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### LETTERS

## Nuclear Magnetic Resonance Investigation of a Sodium Dibutyl Phosphate/Water Lyotropic Mesophase

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<sup>2</sup>H and <sup>31</sup>P NMR have shown that concentrated aqueous solutions of sodium dibutyl phosphate (NaDBP) give rise to a lamellar mesophase for NaDBP mole fractions varying from 0.1 to 0.2 in a temperature range T =285-340 K. By cooling the samples from the isotropic phase in a magnetic field the formation of a discotic DM II mesophase is observed. Different models of water reorientation are proposed to account for the <sup>2</sup>H and <sup>17</sup>O quadrupole splittings. Nuclear relaxation experiments show that, in this particular system, water molecules reorient preferentially about the direction of an oxygen lone pair orbital.

#### Introduction

A magnetic resonance study on micellar aqueous solutions of sodium dibutyl phosphate (NaDBP) has revealed the formation of a lyotropic mesophase at high substrate concentration.<sup>1</sup> This unexpected behavior from such a short-chain aliphatic molecule prompted us to perform further investigations on the orientation and dynamical behavior of NaDBP in the liquid crsytalline state, by means of NMR and ESR techniques. We report here the main features of the <sup>31</sup>P, <sup>2</sup>H, and <sup>17</sup>O NMR works on this system which are in progress in our laboratory. These nuclei are indeed sensitive probes for delineating the phase diagram together with polarizing microscope observations and X-ray diffraction and they provide useful information on the orientational order at the molecular scale.

#### **Experimental Section**

The dibutyl ester of phosphoric acid (HDBP) from OSI (France) was purified as previously reported.<sup>1</sup> The sodium salt was prepared by addition of concentrated NaOH solution to HDBP, the water being removed by distillation of its benzene azeotrope followed by extensive drying under vacuum. The liquid crystalline samples were directly prepared in 10-mm o.d. NMR tubes by warming for several hours the NaDBP- $^{2}$ H<sub>2</sub>O heterogeneous mixtures at 70 °C, the NaDBP mole fraction varying from  $X_{\rm M} = 0.106$  to  $X_{\rm M}$ = 0.214. Most of the <sup>2</sup>H and <sup>31</sup>P experiments were performed on a Bruker WH 90 spectrometer operating in the gated <sup>1</sup>H decoupling mode. The <sup>17</sup>O water NMR spectra were recorded at 67.77 MHz on 10% enriched samples by means of a Bruker WM 500 spectrometer, the baseline distortion being reduced by use of a quadrupolar echo sequence and by taking numerically the first derivative of absorption signals.

#### **Results and Discussion**

Phase Diagram. The <sup>31</sup>P and water <sup>2</sup>H NMR spectra were recorded in the temperature range 275–350 K. Some typical spectra are shown in Figure 1. At room temperature before warming, the spectra of both nuclei show the powder pattern typical of cylindrically symmetric magnetic tensors with <sup>2</sup>H quadrupolar splitting and <sup>31</sup>P chemical shift anisotropy  $|\Delta \nu_q| = 1800$  Hz and  $\Delta \sigma = 18$  ppm, respectively. When the temperature is progressively raised

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Figure 1. <sup>17</sup>O, <sup>2</sup>H, and <sup>31</sup>P experimental and calculated NMR spectra of NaDBP/<sup>2</sup>H<sub>2</sub>O iamellar mesophase ( $X_{\rm M} = 0.165$ , T = 300 K) before (I) and after warming (II) at 340 K and cooling in a magnetic field of 21.15 kG (for  $^{2}$ H and  $^{31}$ P) and 117.47 kG (for  $^{17}$ O). Spectra I correspond to a random orientation of the magnetic tensors while spectra II are indicative of an average orientation of the cylindrical symmetry axis of these tensors perpendicular to the magnetic field with a narrow angular distribution (15-20°). The <sup>17</sup>O spectra are recorded as the first derivative of the absorption to minimize baseline distortions.



Figure 2. Temperature dependence of water <sup>17</sup>O and <sup>2</sup>H quadrupole splittings and <sup>31</sup>P chemical shift anisotropy for a NaDBP/<sup>2</sup>H<sub>2</sub>O sample with  $X_{M} = 0.165$ : (•) increasing temperatures; (O) decreasing temperatures. The lowest lines correspond to the isotropic components of the <sup>2</sup>H and <sup>31</sup>P spectra.

to ca. 320 K, both  $\Delta v_{\alpha}$  and  $\Delta \sigma$  steadily increase as a result of an apparent molecular order enhancement (Figure 2). The <sup>17</sup>O quadrupole splitting behaves similarly.

The isotropic phase labeled II in Figure 3 appears at temperatures varying from 300 to 340 K according to the concentration, the transition domain labeled I + II corresponding to a mixture of liquid crystalline and isotropic phases (Figure 3). The <sup>31</sup>P line shape  $(\sigma_{\parallel} - \sigma_{\perp} \sim -18 \text{ ppm})$ suggests that we are dealing with a lamellar  $L_{\alpha}$  mesophase (see, for instance, ref 2), as confirmed by X-ray diffraction, which corresponds to hydrocarbon bilayers separated by polar domains of thicknesses  $9 \pm 1$  and  $8.5 \pm 0.5$  Å, respectively.

By cooling the samples from the isotropic phase, the <sup>2</sup>H and <sup>31</sup>P NMR spectra become typical of an alignment of the averaged quadrupolar and chemical shift tensors perpendicular to the magnetic field, with a narrow angular distribution about the direction of the magnetic field (Figure 1). The width of the angular distribution as well as  $\Delta \nu$ <sup>(2</sup>H) and  $\Delta \sigma$ <sup>(31</sup>P) are concentration dependent, the optimum alignment occurring for  $X_{\rm M} = 0.15$ . It should be pointed out that the orientations of samples with 0.15  $\leq X_{\rm M} \leq 0.17$  may be kept a few hours after removing the samples from the magnetic field.

This orientation effect seems to be characteristic of a discotic lyomesophase of DM II type<sup>3</sup> formed by aggre-



Figure 3. Dependence of <sup>2</sup>H quadrupole splitting and <sup>31</sup>P chemical shift anisotropy with samples composition (T = 295 K). Partial phase diagram drawn from the <sup>2</sup>H and <sup>31</sup>P NMR spectra evolution: I, lamellar mesophase; II, isotropic phase; III, heterogeneous phase (coagel).

gation in the magnetic field of large disklike micelles, the plane of which is on the average oriented parallel to the field.

When the sample is cooled from 295 K, the deuteron splitting as well as the <sup>31</sup>P chemical shift decreases rapidly. In a narrow temperature range about 280 K, an isotropic line is superimposed on both  ${}^{\bar{2}}H$  and  ${}^{31}P$  spectra and likely corresponds to the formation of NaDBP crystals separated by bulk water (coagel labeled as phase III). A careful investigation of samples with NaDBP mole fractions  $X_{M}$  $\sim$  0.15–0.17 shows that the <sup>2</sup>H quadrupole splitting increases sharply about 282-284 K. This behavior is typical of a liquid crystal  $\Rightarrow$  coagel phase transition, the change in the <sup>2</sup>H splitting being independent of the macroscopic orientation of the sample. No such variation of the anisotropy is found in the <sup>31</sup>P spectra.

On varying the NaDBP concentration we did not observe the formation of another mesophase, e.g., a hexagonal phase which should be characterized by a smaller <sup>31</sup>P chemical shift anisotropy of opposite sign.<sup>2</sup> Another striking feature which is not understood up to now is the increase of the <sup>2</sup>H quadrupole splitting when the  ${}^{2}H_{2}O/$ NaDBP molar ratio is varied from 4 to 8 (Figure 3), in contrast with most of the lyotropic systems. A similar behavior has, however, been reported for the potassium  $laurate/{}^{2}H_{2}O$  lamellar phase.<sup>4</sup>

Reorientation of Water Molecules. Several recent works deal with the deuteron and oxygen-17 quadrupole splittings in lyotropic mesophases.<sup>5-8</sup> A striking feature of these studies is that in all cases the  $|\Delta\nu(^{17}O)/\Delta\nu(^{2}H)|$  ratio of the splittings is close to 6. Table I shows that the same ratio is also observed in the system under study. In order to account for this value, we have considered several models of anisotropic motion of water molecules, labeled I through IV in Table I. Model I corresponds to a reorientation about the axis of a lobe of the oxygen lone pair orbital which coincides likely with the hydrogen bonding direction in water<sup>9</sup> or with the



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TABLE I: Calculated Values of Water <sup>17</sup>O and <sup>2</sup>H Quadrupolar Splittings According to Different Motional Models<sup>a</sup>

	hydration of Na <sup>+</sup> ions	hydration of phosphate groups				
		ІІ о ²н)²н.			IV Zo <sup>2</sup> H O <sup>2</sup> H	
$\frac{\Delta \nu_{q}({}^{17}\text{O}), {}^{b}\text{Hz}}{\Delta \nu_{q}({}^{2}\text{H}), {}^{b}\text{Hz}}{\Delta \nu_{q}({}^{17}\text{O})/\Delta \nu_{q}({}^{2}\text{H})}$	$-3.81 \times 10^{5}$ $6.50 \times 10^{4}$ -5.86	$\begin{array}{c} 4.83 \times 10^{5} \\ -7.34 \times 10^{4} \\ -6.58 \end{array}$	$\begin{array}{c} 3.08 \times 10^{5} \\ -5.17 \times 10^{4} \\ -5.96 \end{array}$	$1.75  imes 10^4 \ -1.53  imes 10^4 \ -1.14$	$-5 \times 10^{5}$ 8.89 × 10 <sup>4</sup> -5.62	
T, K $\Delta \nu_{q}({}^{17}\text{O})/\Delta \nu_{q}({}^{2}\text{H}) \text{ (exptl)}$	300 6.25	305 6.02	310 6.06	315 6.0	320 5.92	

<sup>a</sup> For comparison, the experimental quadrupolar splittings ratios at different temperatures are given for a NaDBP molar ratio  $X_{\rm M} = 0.165$ . <sup>b</sup> Calculated for  $\overline{P}_2 (\cos \beta') = 1$ .

TABLE II: <sup>1</sup>H and <sup>2</sup>H Longitudinal Relaxation Rates and <sup>17</sup>O Line Widths in NaDBP/Water ( $X_M = 0.165$ )

Т, К		300	305	310	315	320
$\overline{T_1^{-1}}$ ( <sup>1</sup> H), s <sup>-1</sup>	exptla	5.10	3.94	2.99	2.46	2.0
	$calcd^d$	4.97	4.00	3.21	2.57	2.06
$T_1^{-1}$ ( <sup>2</sup> H), s <sup>-1</sup>	exptl <sup>b</sup>	47.6	33. <del>9</del>	26.7	20.4	17.2
	$calcd^d$	<b>42.4</b>	33.4	26.3	20.7	16.5
$\Delta \nu_{1/2}(^{17}\text{O}), \text{Hz}$	exptl <sup>c</sup>	2833	2250	1583	1167	935
	$calcd^d$	2607	2072	1646	1311	1048

<sup>a</sup> H<sub>0</sub> = 21 150 G, perdeuterated NaDBP/<sup>1</sup>H<sub>2</sub>O. <sup>b</sup> H<sub>0</sub> = 117 500 G. <sup>c</sup> H<sub>0</sub> = 177 500 G, −1/2 ↔ 1/2 transition. <sup>d</sup> Calculated for model I with  $\theta$  = 28.5° and correlation times  $\tau_{\perp}$  = 8.9 × 10<sup>-17</sup> exp(2300/T),  $\tau_{\parallel}$  = 5.5 × 10<sup>-21</sup> exp(3200/T) s.

direction. Models II and II' are related to the hydrogen bonding of water with two adjacent phosphate groups or one phosphate group, respectively, the latter being consistent with theoretical calculations on the hydration of the dimethyl phosphate anion.<sup>10</sup> Lastly, we have considered the reorientation about the bisector of the H-O-H angle (model III) and the normal to the molecular plane (model IV).

For an anisotropic reorientation in a liquid cristalline phase, the quadrupole splitting of a nucleus i of spin I is given by

$$\Delta \nu_{\mathbf{q}}^{(i)} = \frac{3\chi_{\mathbf{q}}^{(i)}}{4I(2I-1)} (3\cos^2 \Psi - 1)\bar{P}_2(\cos \beta') \times [\frac{1}{2}(3\cos^2 \theta_i - 1) + \frac{1}{2}\eta \sin^2 \theta_1 \cos 2\phi_i]$$
(1)

where  $\Psi$  is the angle between the static magnetic field and a local director  $\Delta_{\rm L}$ ,  $\beta'$  the time-dependent angle between the molecular axis of reorientation  $\Delta_{\rm m}$  (Figure 4), and  $\bar{P}_2$ (cos  $\beta'$ ) the molecular order parameter.  $\theta_{\rm i}$  and  $\phi_1$  are the polar and azimuthal angles of  $\Delta_{\rm m}$  in the frame of the principal axes of the electric field gradient tensors of <sup>2</sup>H or <sup>17</sup>O nuclei. The quadrupole splittings were calculated with the quadrupole coupling constants and asymetry parameters  $\chi_q(^{17}{\rm O}) = 6.67$  MHz,  $\chi_q(^{2}{\rm H}) = 213$  kHz, and  $\eta(^{17}{\rm O}) = 0.93$ ,  $\eta(^{2}{\rm H}) = 0.11^{11,12}$  for  $\angle{\rm H}{\rm -O}{\rm -H} = 104.5^{\circ}.^{9}$  The calculated values of  $\Delta\nu_q(^{17}{\rm O})/\Delta\nu_q(^{2}{\rm H})$  given in Table I show that only model III is clearly inconsistent with the experimental ones.



**Figure 4.** Principal axes systems for the electric field gradient tensors of deuterium and oxygen nuclei in the water molecule ( $Y_{2_{\rm H}}$  and  $Z_0$  are perpendicular to the molecular plane).  $\Delta_{\rm L}$  is the local director and  $\Delta_{\rm m}$  the axis of molecular reorientation.

An unambiguous selection between the other models has been performed by relaxation measurements on water <sup>1</sup>H, <sup>2</sup>H, and <sup>17</sup>O nuclei (Table II). From these experiments, it appears that, in the system under study, only model I holds, with an angle  $25^{\circ} < \theta < 30^{\circ}$  between the  $\Delta_{\rm m}$  and  $Z_0$  axes in the molecular symmetry plane (Figure 4), suggesting that the interstitial water molecules reorient about the direction of an oxygen lone pair orbital which is likely that of binding to a cationic site.

Additional experimental data as well as the calculations of relaxation rates for different models or reorientation of water will be reported in a forthcoming paper.

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