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^{2}H AND ^{14}N NMR OF CETYLPYRIDINIUM BROMIDE LYOTROPIC AND THERMOTROPIC LIQUID CRYSTALS

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^{2}H and ^{14}N NMR spectra of the cationic head group have been recorded for liquid crystalline systems of CPB (cetylpyridinium bromide), pentanol and NaBr brine, at low surfactant content. The ^{2}H quadrupolar splittings provided the order parameters of the aromatic ring at various temperatures. Using these order parameters, the experimentally determined ^{14}N quadrupolar splittings allowed the evaluation of the principal values of the nitrogen quadrupole coupling tensor, $|C_Q| = 0.41$ MHz and $\eta = 0.39$. ^{2}H quadrupolar splittings measured for the thermotropic liquid crystal given by pure CPB above 71°C allowed to calculate the ring order parameters also for this phase. These parameters and the ^{14}N $|C_Q|$ and η values led to ^{14}N splitting values in very good agreement with those actually observed for this thermotropic ionic liquid crystal.

Keywords: ^{2}H NMR; ^{14}N NMR; cetylpyridinium bromide; swollen lamellar phase; thermotropic ionic liquid crystal; ^{14}N quadrupole coupling

INTRODUCTION

NMR spectroscopy of quadrupolar nuclei is widely employed in the study of lyotropic liquid crystals (LC), which are formed by amphiphiles in the presence of solvent. Most commonly exploited are the residual quadrupolar splittings ($\Delta\nu$) of ^{2}H and ^{17}O [1–3], as water is by far the most important solvent and heavy water is of widespread use. Unfortunately these investigations are complicated by temperature dependent changes in the reorientational motion of water and in the hydration degree of the amphiphilic molecules [4,5]. Furthermore, the magnitude of the quadrupolar splittings is often reduced by fast exchange between bound water and bulk water, which reorients isotropically [6]. More faithful information on these anisotropic phases can be gained by means of NMR spectroscopy of the quadrupolar nuclei of the surfactant molecules. Very often, to this end, either the whole alkyl chain or a few selected positions are isotopically enriched

with deuterium [7–9]. In this way interesting pictures of the interior of the aggregates have been obtained [10]. Usually the order parameters decrease from the first or second methylene of the alkyl chain towards the end. In the innermost part of the aggregate the chain possesses a very high mobility, related to the huge number of its degrees of freedom. The methylene group next to the surface is the least mobile one and therefore it is considered to be the most informative about the order of the aggregates. For this reason many studies of the phase diagram and of the properties of lyotropics rely on the deuteration of the first methylene group of the surfactant, co-surfactant or co-aggregate.

A relation between the order parameters of the first chain segment and the order parameters of the head group is established by the molecular geometry. It should be noted that the properties of amphiphilic molecules are determined both by the chain and the head group, and that the latter plays a fundamental role being the moiety in direct contact with the solvent. Indeed also the quadrupolar nuclei of the head group are used to investigate lyotropic systems. Sometimes this is achieved by introducing deuterium, e. g. by using deuterated pyridinium salts [11–13]. In other cases it is possible to exploit the quadrupolar nuclei naturally present. The latter case is represented by cationic surfactants with a quaternary nitrogen atom. ^{14}N is a very convenient quadrupolar nucleus ($I = 1$), with a moderate nuclear quadrupole moment ($Q = 20.45$ mb) [14] and the possibility to work without isotopic enrichment (natural abundance 99.63%) [15]. Indeed ^{14}N NMR spectroscopy was used to define the phase diagrams of binary CTAC-H_2O [8] (CTAC = cetyltrimethylammonium chloride, cetyl = n-$C_{16}H_{33}$) and CTAB-formamide [16] (CTAB = cetyltrimethylmethylammonium bromide) systems. It was also employed to study the temperature dependence of the alignment in the magnetic field both for a hexagonal phase of the binary system CTAB-D_2O [17] and for a pseudoternary system CTAB-pentanol- NaBr brine [18], which forms anisotropic phases at brine concentration up to 95–98%, in other words at extremely high dilution. In CTAB the electric field gradient (EFG) at the nitrogen atom is weak, approximately axially symmetric and the z axis of its principal axes system (PAS) is along the N-$C(1)_{alkyl}$ bond direction.

In this paper we want to test the significance of the ^{14}N NMR spectroscopy in a case where the EFG is expected neither to be axially symmetric nor to have the PAS z axis along the N-$C(1)_{alkyl}$ bond direction. For this purpose we took into consideration two extreme LC situations for the CPB (CPB = cetylpyridinium bromide), namely the swollen lamellar phase at very low surfactant concentration and the LC given by the pure compound at temperatures higher than the melting point. The swollen lamellar phases have several interesting properties: quick and easy preparation, low viscosity and rapid alignment in the magnetic field already at room

temperature. Similar systems with hexanol instead of pentanol as co-surfactant have been thoroughly investigated, mainly by means of diffraction techniques [9,19,20], which assessed that these phases consist of extended bilayers separated by a large layer of brine, the thickness of which depends on the brine content. In addition, the studies showed that these phases exist in a narrow range of co-surfactant/surfactant ratios and that the properties of the bilayers depend sensitively on this ratio.

Here we report the order parameters of pyridinium evaluated from the ^{2}H residual quadrupolar splittings of the isotopically enriched aromatic ring for the swollen lamellar phase CPB, pentanol, NaBr brine, and for the CPB thermotropic LC at various temperatures. Furthermore we report the ^{14}N NMR results and discuss them using the above order parameters. From these we could determine the cetylpyridinium ^{14}N quadrupole coupling tensor, the knowledge of which is necessary to assess the role which the ^{14}N probe nucleus can play in the study of these phases.

EXPERIMENTAL

Preparation of the Samples

Deuterated CPB was prepared by direct condensation of pyridine-d_5 and cetylbromide, keeping the thoroughly mixed reagents in a boiling water bath for 6 hours The product was crystallised from ethylacetate.

The samples were prepared by weighing in 10 mm NMR tubes the appropriate amounts of CPB (20% deuterated compound), NaBr (0.2 M solution) and pentanol, which was added dropwise. The samples were then equilibrated at room temperature for at least 12 hours. The presence of the LC phase was checked by means of ^{14}N NMR. Then the samples were transferred to 5 mm NMR tubes, which were sealed off to prevent pentanol evaporation.

The compositions of the samples examined are reported in Table I.

TABLE I Weight Percent Composition of Lyotropic Samples

	CPB/%	pentanol/%	brine/%
sample a	8.93	6.15	84.91
sample b	8.84	5.92	85.23
sample c	8.51	6.36	85.13
sample d	5.28	3.64	91.07

NMR Spectra

The NMR spectra were recorded on a Jeol Eclipse 400 (9.4 T) spectrometer operating at 61.37 MHz for ^{2}H and at 28.88 MHz for ^{14}N. ^{2}H NMR spectra were acquired with the deuterium field frequency lock turned off. Temperature was controlled within $\pm 0.5°C$ by means of a Jeol NM-EVTS3 variable temperature unit.

Typically, 15000 transients were acquired for ^{14}N (one every 0.1 sec) and 8000 transients were acquired for ^{2}H (one every 0.3 sec). Prior to FT the ^{2}H data were zero-filled. Digital resolutions were: 14.11 Hz per point for ^{14}N and 2.50 Hz per point for ^{2}H.

The samples of the swollen lamellar phase were left in the magnet for at least 15' at 30°C before recording the spectra, so that the alignment process of the aggregates could take place. The ^{14}N NMR spectra were recorded from 5 mm tubes placed in 10 mm tubes containig water.

The samples of pure CPB, representing a thermotropic LC, were first heated in the magnet to 90–100°C for at least 30' to allow for the alignment. Then the spectra were acquired after cooling to the desired temperature. The ^{14}N NMR spectra were acquired for non-deuterated CPB, from 10 mm tubes, and for deuterated CPB from 5 mm tubes. The results obtained did not differ significantly.

The regression analyses were carried out by the software Microsoft® Excel97.

RESULTS

Swollen Lamellar Phase

^{2}H NMR Spectra

All the samples considered corresponded to a pure phase as confirmed by the presence of just one doublet for D_2O with a quadrupolar splitting, $\Delta\nu(^{2}H)$, of 20–30 Hz.

The signals arising from the deuterated CPB head groups appeared outside the water doublet because of the much larger splitting indicating that the alignment of the surfactant molecule was quite strong (Figure 1). Similarly to previous NMR studies on surfactants with deuterated pyridinium head groups [11–13], three different doublets were observed corresponding to the aromatic positions (2), (3) and (4) (Figure 2), in line with a fast reorientation of the ring about its C_2 axis. The assignments were made on the basis of chemical shifts, the one for position (4) being obvious because of the smaller intensity. From the NMR spectra only the absolute values of the splittings are obtained. All splittings increased

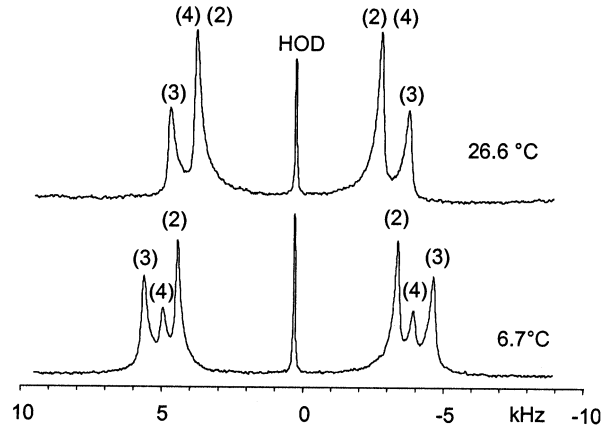

FIGURE 1 ^{2}H NMR spectra of sample a at 26.6°C (upper trace) and at 6.7°C (lower trace).

with decreasing temperature, but with different slopes. $\Delta\nu(^{2}H(3))$ was always larger than $\Delta\nu(^{2}H(2))$. $\Delta\nu(^{2}H(4))$ was the splitting most sensitive to temperature.

The $^{2}H(4)$ resonances were close to the ones of $^{2}H(3)$ at low temperature, while at high temperature they were closer to those of $^{2}H(2)$, overlapping with them in sample a (Fig. 1).

The difference between $\Delta\nu(^{2}H(2))$ and $\Delta\nu(^{2}H(3))$ is due to the distortions of the geometry of the pyridinium ring from a regular hexagon. A more detailed explanation of this effect can be obtained by considering that the observed ^{2}H quadrupolar splittings may be written as:

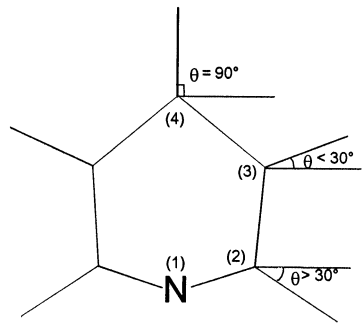

FIGURE 2 Distortions of a pyridinium ring from the regular hexagonal geometry.

$$\Delta\nu(^2H(i)) = -\frac{3}{4}C_{Q(i)}\left(1+\eta_{(i)}\right)S_{zz} + \frac{3}{4}C_{Q(i)}\left(1-\frac{\eta_{(i)}}{3}\right)\cos(2\theta_{(i)})\left(S_{xx}-S_{yy}\right) \quad (1)$$

where i = 2, 3, 4 and S_{xx}, S_{yy}, S_{zz} are the principal components of the order tensor for the pyridinium ring using the axis system depicted in Figure 3, $C_{Q(i)}$ and $\eta_{(i)}$ are the quadrupole coupling constant and asymmetry parameter of deuteron (i). The angle $\theta_{(i)}$ describes the orientation of the axes of the EFG PAS at the deuterium nucleus (i) (in which the $z_{(i)}$ axis coincides with the C(i)-D(i) bond direction and the $y_{(i)}$ axis is orthogonal to the ring plane). $\theta_{(4)}$ is 90°, whereas both $\theta_{(2)}$ and $\theta_{(3)}$ would be 30° in the case of regular hexagonal geometry.

Tracey found out that, under the assumption of $\eta = 0$ and $C_{Q(1)} = C_{Q(2)} = C_{Q(3)}$, the following relation holds:[11]

$$\frac{|\Delta\nu(^2H(3)) - \Delta\nu(^2H(4))|}{|\Delta\nu(^2H(2)) - \Delta\nu(^2H(4))|} = \left(\frac{\cos\theta_{(3)}}{\cos\theta_{(2)}}\right)^2 \quad (2)$$

The ratio given in equation 2 should be constant and larger than one, owing to the actual geometry of the pyridinium ring where $\theta_{(2)} > 30°$ and $\theta_{(3)} < 30°$ (Fig. 2). Our experimental data (Table II), in line with other CPB NMR studies [11,12], lead to a constant ratio only if $\Delta\nu(^2H(4))$ has an opposite sign with respect to $\Delta\nu(^2H(2))$ and $\Delta\nu(^2H(3))$. Furthermore the ratio is larger than one only for $|\Delta\nu(^2H(3))| > |\Delta\nu(^2H(2))|$, in agreement with the above assignments of the signals. In the following we choose $\Delta\nu(^2H(2))$ and $\Delta\nu(^2H(3))$ to be positive and $\Delta\nu(^2H(4))$ to be negative. The signs of the order parameters derived are based on this choice.

From the experimental splittings, $\Delta\nu(^2H(2))$, $\Delta\nu(^2H(3))$ and $\Delta\nu(^2H(4))$, the order parameters for the pyridinium ring, S_{zz} and $(S_{xx}\text{-}S_{yy})$, have been determined for each sample as a function of temperature. Indeed, in the aromatic rings the C_Q values do not differ much and the η values are small. Assuming $C_Q = 185$ kHz and $\eta = 0.05$ for all the positions [11], for each

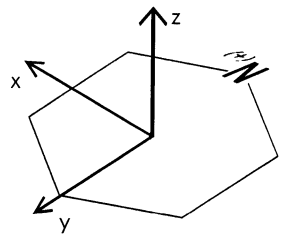

FIGURE 3 Axis system used for the pyridinium ring.

TABLE II ^{2}H and ^{14}N Experimental Quadrupole Splittings for the Samples of the Lyotropic Phase

T/°C	$\Delta\nu(^{2}H(2))$/kHz	$\Delta\nu(^{2}H(3))$/kHz	$\Delta\nu(^{2}H(4))$/kHz	$\Delta\nu(^{14}N)$/kHz
		sample a		
26.6	6.595	8.520	6.595	19.40
24.7	6.705	8.650	−6.705	19.50
22.0	6.900	8.925	−6.900	
17.7	7.185	9.330	−7.520	
14.7	7.335	9.535	−7.770	21.00
11.7	7.575	9.905	−8.290	21.55
9.7	7.590	9.910	−8.310	21.55
6.7	7.820	10.300	−8.910	21.95
4.7	7.850	10.310	−8.955	22.05
		sample b		
29.8	6.445	8.330	−6.560	17.80
24.5	6.860	8.925	−7.200	19.45
14.7	7.545	9.895	−8.530	
9.7	7.910	10.450	−9.385	21.90
		sample c		
29.7	5.880	7.550	−5.660	17.35
26.7	6.125	7.910	−5.980	18.20
24.8	6.270	8.110	−6.110	18.65
14.7	6.930	8.940	−6.930	20.20
11.7	7.170	9.275	−7.390	20.60
9.7	7.275	9.435	−7.825	20.80
6.7	7.430	9.690	−7.890	
4.7	7.535	9.850	−8.235	21.45
		sample d		
29.7	5.110	6.610	−5.370	13.75
26.7	5.545	7.210	−5.980	
24.9	5.835	7.615	−6.380	16.50
17.7	6.500	8.540	−7.515	
14.7	6.740	8.880	−8.020	18.70
9.7	7.240	9.615	−9.265	19.85
4.7	7.620	10.290	−10.290	20.25

temperature the three data points with coordinates $\cos(2\theta_{(i)})$ and $\Delta\nu(^{2}H(i))$ were fitted to a straight line, by means of the least squares method. The values of 28° for $\theta_{(3)}$ [11], of 34.4° for $\theta_{(2)}$, (from the splittings ratio (1.070) of equation 2), and of 90° for $\theta_{(4)}$ were used. The order parameters obtained for the sample d are reported in Figure 4.

Close values for the order parameters could be obtained, through bilinear regression, using for pyridinium the deuterium quadrupole parameters $C_{Q(2)} = 183$, $\eta_{(2)} = 0.03$, $C_{Q(3)} = 185$, $\eta_{(3)} = 0.03$, $C_{Q(4)} = 188$, $\eta_{(4)} = 0.01$, reported for pyridine [21].

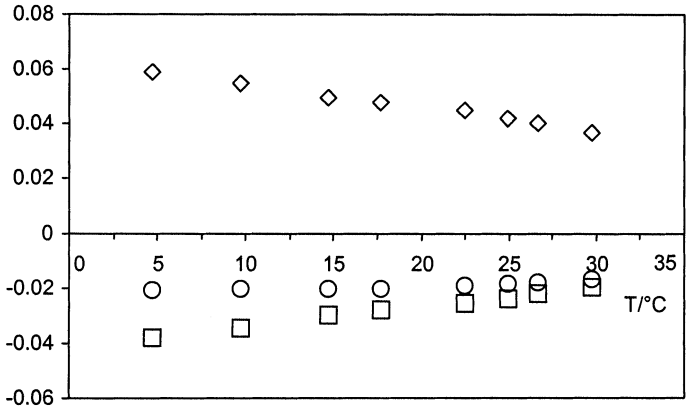

FIGURE 4 Plot of the order parameters of the pyridinium ring in swollen lamellar phase sample d vs. temperature: ◇ S_{xx}, □ S_{yy}, ○ S_{zz}.

The absolute values of the three order parameters resulted to increase on lowering temperature for all the lyotropic samples investigated. An example of the trends is reported in Figure 4.

^{14}N NMR Spectra

The ^{14}N NMR spectra consisted of the doublet expected for a single anisotropic phase. The corresponding splitting $|\Delta\nu(^{14}N)|$ decreased upon dilution with brine. $|\Delta\nu(^{14}N)|$ decreased also upon increasing the pentanol/surfactant ratio at constant brine content.

Lowering the temperature led to a monotonical increase of $|\Delta\nu(^{14}N)|$, which suggests a higher degree of alignment of the pyridinium head group.

TABLE III ^{2}H and ^{14}N Experimental Quadrupole Splittings for the CPB Thermotropic Liquid Crystal

T/°C	$\Delta\nu(^{2}H(2))$/kHz	$\Delta\nu(^{2}H(3))$/kHz	$\Delta\nu(^{2}H(4))$/kHz	$\Delta\nu(^{14}N)$/kHz
89.6	13.180	18.000	−17.590	34.85
86.7	13.130	18.060	−18.060	34.45
83.7	13.110	18.110	−18.110	34.20
80.6	12.810	17.930	−19.090	33.90
77.7	12.760	17.940	−19.560	33.55
74.7	12.750	17.930	−19.890	
71.7	12.710	17.940	−20.170	

The splitting $\Delta\nu(^{14}N)$ can be expressed as:

$$\Delta\nu(^{14}N) = \frac{3}{2} C_{QN}\left[S_{zzN} + \frac{\eta_N}{3}\left(S_{xxN} - S_{yyN}\right)\right] \quad (3)$$

where C_{QN} and η_N are the quadrupole parameters of the ^{14}N nucleus, which were unknown for CPB, and S_{xxN}, S_{yyN} and S_{zzN} are the order parameters of its EFG PAS, which coincides with the axis system of the pyridinium ring apart from possible axes permutations.

Using the experimentally determined $\Delta\nu(^{14}N)$ values and the order parameters obtained for the pyridinium ring, we calculated the C_{QN} and η_N values on the basis of a linear regression method. The values resulted in $C_{QN} = -0.405$ MHz and $\eta_N = 0.39$, or $C_{QN} = -0.413$ MHz and $\eta_N = 0.39$, the latter values being obtained using the ^{2}H quadrupole couplings of pyridine. The EFG PAS at ^{14}N has the x and y axes interchanged with respect to the molecular axis system of Figure 3.

If the $\Delta\nu(^{14}N)$ splitting had a negative sign C_{QN} would be positive, i.e. from our data just the absolute value of C_Q can be obtained.

Thermotropic Ionic Liquid Crystal

Pure CPB is a thermotropic LC which forms an anisotropic phase over a wide temperature range above its melting point at 71°C, i.e. CPB belongs to the class of ionic liquids, which exhibit anisotropic phases such as other alkylpyridinium salts [22,23].

^{2}H NMR Spectra

^{2}H NMR spectra of pure CPB showed a pattern of partial alignment in the magnetic field (Fig. 5).

The deuterium splittings $|\Delta\nu(^{2}H(2))|$ are about twice as large as those shown by the swollen lamellar phase at about 50°C lower temperature. The dependence of the splitting on temperature is weaker than for the lyotropic LC.

The order parameters for the pyridinium ring were obtained as described above; the value of 34.9° was used for the $\theta_{(2)}$ angle. According to the larger splitting $\Delta\nu(^{2}H)$, the values for the order parameters were about twice as large as those in the lyotropic phase. As demonstrated in Figure 6, $|S_{yy}|$ and $|S_{zz}|$ showed opposite dependence on the temperature, and $|S_{xx}|$ was almost independent.

^{14}N NMR Spectra

The quadrupolar splitting of the ^{14}N nucleus, $\Delta\nu(^{14}N)$, too was roughly twice as large as that in the lyotropic phase. Similar to the ^{2}H results, the $\Delta\nu(^{14}N)$ values showed a much weaker dependence on the temperature

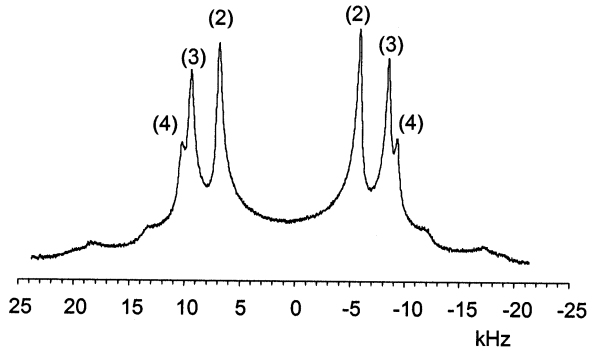

FIGURE 5 ^{2}H spectrum of pure CPB at 77.7°C.

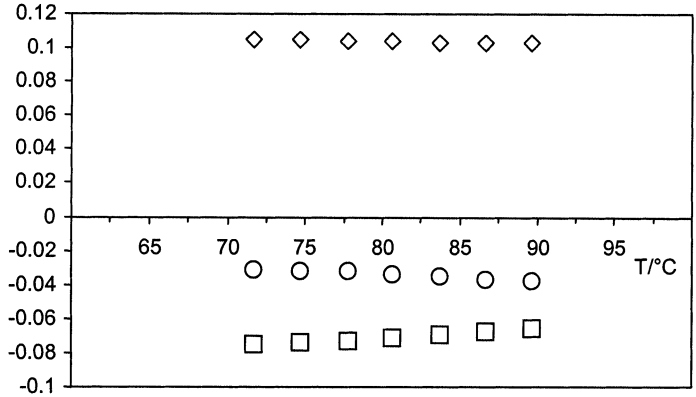

FIGURE 6 Plot of the order parameters of the pyridinium ring for the thermotropic LC phase vs. T: ◇ S_{xx}, □ S_{yy}, ○ S_{zz}.

than those observed for the lyotropic phase. But somewhat surprisingly, the splitting decreased with decreasing temperature (Fig. 7).

The values for $|\Delta\nu(^{14}N)|$ were reproduced successfully using both sets of quadrupolar parameters obtained from the lyotropic phase and the order parameters from the ^{2}H NMR study, confirming the ^{14}N quadrupole values (Fig. 7).

DISCUSSION

The quadrupole coupling constant, C_Q, obtained for the ^{14}N nucleus of the pyridinium moiety is small compared to the one of free pyridine [24], as

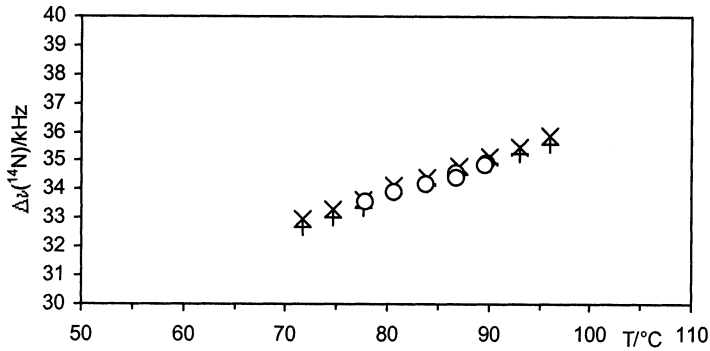

FIGURE 7 Plot of $\Delta\nu(^{14}N)$ values for the thermotropic LC phase vs. T: ○ experimental values, + calculated values from $|C_{QN}| = 0.405$ MHz and $\eta_N = 0.39$, × calculated values from $|C_{QN}| = 0.413$ MHz and $\eta_N = 0.39$.

expected because of the engagement of the nitrogen lone pair in chemical bonding and in line with that of pyridine N-oxide [25].

For CPB the ^{14}N quadrupole parameters, C_Q and η, are necessary for the interpretation of the nitrogen quadrupolar splittings used to provide information about the LC phases.

The ^{14}N quadrupolar splitting has been widely employed to study lyotropic LC of cetyltrimethylammonium derivatives [8,16–18]. In the latter case the principal axis points along the N-C(1)$_{alkyl}$ direction. The order parameter of this direction with respect to the magnetic field is the most immediate as far as the order of the surfactant head group is concerned, even if it is not a direct measure of the alignment of the aggregates.

Various processes determine the observed order parameters, namely the alignment of the director perpendicular to the magnetic field (negative diamagnetic anisotropy), the lamellae fluctuations about the director of the mesophase, the motion of the N-C(1)$_{alkyl}$ axis and the segmental motion of the chain; probably in these quite extended bilayers the edge diffusion contributes to a minor extent [26].

In CPB the N-C(1)$_{alkyl}$ direction corresponds to the C_2 axis of the aromatic ring, that is to the y axis shown in Figure 3. Therefore, in this case, the most important quadrupolar splitting is the one of $^{2}H(4)$, because it best reflects the S_{yy} order parameter of the ring. On the other hand, the ^{14}N quadrupole splittings, $\Delta\nu(^{14}N)$, owing to the EFG PAS orientation, reflect the S_{zz} ring order parameter, which, in contrast to S_{yy}, is affected also by librations and rotations of the aromatic moiety about the C_2 axis. Thus the ^{14}N nucleus appears to give a less immediate description of the order than $^{2}H(4)$.

Luckily, in the lyotropic system the three order parameters exhibit a similar temperature dependence, so that $|\Delta\nu(^{14}N)|$, reflecting S_{zz}, is a

qualitative indicator of the temperature dependence of the overall order of the surfactant head group. However, to obtain the values of the order parameters of the head group, ^{2}H data from the isotopically enriched molecules must be employed.

The order parameters determined for the pyridinium head group in the swollen lamellar phase, especially in the range from 5 to 10°C, are very similar to the values reported for the discotic phase consisting of 5.08% hexadecylpyridinium chloride, 26.61% hexadecylammonium bromide, 6.44% decanol and 61.86% NaCl brine [11]. S_{xx} values much larger than S_{yy} and S_{zz} values appear to be a common trend in such systems, probably connected with the packing of the surfactant (and co-surfactant) molecules. Such behaviour is also observed when the pyridinium cation enters the surfactant aggregates as a guest [13].

It is interesting to compare the order parameters of the pyridinium ring in the two extreme situations: the swollen lamellar phase, in which the surfactant concentration is low and the molecules are in contact mainly with pentanol and water, and the thermotropic LC, in which only the surfactant is present. Possibly, the latter phase is a smectic A phase, consisting of layers of molecules in which the aliphatic chains are interdigitated, in analogy with the solid state structure [27] and with the structure of the thermotropic phase of cetylpyridinium hexafluorophosphate [23]. In the thermotropic phase the values of the three order parameters are higher than those in the lyotropic phase, but still the order $|S_{xx}| > |S_{yy}| > |S_{zz}|$ holds. The most characteristic feature is the different temperature dependence: $|S_{xx}|$ changes very little, $|S_{yy}|$ increases and $|S_{zz}|$ decreases with temperature. This behaviour reflects different motional degrees of freedom.

CONCLUSIONS

For the system CPB, pentanol, NaBr brine, the ^{14}N NMR spectra show large residual quadrupolar splittings and are very effective in indicating the presence of anisotropic phases, as found for the analogous CTAB system [18]. In the former system, however, the EFG at the nitrogen nucleus is not axially symmetric and the z axis of its PAS is not along the $N\text{-}C(1)_{alkyl}$ direction. It follows that the order parameters of the EFG PAS cannot be calculated using only ^{14}N NMR spectra.

Order parameters for the aromatic ring can satisfactorily be obtained, after deuteration, from the deuterium splittings, $\Delta\nu(^2\text{H})$. Once this has been accomplished, the ^{14}N quadrupole splittings can advantageously be used to evaluate the principal values of the ^{14}N quadrupole coupling tensor.

Pure CPB forms also a thermotropic LC above its melting point. The order parameters calculated from the ^{2}H splittings of this phase are larger

than those of the lyotropic phase. From these order parameters and the above C_{QN} and η_N values one can calculate ^{14}N quadrupolar splittings, that are in very good agreement with those measured for this phase.

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