameters of chain segments of the surfactants in the hydrophobic region of both nematic phases are compared. This also applies to SDS/H_3PO_4 and SDS/H_2O nematic phases with $\Delta\chi < 0$. Such studies would also make it possible to understand the effect of H_3PO_4 in the aqueous layers of nematic phases in detail. These investigations are envisaged.

3.4. *N.M.R. spectroscopy*

The same systems have also been studied using the ^{23}Na quadrupolar splittings and the ^{31}P chemical shifts of phosphoric acid. The results for the ^{23}Na quadrupolar

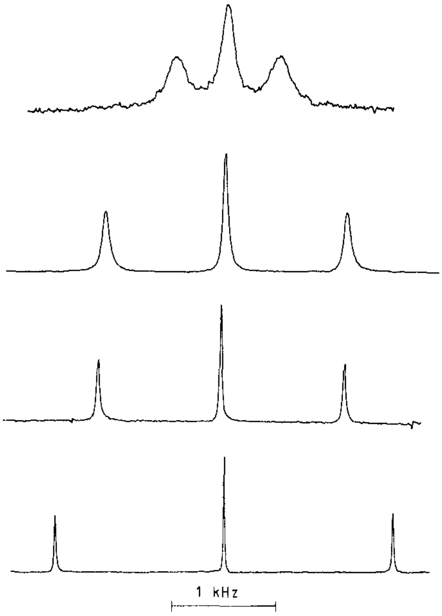

Figure 4. ^{23}Na quadrupolar splittings of DACl/H_3PO_4 systems. N.M.R. spectra from the bottom to the top were obtained from the micellar nematic phases, containing 10, 30, 50 and 70 per cent H_3PO_4 in the solvent, respectively.

splittings are summarized in figures 4, 5, 6 and 7. As expected, in ordered media these spectra contain three lines [6, 16] except for the decanol/H_3PO_4 system. If the ^{23}Na quadrupolar splittings of DACl nematic phases are examined, two effects can be recognized. As the concentration of H_3PO_4 in the solvent increases, the linewidth at half height increase but the quadrupolar splittings decrease, see figure 4. The ^{23}Na quadrupolar splitting of the DACl nematic phase with 10 per cent H_3PO_4 was 3300 Hz, but it was 1000 Hz with 70 per cent H_3PO_4. The nematic systems with 30 and 50 percent H_3PO_4 gave ^{23}Na quadrupolar splittings of 2415 Hz and 2370 Hz, respectively. These two results may be explained by a decrease of the availability of specific binding sites for sodium ions [17, 18] as the concentration of H_3PO_4 in the solvent is varied from 10 to 70 per cent. In this case, sodium ions are subjected to more tumbling, and this leads to smaller quadrupolar splittings and also to line broadening, as observed in the DACl systems.

^{23}Na quadrupolar splittings of the $DAPH_2$ nematic phase (3550 Hz), the SDS nematic phase (11 700 Hz) and the dec/H_3PO_4 system are illustrated in figures 5, 6 and 7, respectively. The latter system gives no ^{23}Na quadrupolar splitting indicating that the sodium ions in this system possess no preferential orientation, and consequently a random alignment of the director of the mesophase, even if the sample was heated above the isotropic transition (50°C) and measured after cooling at 40°C. ^{31}P N.M.R. spectra of H_3PO_4 in the micellar nematic phases of DACl and $DAPH_2$ systems contain a symmetric singlet, therefore the chemical shift of H_3PO_4 in these anisotropic systems is isotropic. Such a singlet of H_3PO_4 in the $DAPH_2$/H_3PO_4 nematic phase and that of 85 per cent H_3PO_4 are shown in figure 5. The ^{31}P N.M.R. spectrum of the SDS nematic phase stems from the bonded phosphate group in the surfactant, PDE. Therefore, the ^{31}P N.M.R. spectrum in this micellar nematic phase shows by and large

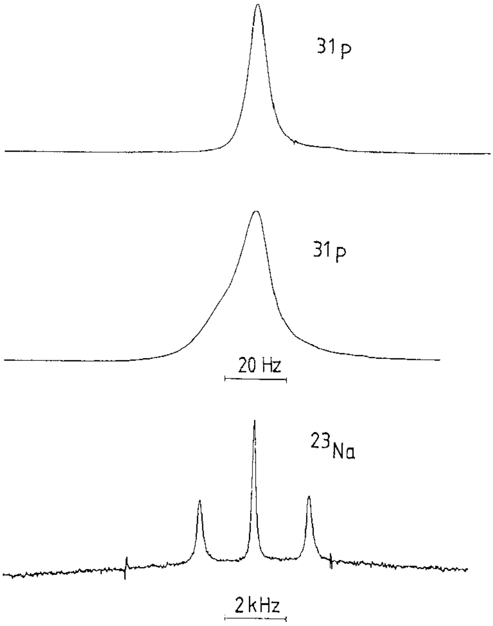

Figure 5. ^{23}Na quadrupolar splitting and ^{31}P chemical shift (upper spectrum) of the nematic $DAPH_2/H_3PO_4$ system. ^{31}P N.M.R. spectrum in the middle is of the solvent, 85 per cent H_3PO_4.

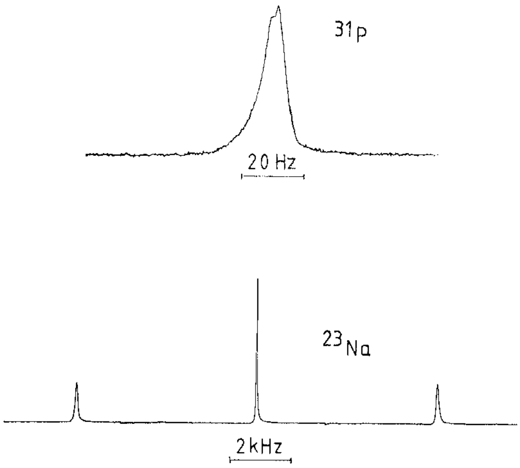

Figure 6. ^{23}Na quadrupolar splitting of the nematic phase, SDS/H_3PO_4 system and ^{31}P N.M.R. chemical shift of PDE in the same phase.

an asymmetric shape at the top on the left hand side of the spectrum, see figure 6. Since ^{31}P N.M.R. spectra are used to differentiate between the motions of phospholipid molecules in L_α, H_α and isotropic phases [19, 20, 21], we assume tentatively that the ^{31}P N.M.R. spectrum of PDE in the micellar nematic phase of SDS system reflects some ^{31}P chemical shift anisotropy, i.e. not all the motions of the phosphate group of PDE in this nematic phase are isotropic, and therefore a small chemical shift anisotropy is measured. It should be mentioned that the asymmetric shape of the ^{31}P N.M.R. spectrum in the nematic phase of SDS does not come from unreacted H_3PO_4.

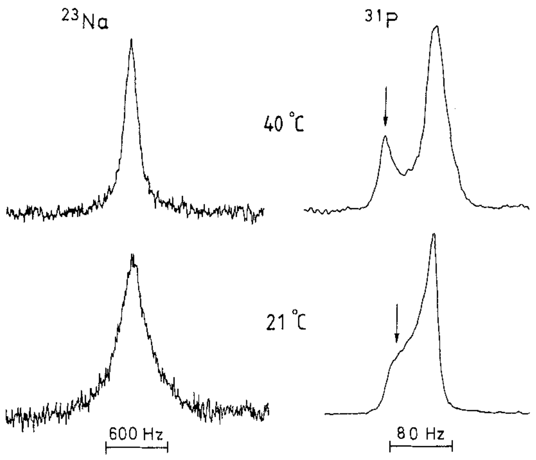

Figure 7. ^{23}Na and ^{31}P N.M.R. spectra of the decanol/H_3PO_4 lamellar phase. Spectra at the bottom before heating the sample above the isotropic transition (50°C). Spectra at the top after heating the sample and cooling to 40°C. The arrows indicate the isotropic phase spectra.

If in a micellar nematic system free and bonded H_3PO_4 exist, then two ^{31}P N.M.R. peaks are obtained as can be shown in acidolysis reactions of amphiphilic esters and H_3PO_4 [8]. The observation of ^{31}P chemical shift anisotropy in micellar nematic phases depends probably on the micelle size, the diamagnetic anisotropy of the nematic phase, the nature of the bonded phosphate group and its interactions with its environment. Therefore, we feel that this problem deserves particular attention and must be studied in a separate work.

The ^{31}P N.M.R. measurement of the decanol/H_3PO_4 system at 21°C gave a singlet with an asymmetric shape on the left hand side as in figure 7. But as this system was heated over the isotropic transition (50°C) and was let to cool, a separation in two phases occured. ^{31}P N.M.R. spectrum measured after cooling to 40°C consisted of two peaks each corresponding to the one phase of this system. The separation between the two peaks in the ^{31}P spectrum at 40°C looks larger than any potential separation in the spectrum at 21°C. This indicates, however, that the chemical shift of H_3PO_4 in the isotropic phase is notably different from the chemical shift of H_3PO_4 in the lamellar phase. Visual inspection of the N.M.R. sample showed a clear phase separation, the lower isotropic phase being a smaller portion and the upper phase being anisotropic.

4. Concluding remarks

The results presented in this work indicate that aqueous orthophosphoric acid is a convenient solvent for cationic surfactants to form micellar nematic phases. Compared to pure water, H_3PO_4 appears to possess a better solubilizing capacity as shown for the $DAPH_2/H_3PO_4$ and the decanol/H_3PO_4 systems. The latter system is interesting in showing interactions between neutral surfactants (long chain alkanols) and H_3PO_4 which give rise to micellar liquid-crystalline systems. The use of H_3PO_4 as a solvent for anionic surfactants to form micellar liquid-crystalline phases is either not possible (e.g. sodium decanoate due to hydrolysis reaction) or restricted (e.g. sodium decylsulphate). In the latter case, the formation of a micellar nematic phase occurs as a result of a replacement reaction.

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