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Quadrupole Splittings in Deuterium NMR-Spectra of the Hexagonal Phase in the System Sodium Octanoate-d_{15}-Water-Carbontetrachloride†

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The hexagonal phase of the system $C_7D_{15}COONa$-H_2O-CCl_4 has been studied by deuterium magnetic resonance. Order parameters for the different CD_2-groups have been determined from the observed deuterium splittings in powder spectra. The order parameters range from 0.02 to 0.13. The order parameters decrease when CCl_4 is solubilized, implying an increased motional freedom of the alkyl chain. For some samples a central, unsplit peak is observed originating from isotropic metastable aggregates.

INTRODUCTION

The deuterium nucleus has a spin quantum number $I = 1$ and consequently an electric quadrupole moment. The quadrupole moment of the deuteron interacts with the electric field gradient at the place of the nucleus. In a magnetic field the interaction perturbs the Zeeman energy levels of the deuteron and gives rise to splittings in the deuterium NMR spectra of solids. For the case with a cylindrically symmetric electric field gradient (which is the case for a C—D single bond) two resonance lines with the separation Δ is obtained.[1] Δ (in Hz) is given by:

$$\Delta = \frac{3}{4}\frac{e^2Qq}{h}(3\cos^2\theta - 1) \tag{1}$$

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† Paper presented at the Fifth International Liquid Crystal Conference, Stockholm 1974.

where e^2Qq/h is the quadrupole coupling constant and θ is the angle between the magnetic field and the symmetry axis of the electric field gradient (in our case the direction of the C—D bond).

If molecular motions that are fast compared to the inverse of the quadrupole coupling constant are present the angle dependent factor in equation (1) should be replaced by its time average. For the case of liquid crystals the splitting is given by[2]

$$\Delta = \frac{3}{4}\frac{e^2qQ}{h}|S| \cdot |(3\cos^2\phi - 1)| \tag{2}$$

where ϕ is the angle between the magnetic field and the director and S is the order parameter defined as[3,4] $S = (\overline{\tfrac{3}{2}\cos^2\xi - \tfrac{1}{2}})$, where ξ is the angle between the C—D bond and the director.

In a powder sample where all values of cos ϕ are equally probable, the observed NMR-spectrum consists of a broad distribution of frequencies with two marked peaks with the separation Δ_{powder} given by:[2]

$$\Delta_{\text{powder}} = \frac{3}{4}\frac{e^2Qq}{h} \cdot |S| \tag{3}$$

The order parameter S characterizes the molecular alignment with respect to the director.[5] For an ordered rigid system where the molecular orientation does not change very much with time, S can have values from 1 (parallel alignment) to $-\frac{1}{2}$ (perpendicular alignment).[5] For the case of a liquid crystal with anisotropic molecular motions, the magnitude of S will also depend on the degree of anisotropy of the motions.[2]

In liquids where the motions of the molecules are isotropic, all directions of the C—D bond with respect to the magnetic field are equally probable which implies that $(\overline{3\cos^2\theta - 1}) = 0$ and the splitting is reduced to zero and a single line is observed.

RESULTS AND DISCUSSION

We have studied the deuterium NMR-spectra of the perdeuterated alkyl chain in the hexagonal phase of the system $C_7D_{15}COONa—H_2O—CCl_4$ at 27°C. The phase diagram of this system is shown in Figure 1.[6] The hexagonal phase (marked E in Figure 1) consists of long cylindrical rods arranged in a hexagonal lattice.[6]

The deuterium NMR-spectra were recorded using a pulsed NMR spectrometer Bruker B-KR 322s operating at 13.83 MHz equipped with a Bruker computer BNC 12. The absorption spectra were obtained as the Fourier transforms of the registered free precession signals. The spectrum of a binary

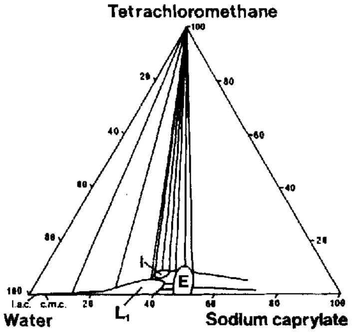

FIGURE 1 The phase diagram of the system $C_7H_{15}COONa$-H_2O-CCl_4 at 20°C from reference 6. The composition is given in weight-%.

mixture of $C_7D_{15}COONa$ and H_2O with the mole ratio 1:9.65 is shown in Figure 2. This spectrum is a powder spectrum and it shows six resolved doublets. The spectrum clearly shows that there are different order parameters along the alkyl chain. This has also been found for alkyl chains in some nematic liquid crystals.[7] The doublet with the smallest separation has a higher intensity and is assigned to the CD_3-group. The doublet with the second biggest splitting is most likely due to over-lapping signals from two CD_2-groups. From the spectrum of a perdeuterated molecule it is not possible to assign the spectrum unambigously. However, if it is assumed that the order parameter in the alkyl chain decreases from the polar group to the methyl group we can attribute each doublet to a specific CD_2-group and calculate the absolute values of the order parameter for the C—D bonds in the different methylene groups in the chain from eq. (3). The value used for

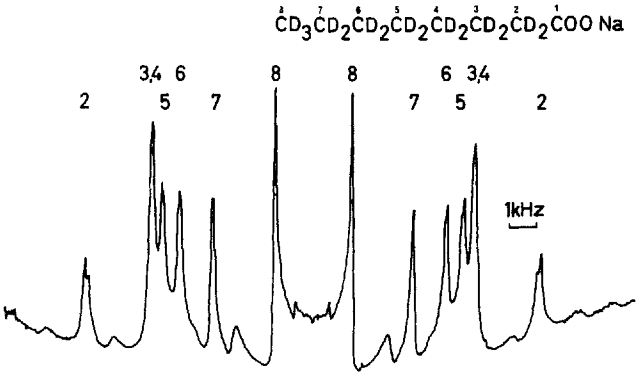

FIGURE 2 Deuterium magnetic resonance spectrum of an unoriented sample of a binary mixture of $C_7D_{15}COONa$ and H_2O. Mole ratio 1:9.65.

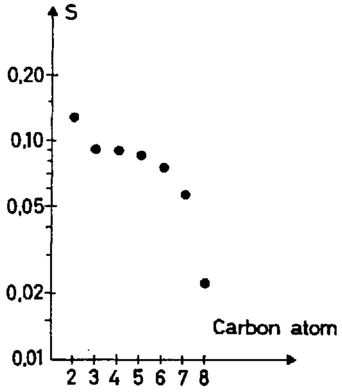

FIGURE 3 The absolute value of the order parameter S for different C—D bonds for a binary mixture of $C_7D_{15}COONa$ and H_2O. Mole ratio 1:9.65.

e^2Qq/h is 167 kHz as obtained from deuterium magnetic resonance spectra of solid hexane.[8] The results are shown in Figure 3 and in Table I. The shape of the curve in Figure 3 is similar to that obtained for the lamellar phase of the potassium laurate-water system by Charvolin *et al.*[9] The absolute values of the order parameters are about a factor 2 larger for the lamellar phase. If, however, the molecules diffuse rapidly along the surfaces of the cylinders in the hexagonal phase, this motion gives rise to an additional averaging of the static quadrupole interaction. In the lamellar phase, diffusion along the lamellae gives no averaging effect. By geometrical considerations it can be shown that rapid diffusion over a cylindric surface reduces the order parameter by a factor 2.[2,10] If the observed factor 2 is due to diffusion it is possible to give an upper limit for the correlation time for the translational motion

$$\tau_c \lesssim 5 \cdot 10^{-5}\ s.$$

TABLE I

The absolute value of the order parameter S for different mole ratios $C_7D_{15}COONa:H_2O:CCl_4$ of the hexagonal phase

Carbon atom number	Mole ratio			
	1:9.65:0	1:9.08:0	1:8.75:0	1:9.65:0.14
2	0.130	0.131	0.134	0.121
3,4	0.0918	0.0928	0.0960	0.0880
5	0.0861	0.0864	0.0906	0.0813
6	0.0762	0.0765	0.0806	0.0717
7	0.0570	0.0571	0.0608	0.0531
8	0.0221	0.0221	0.0237	0.0202

If τ_c is considered to be the time it takes for a molecule to move the distance πr, where r is the cylinder radius, a lower limit for the diffusion constant can be calculated, $D \gtrsim 10^{-8}$ cm^2/s. *cf.*[10,11]

Similarly as for the lamellar phase of the potassium laurate-water system[9] it is seen that the order parameters are practically constant for the three methylene groups nearest the α-CD_2. This indicates similar motions for these methylene groups, which might be due to strong coupling between these parts of the alkyl chains. The order parameter for the end CD_3-group is slightly more than $\frac{1}{3}$ of the value for the preceeding CD_2-group. This reduction factor is probably due to the almost free rotation of the C—D bonds in the methyl group about the last C—C bond in the alkyl chain.[12]

Recently deuterium splittings have also been studied in some lamellar phases containing solubilized alcohols.[13] The results are in line with those presented here and those of Charvolin *et al.*[9] Order parameters for alkyl chains in lipid bilayers have been calculated theoretically by Marčelja using the molecular field approximation.[14] The agreement with the experimental results appears satisfactory.

Order parameters in similar systems have also been measured by ESR using spin labels.[15,16] The ESR-measurements indicate, in contrast to the results from deuterium splittings, an exponential decrease of the order parameter along the alkyl chain. The difference might be attributed to the perturbing effect of the spin label.[9]

Our samples were equilibrated for about 24 *h* at the highest possible temperature where the hexagonal phase exists and were then allowed to slowly cool down to room temperature. Some samples were heated to such a high temperature that an isotropic micellar solution was obtained and were then cooled down rather slowly but without equilibrating the hexagonal phase at a high temperature. Spectra of these latter samples showed a sharp peak at the Larmor frequency. An example of such a spectrum is shown in Figure 4. The peak must originate from molecules in the sample that move isotropically. The most probable explanation is that in these samples micellar aggregates are present in metastable equilibrium with the hexagonal phase.

As can be seen from Table I the order parameters for the C—D bonds in the different methylene groups do not change very much with the mole ratio sodium octanoate:water. For the sample with the mole ratio 1:8.75 we have not succeeded, in spite of careful thermal treatment, to get rid of the isotropic part of the sample. This might imply that the composition of the hexagonal phase present is not exactly the same as the mean composition of the sample.

The order parameters for a sample where carbon tetrachloride has been solubilized in the hexagonal phase (see Figure 1) is also given in Table I. Also for this sample it was not possible to get rid of the isotropic parts of the

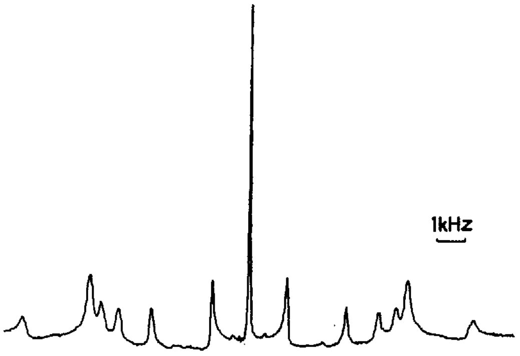

FIGURE 4 Deuterium magnetic resonance spectrum of an unoriented sample of a binary mixture of $C_7D_{15}COONa$ and H_2O. Mole ratio 1 : 9.65. This spectrum shows a central isotropic peak (see text).

sample. It can be seen that the order parameters are significantly smaller for all the methylene groups implying an increased motional freedom of the alkyl chain when CCl_4 is solubilized in the hexagonal phase.

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