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A Multinuclear NMR Approach to the Study of the Lyotropic System CTAB-D_2O

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CTAB-D_2O liquid crystalline phase (CTAB = cetyltrimethylammonium bromide), type I according to magnetic anisotropy, has been investigated by means of ^2H, ^{14}N and ^{17}O NMR at variable temperature. The residual quadrupolar splittings of all these nuclei evidenced the alignment of the phase in the magnetic field. The interpretation of the data of D_2O quadrupolar nuclei, commonly used in the study of lyotropic liquid crystalline phases, is complicated because of water reorientation, exchange processes and variations of the hydration degree. The ^{14}N quadrupolar splittings are much more reliable indicators of the orientation of surfactant aggregates since their interpretation in terms of the order parameter is straightforward in this case because the nitrogen nucleus is subject to an electric field gradient of axial symmetry and resides just in the head of the amphiphile.

Key words: liquid crystals, NMR spectroscopy, quadrupolar nuclei, surfactants.

INTRODUCTION

Binary systems formed by ionic surfactants and water at temperatures higher than the Krafft point produce a wealth of phases,[1] the most representative ones being: the micellar solution, the hexagonal phase, the cubic phase, the lamellar phase. They are differentiated by the type of packing of amphiphile molecules; for instance, the hexagonal phase is made up of ex-

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tremely long cylindrical micelles arranged in a hexagonal lattice while the lamellar phase is the stacking of surfactant bilayers and aqueous layers. Both these phases exhibit liquid crystalline behavior and, since the latter is mainly connected to the surfactant/solvent ratio, they are termed lyotropic, to distinguish them from the thermotropic liquid crystals, whose properties are generally controlled by the molecular structure.

Lyotropic liquid crystals have been extensively investigated by low angle X-ray diffraction,[1,2] optical microscopy, NMR, light scattering.[2]

The basic units that must be considered in a lyotropic liquid crystal are molecular aggregates. The relevant property of aggregates for NMR investigation is their magnetic anisotropy which allows their alignment in a magnetic field. If it is positive, the principal axis of the aggregate tends to stand parallel to the magnetic field and the phase is known as type I, while if it is negative, the principal axis of the aggregates tends to lie perpendicular to the magnetic field and the phase is known as type II.[1]

As a result of the preferred molecular orientation, quadrupolar splittings may be detected in the NMR spectra of quadrupolar nuclei. In fact, they are the most informative parameters in the NMR spectra of quadrupolar nuclei.

A nucleus with a spin quantum number $I \geq 1$ possesses a nuclear quadrupole moment, which couples with the electric field gradient present at the nuclear site. Thus, the quadrupole interaction must be added to the Zeeman one and, usually, it can be considered as the first order perturbation.[3] In this case, the resonance of a quadrupolar nucleus in a molecule with a fixed orientation with respect to the magnetic field splits into $2I$ lines with the separation given by the following expression for an electric field gradient (EFG) with axial symmetry:

$$\Delta\nu = \frac{3C_Q}{2I(2I-1)}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

where θ is the angle between the Z axis of the EFG principal axes system (PAS) and the magnetic field, while C_Q is the quadrupole coupling constant:

$$C_Q = \frac{eQV_{zz}}{h}$$

where e is the absolute value of the electron charge, Q is the nuclear quadrupole moment, V_{ZZ} is the value of the largest component of the EFG tensor in its PAS and h is the Planck constant.

In a liquid phase, θ changes very fast because of molecular motion. In an ordinary isotropic solution, the completely random motion succeeds in averaging out the effects of the quadrupolar interaction, while in an oriented liquid crystalline phase the molecular motion, though still fast, is anisotropic, which results in a residual quadrupole splitting. Its magnitude is given by the former equation, provided the second Legendre polynomial is averaged.[4] This time average is equivalent to the ensemble average and is better known as the order parameter (S),[5] since it provides information on the orientational distribution of the Z axis of the EFG PAS with respect to the magnetic field. S lies in the range $-0.5 < S < 1$.

$$\left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle = S$$

Since 1967, when the alignment of a lyotropic liquid crystalline mesophase in a magnetic field was revealed for the first time,[6] a very important investigation tool of lyotropic mesophases has been the quadrupolar splitting of the water deuterium ($\Delta\nu(^2H)$).[7,8] Unfortunately, its interpretation is far from straightforward, since it is a result of multiple averaging processes, which take place on different time scales.[9] The first process is the exchange between bound and free water:

$$\Delta\nu = p_b \Delta\nu_b + p_f \Delta\nu_f$$

where p_b and p_f are the fractional populations of bound and free water, respectively. The splitting of free water is averaged out by the isotropic reorientation, therefore $\Delta\nu_f = 0$. [10]

The $\Delta\nu_b$ is averaged over various sites, in which it may have different magnitudes and signs:

$$\Delta\nu_b = \sum_i p_{bi}\, \Delta\nu_{bi}$$

Furthermore, the splitting at each i site is a result of the averaging due to the reorientation of the water molecule at that site.

In order to gain a deeper understanding of the orientational distribution of water molecules on the surface and of their reorientation dynamics, the quadrupolar splitting of ^{17}O ($\Delta\nu(^{17}O)$) has been taken into consideration,[11,12] as well, but it appears to be conclusive just in a few peculiar cases.[10]

Therefore, we decided to investigate to which extent the quadrupolar nitrogen nucleus present right in the head of the amphiphile can be useful in the NMR study of these systems. The most abundant isotope of nitrogen, ^{14}N, (natural abundance 99.63%) has a spin quantum number $I = 1$ and a quadrupole moment $Q = 1.6 \times 10^{-30}$ m^2.[13] We used the cationic surfactant CTAB (cetyltrimethylammonium bromide, where cetyl stands for hexadecyl), for which the binary phase diagram with water is well known.[14] The concentration employed corresponds to a hexagonal liquid crystalline phase.[15] Thus, for this system, we studied the NMR spectra of ^{14}N besides those of ^{2}H and ^{17}O of water.

EXPERIMENTAL

The samples of CTAB in D_2O at a molality of 1.3 mol kg^{-1} were prepared directly in the NMR tubes, 10 mm for the ^{14}N measurements and 5 mm for the ^{2}H and ^{17}O ones, by mixing at elevated temperatures. Samples were then kept in a thermostat at 25 °C for equilibration for at least one week. The presence of the liquid crystalline phase was confirmed by the observation of birefringence by means of a Leitz Wetzlar RME 5 microscope with crossed Nicols. In order to measure NMR spectra from anisotropic phases aligned in the magnetic field, the sample, after being placed into the magnet, was heated to 368 K, where an isotropic phase is stable, and then slowly cooled down.

^{2}H, ^{14}N and ^{17}O spectra were recorded on a JEOL EX-400 spectrometer operating at 9.4 T (^{2}H at 61.369 MHz, ^{14}N at 28.889 MHz, ^{17}O at 54.196 MHz).

All spectra were acquired under the proton broad band decoupling with digital resolutions of 0.49 Hz/pt for ^{2}H, 4.88 Hz/pt for ^{14}N and 3.91 Hz/pt for ^{17}O, respectively.

RESULTS AND DISCUSSION

In the NMR studies of lyotropic liquid crystalline phases,[7,8] a common procedure, related to the very slow kinetics of orientation,[15] is to heat the sample and to leave it to cool down slowly.

Thus, at 368 K, the ^{2}H spectrum gave a singlet, confirming the presence of just the isotropic phase. At 363 K, a doublet began to appear on the sides of the parent signal. At 353 K, the singlet had almost completely disappeared in favor of the doublet. The latter reflects the incomplete averaging of the ^{2}H ($I = 1$) quadrupole splitting and is diagnostic of the presence of one liquid crystalline phase aligned in the magnetic field. The temperature dependence of the quadrupole splitting (Figure 1) is almost linear, indicating that no further phase transition is taking place, at least till 303 K. The positive slope of $\Delta\nu(^{2}H)$ against temperature is noteworthy although one might expect a negative one since the quadrupole splittings reflect the degree of order. However, this somewhat surprising behavior is not unusual for lyotropic phases[4] and it is attributed to strong variations in the degree of hydration and to changes of the populations p_{bi} at the various sites.

In ^{17}O NMR spectra of heavy water at 368 K, as in spectra of ^{2}H, we found just a singlet, then on cooling, corresponding to the onset of the liquid crystalline phase, four further signals appeared, two on each side of the

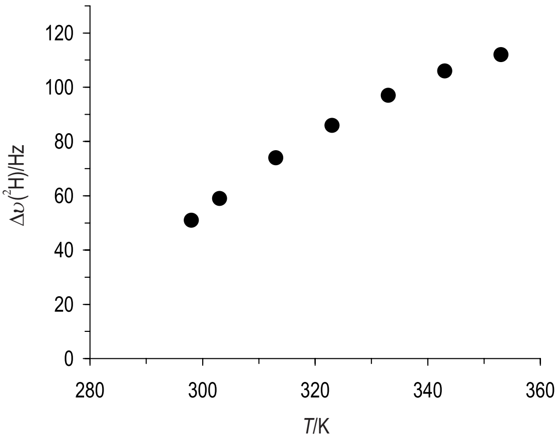

Figure 1. ^{2}H quadrupolar splitting *vs.* temperature.

original one. Since spin quantum number of ^{17}O is 5/2, in an oriented anisotropic phase there is a quintet due to the residual quadrupolar splitting. Integrated intensities of the single lines of the multiplet are proportional to $I(I+1) - m(m+1)$, *i.e.* in the oxygen case their ratios are 5:8:9:8:5. The outer lines are broader (Figure 2) owing to the differences in relaxation rates.[11] Because of the rather high C_Q value, the quadrupolar relaxation mechanism is quite efficient and the signals broadened substantially on cooling and coalesced already near room temperature.

The magnitudes of $\Delta\nu(^{17}O)$ and $\Delta\nu(^2H)$ at 303 K, amounting to 360 Hz and 60 Hz, respectively, reflect the higher C_Q of ^{17}O and the differences in order parameters for the two nuclei. Since the values of C_Q for ^{17}O and ^{2}H in

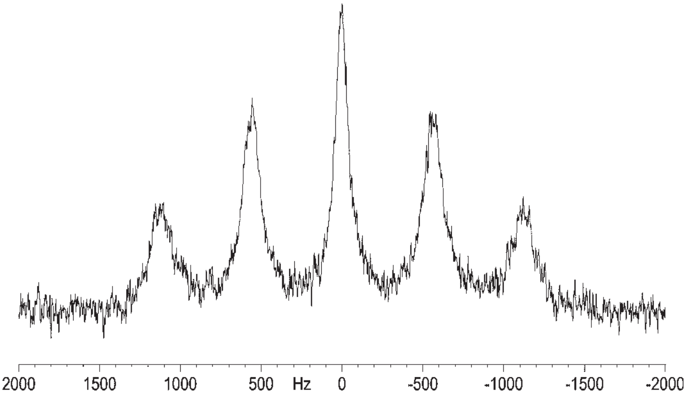

Figure 2. ^{17}O NMR spectrum at 323 K.

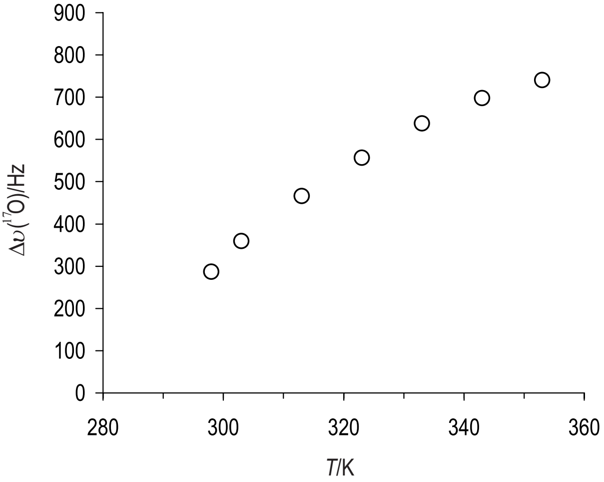

Figure 3. ^{17}O quadrupolar splitting *vs.* temperature.

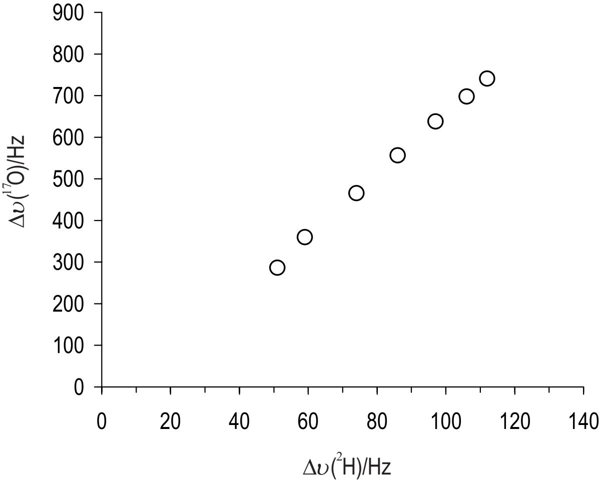

Figure 4. ^{17}O *vs.* ^2H quadrupolar splittings at various temperatures.

D_2O are known with quite enough confidence, 6.65 MHz and 0.222 MHz,[11] and the orientation of the two EFG principal axes systems is constrained by the molecular geometry; in principle, it should be possible to obtain additional information from the comparison of the two values. Unfortunately, the ratio $\Delta\nu(^{17}O)/\Delta\nu(^2H)$ is 6, which is the value compatible with too many reorientation mechanisms.[14] Moreover, the temperature dependence of $\Delta\nu(^{17}O)$ (Figure 3) is of the kind already found for $\Delta\nu(^2H)$ and their ratio is conserved at all the temperatures examined (Figure 4).

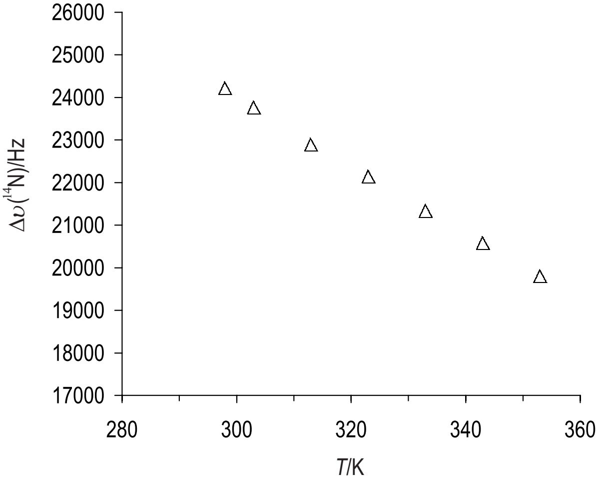

Figure 5. ^{14}N quadrupolar splitting *vs.* temperature.

At a high temperature only a singlet was observed in the ^{14}N spectrum, while a doublet appeared upon decreasing the temperature. The splitting (23770 Hz at 303 K) is by far larger than those in water nuclei, notwithstanding the weakness of EFG at nitrogen in ammonium ions,[16] indicating a large order parameter for the surfactant molecules. $\Delta\nu(^{14}N)$ increases with decreasing the temperature (Figure 5) and therefore it seems to be a more reliable indicator of the degree of alignment of the lyotropic liquid crystal than the water $\Delta\nu(^{2}H)$ and $\Delta\nu(^{17}O)$.

The order parameters listed in the Table I were obtained from the experimental data, using the above equations, using the C_Q value of 111.3 kHz reported in literature for CTAB.[17] One must be aware that they are products

TABLE I

Quadrupolar splittings and $|S|$ values from $\Delta\nu(^{14}N)$ at various temperatures

T/K	$\Delta\nu(^{2}H)$/Hz	$\Delta\nu(^{17}O)$/Hz	$\Delta\nu(^{14}N)$/Hz	$\lvert S\rvert$
353	112	741	19810	0.12
343	106	698	20590	0.12
333	97	638	21340	0.13
323	86	557	22150	0.13
313	74	466	22900	0.14
303	59	360	23770	0.14
298	51	287	24220	0.15

of a few factors, the main ones being: the order parameter associated with the orientation of the long axis of the micelle and the order parameter associated with the reorientation of the Z axis of the nitrogen EFG PAS about the radius of the micelle cylinder.[18] In the present case, we consider the EFG to be axially symmetric and with the Z axis coincident with the nitrogen-cetylic carbon direction. Thus, the order parameters contain information both on the orientation of the aggregates with respect to the magnetic field and on the surfactant molecules with respect to the aggregate.

CONCLUSIONS

It may be concluded that, since the ^{14}N NMR spectrum is directly connected to the orientation of the aggregates, ^{14}N, much more than either ^{2}H or ^{17}O of water, is a reliable tool to study the properties of lyotropic mesophases based on cationic surfactants. Futhermore, it is likely that the increase of the order parameter on decreasing the temperature, detected through ^{14}N NMR, is mainly due to an increase of the alignment of the micellar axes with the magnetic field, in analogy with other lyotropic systems.[18] Such a trend is in agreement with the Boltzmann distribution for the magnetic orientational energy of the micelles.

In so far as $\Delta\nu(^{14}\mathrm{N})$ is such a good indicator of the degree of alignment of the micelles in the magnetic field, it also looks promising in furnishing information about the size of the aggregates.

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SAŽETAK

Multinuklearni NMR pristup u proučavanju liotropnog sustava CTAB-D_2O

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Tekući kristal CTAB-D_2O (CTAB = cetiltrimetilamonijev bromid) istražen je primjenom tehnika ^2H, ^{14}N i ^{17}O NMR pri varijabilnoj temperaturi. Kvadrupolno cijepanje uzrokovano tim jezgrama upućuje na preferirane molekularne orijentacije u vanjskom magnetnom polju. Međutim, interpretacija podataka vezanih uz kvadrupolne jezgre D_2O otežana je zbog reorijentacije vode, procesa izmjene te zbog promjena u hidrataciji. Cijepanje uzrokovano kvadrupolnim jezgrama ^{14}N pokazalo se mnogo korisnijim u tom pogledu.