

## Counter-ion Quadrupole Splittings in Lyotropic Liquid Crystals. Determination of the Sign of the Order Parameter

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Many recent investigations have utilised the occurrence of static effects in nuclear magnetic resonance (NMR) spectra to obtain information on ionic interactions in liquid crystals and model membranes.<sup>1-9</sup> A theoretical approach based on a simple electrostatic model has been used to explain the quadrupole splittings observed for different counter-ions in various liquid crystalline (l.c.) phases.<sup>10</sup> The l.c. phases of the sodium octanoate-decanol-water system have been well documented in the classic studies of Ekwall *et al.*,<sup>11</sup> making this system the obvious starting point for systematic investigations of ion quadrupole splittings. However, <sup>23</sup>Na splittings for the lamellar (D) phase were an order of magnitude smaller than predicted by the theory and were temperature dependent,<sup>4,10</sup> decreasing to zero at higher temperatures.<sup>4</sup> Also, the <sup>23</sup>Na splittings observed for powder and aligned samples were not in agreement with theoretical equations.<sup>4</sup> In addition, the <sup>23</sup>Na splittings were consistent<sup>4</sup> with a non-lamellar structure<sup>11</sup> for the C phase although this appeared to be unlikely from previous NMR studies.<sup>12</sup> These difficulties have been resolved in the present investigation, and the sign of the sodium ion order parameter (*S*), previously unknown, has been deduced.

Sodium splittings have been determined for C and D phase samples using continuous-wave and spin-echo techniques. Sample preparation and continuous-wave measurements were carried out as described previously.<sup>4,12</sup> Spin-echo measurements were made using a Bruker Bkr 322-S pulsed spectrometer operating at 23.81 MHz, with the splitting being obtained from the modulation of the free induction decay following a  $\pi/2$  pulse.

Both aligned and powder samples were examined as a function of temperature and phase structures were checked using a polarising microscope with hot stage attachment.

The quadrupole splittings ( $\Delta$ ) of the sodium resonance in aligned and powder samples are given<sup>10</sup> by equations (1) and (2), respectively.

$$\Delta = |(3 \cos^2 \theta_{LD} - 1) \sum_i P_i \nu_Q^i S_i| \quad (1)$$

$$\Delta = |\sum_i P_i \nu_Q^i S_i| \quad (2)$$

where  $\nu_Q = e^2 q Q / 4h$  is the effective quadrupole coupling constant;  $P_i$  is the fraction of sodium ions in site *i*;

$S = 1/2 (3 \cos^2 \theta_{DM} - 1)$  if the asymmetry parameter is neglected.

$\theta_{LD}$  and  $\theta_{DM}$  are the angles between director and magnetic field and between director and electric field gradient, respectively. Note that in general only the absolute value of *S* may be obtained from the splitting.

The results can be summarised as follows:

(a) If water evaporation during sample preparation is avoided then values of  $\Delta$  for powder and aligned samples are related by equations (1) and (2) at all temperatures.

(b) The splittings are a complex function of temperature and composition. (See Figs. 1 and 2; similar results have been obtained elsewhere.<sup>13</sup>)

(c) Values of  $\Delta$  for the C phase are similar to those of adjacent D phase samples.

For the discussion of these data it is important to note that the <sup>23</sup>Na splittings of the sodium octanoate-decanol-water system are considerably smaller than those obtained with soaps having a sulfate end-group. If the electrostatic model discussed in Ref. 10 is used in combination with counter-ion association degrees of Ref. 14 the order parameter of the bound sodium ions is obtained to be considerably less than unity for the present system. The

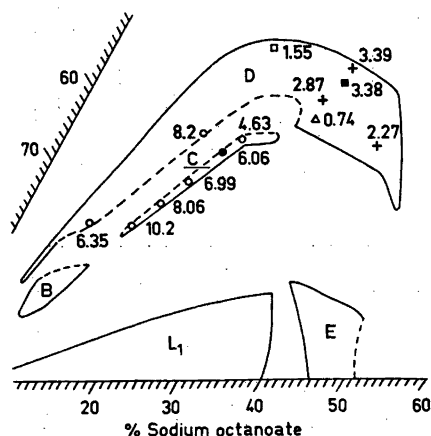


Fig. 1. Partial phase diagram (from Ref. 11) showing sample compositions and measured splittings. Temperatures of measurements were  $300 \pm 1$  K and  $294 \pm 1$  K for D and C phases, respectively. A  $\Delta$  value of 8.06 kHz was measured at 303 K for the C phase sample indicated by ●.

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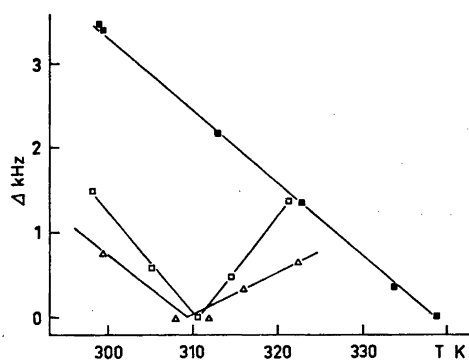


Fig. 2. Temperature dependence of the  $^{23}\text{Na}$  quadrupole splitting of three lamellar powder samples in the sodium octanoate-decanol- $\text{D}_2\text{O}$  system. Symbols refer to sample compositions with the same symbols in Fig. 1. As a result of a finite spin relaxation rate very small splittings are unobservable, and the zero splitting means that no modulation of the free induction decay was discernable. (The lines are drawn merely as an aid to the eye; there is no theoretical justification for a linear temperature dependence of the splittings.)

order parameter is zero for  $\theta_{\text{DM}} = 54^\circ 44'$ , the magic angle. Changes in temperature or composition give rise to changes in  $\theta_{\text{DM}}$ . With an average  $\theta_{\text{DM}}$  value which is close to the magic angle both positive and negative  $S$  values may be encountered and that this is so in the present case can be inferred from both the variable temperature and concentrations studies (Figs. 1 and 2). It seems not possible to understand vanishing quadrupole splittings well within the liquid crystal stability ranges in another way. Changes in  $S$  cannot be due to fundamental changes in the structure of the l.c. phase since concurrent changes are not observed in alkyl chain proton resonance<sup>12</sup> or water deuteron quadrupole splittings.<sup>15</sup> If increasing temperature or hydration may be assumed to weaken the amphiphile-counter-ion interaction (cf. Ref. 16) we have here for the first time a method to obtain the sign of the order parameter. Thus if the counter-ion splitting increases with increasing temperature or water content this indicates that the order parameter is positive while in the opposite case a negative order parameter is indicated.

These considerations open the way for using counter-ion quadrupole splittings to obtain unique information on the detailed location of counter-ions at the surface of an amphiphile aggregate. Except for the highest water contents, our observations suggest that over wide concentration and temperature ranges  $\theta_{\text{DM}}$  takes on large values. A location of bound sodium ions between adjacent carboxyl groups

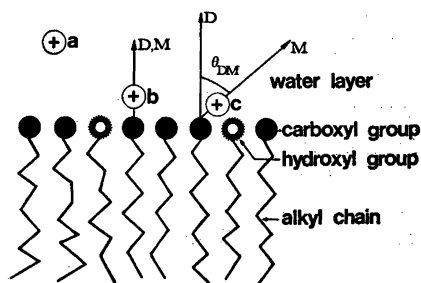


Fig. 3. Schematic drawing of the counter-ion binding at the lamellar surface according to the discussion in the text. The following three possibilities are shown: (a) The counter-ion is moving freely in the water layer. This location is characterized by  $S=0$ . (b) The counter-ion is located symmetrically with respect to the amphiphile polar end-group. In this case the average angle between the director ( $D$ ) and the electric field gradient ( $M$ ) is equal to  $0^\circ$ . (c) The counter-ion is located between amphiphile polar head-groups.

involving hydrogen-bonding between water of counter-ion hydration and surfactant end-group is a plausible model to explain these findings. Our findings with alkyl sulfates or sulfonates correspond to much higher  $S$  values and thus small values of  $\theta_{\text{DM}}$ . This is not unexpected in view of the symmetric end-groups and the low tendency of these end-groups to become involved in hydrogen-bonding. An attempt to visualize different locations of counter-ions at a lamellar surface is presented in Fig. 3. It should be noted that  $S$  is determined not only by the average value of  $\theta_{\text{DM}}$  but also by its range of variation, and that according to eqs. 1 and 2, a zero splitting may result from exchange between sites having different signs of  $S$  or  $\nu_Q$ . However, the general conclusions appear to be independent of these effects since the temperature dependences are large.

Because alkyl chain resonances were similar in C and D phases, it was proposed<sup>12</sup> that the C phase structure was an emulsion of lamellar phase and a small amount of micellar solution rather than the tetragonal rod structure favoured by Ekwall *et al.*<sup>11</sup> Previous  $^{23}\text{Na}$  splittings were consistent with the second structure,<sup>4</sup> but the similarity between values of  $\Delta$  for C and D phases supports the emulsion structure. Further studies are in progress using other techniques to resolve this problem.

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Received May 27, 1975.

## Crystallizations and Transformations of SrCl<sub>2</sub>-Hydrates in H<sub>2</sub>O-Solutions in Quartz Flasks

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The search for materials suitable for energy storage has aroused an interest in the kinetics of nucleation and the growth of salt hydrates.<sup>1</sup> In a previous paper<sup>2</sup> it was shown that SrCl<sub>2</sub>·6H<sub>2</sub>O can, if properly treated, be heated above 61.3 °C – the temperature of transition for the system SrCl<sub>2</sub>·6H<sub>2</sub>O ⇌ SrCl<sub>2</sub>·2H<sub>2</sub>O + sat. solution – without transforming into dihydrate; SrCl<sub>2</sub>·H<sub>2</sub>O is formed at approx. 71 °C.

The system, SrCl<sub>2</sub>·H<sub>2</sub>O + sat. solution, can be supercooled approx. 100 °C in quartz flasks if treated as described below; the temperature of transition for SrCl<sub>2</sub>·2H<sub>2</sub>O ⇌ SrCl<sub>2</sub>·H<sub>2</sub>O + sat. solution is approx. 135 °C. The limit of supercooling – approx. 30 °C where hexahydrate is generated – depends probably on the quartz container used but not on the monohydrate crystals.

The system, SrCl<sub>2</sub>·H<sub>2</sub>O + sat. solution, can also be supercooled – from 61.3 °C down to approx. 20 °C – and the limit, where hexahydrate is formed, depends probably also on the container used and not on the supercooled system (*cf.* results obtained with CaCl<sub>2</sub>-hydrates<sup>3</sup>).

*Experimental details and results.* Sample SrCl<sub>2</sub>, El-chemical, from Merck, Germany. The analysis of the sample and the experimental arrangement is described earlier.<sup>2</sup> The cleaning of the quartz flasks which contained the SrCl<sub>2</sub>-system has been modified as follows: the vacuum grease (Apiezone H) was first removed; the last residue was thoroughly washed away by chloroform. Then the flask was washed with alcohol and water and filled with conc. H<sub>2</sub>SO<sub>4</sub> which contained 25 g NaClO<sub>4</sub> per 1 H<sub>2</sub>SO<sub>4</sub> (analysed reagents). The flask was left for 12 h at 100 °C, and then thoroughly washed with distilled water (sp. conductivity less than 5 × 10<sup>-7</sup> Ω<sup>-1</sup> cm<sup>-1</sup>).

A SrCl<sub>2</sub>-solution was filtered through a filter, type VSWP 04700, white, plain, pore size 0.025 μm; stainless pressure filter holder, type XX4004700. Filter and filterholder from Millipore Corp. U.S.A.; before use they were washed repeatedly with distilled water until the sp. cond. was less than 10<sup>-6</sup> Ω<sup>-1</sup> cm<sup>-1</sup>. The washing and the filtration of the SrCl<sub>2</sub>-solution into a quartz flask was performed in a laminar air flow cabinet; the pore sizes of the air filter were less than 0.6 μm.

Before starting an experiment, a SrCl<sub>2</sub>-solution was heated to 100 °C, cooled and then exhausted four or five times. It proved to be