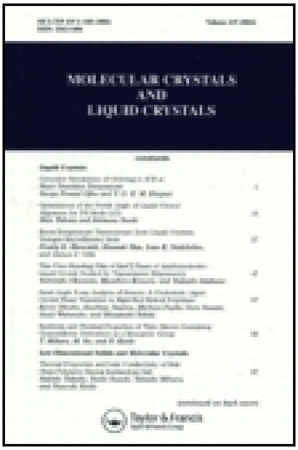

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Ion Binding in Liquid Crystals Studied by NMR V. Static Quadrupolar Effects for Alkali Nuclei†‡

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Abstract—Nuclear magnetic resonance spectra of $^{7}Li^{+}$, $^{23}Na^{+}$, $^{39}K^{+}$, $^{85}Rb^{+}$, $^{87}Rb^{+}$ and $^{133}Cs^{+}$ counter-ions in lyotropic liquid crystalline phases were recorded. For all these nuclei it was observed that static quadrupolar interactions cause splittings of the NMR absorption into component signals. First-order ^{23}Na quadrupole splittings are strongly affected by sample temperature, phase structure, sample composition, macroscopic alignment and amphiphile end-group. The competitive binding of the alkali ions was studied by $^{7}Li^{+}$, $^{23}Na^{+}$ and $^{133}Cs^{+}$ NMR. The splittings were assumed to depend on four factors, i.e. (a) the degree of counter-ion binding to the amphiphilic surfaces, (b) the quadrupole coupling constant, (c) the degree of orientation of the electric field gradients and (d) exchange of counter-ions between microcrystallites. It is found that the rate of exchange between microcrystallites depends strongly on the counter-ions present, that sodium ions exchange more rapidly than water molecules, and that the counter-ion exchange proceeds at a lower rate if D_2O is substituted for H_2O. The presence of the counter-ion exchange process, which was established by comparing the temperature dependences of splittings for powdered and aligned samples, makes it often impossible to interpret splittings obtained with powdered samples solely in terms of molecular interactions. Counter-ion quadrupole splitting studies with phospholipid-containing lamellar samples show that the method constitutes a novel possibility to study ion binding in biological membrane systems as well as models of these.

1. Introduction

The successful use of nuclear quadrupole relaxation for studying alkali ions in macromolecular$^{(1-4)}$ and micellar solutions$^{(5-7)}$ demonstrates that the nuclear electric quadrupole moment can be used as

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† For part IV, see Ref. 11.

‡ Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

a sensitive probe for elucidating interactions between alkali ions and molecules or molecular aggregates of colloidal dimensions. Studies of this type are based on the fact that for many monoatomic ions in amorphous solution, dynamic interactions between the quadrupole moment and electric field gradients constitute the predominant mechanism causing nuclear magnetic relaxation. Apart from the time-dependent quadrupole interactions,(8) and in analogy with solid systems, we would expect for liquid crystalline solutions to encounter effects in the NMR spectrum due to quadrupole interactions not being averaged to zero by the molecular motion. Static quadrupolar effects arise if the nuclear surroundings are anisotropic on a sufficiently long time-scale and lead to splittings of NMR signals into two or more components.

Previously we briefly reported splittings of $^{35}Cl^-$, $^{37}Cl^-$ and $^{23}Na^+$ NMR signals in lyotropic mesophases and showed that they could be explained by static quadrupolar interactions.(9–11) It appears that these quadrupole splittings constitute a novel possibility of studying ion binding in anisotropic mesophases as well as in biological membranes and models of these.

In the present paper, which is concerned with lyotropic mesophases containing ionic amphiphiles, it will be demonstrated that static quadrupolar effects are observable for all alkali ions. Furthermore, attempts will be made to establish the origin of the static quadrupolar effects by studying how the splittings depend on, e.g., temperature, ion competition, phase composition and phase structure.

2. Experimental

NMR MEASUREMENTS

The NMR investigations were performed with a Varian Associates V-4200 wide-line spectrometer equipped with a 12-inch V-3603 magnet and a Varian Mark II Fieldial. The derivative of the NMR absorption curve was observed. In some cases a slight overmodulation was necessary in order to get a sufficiently large signal-to-noise ratio. This overmodulation of the NMR signal caused some broadening of the resonance peaks but was found to have no significant effect on the magnitude of the quadrupole splittings.

The measured quadrupole splittings are the distances between the outer peaks in the NMR spectra for ^{7}Li, ^{23}Na, ^{39}K and ^{87}Rb, whereas for ^{133}Cs the splitting is defined as the distance between the satellites closest to the central peak. The reproducibility of the measured splittings was in most cases better than ± 3%. The splittings were found to depend slightly (up to 10%) on the time elapsed after sample preparation. In order to eliminate this source of error, spectra were recorded at different times. The data reported below refer to experiments where no further change of splitting with time could be detected over a period of some months.

^{7}Li, ^{23}Na and ^{89}Rb measurements were performed at a resonance frequency of 15.82 MHz, whereas the resonance frequency was 2.79 MHz for ^{39}K, 5.78 MHz for ^{85}Rb and 7.85 MHz for ^{133}Cs. The variable frequency oscillator of the wide-line spectrometer was stabilized (except for ^{39}K and ^{133}Cs) within ± 1 Hz by means of a crystal oscillator.

The sample temperature was 27 ± 2 °C if not otherwise specified. In the determinations of the temperature dependence of the splittings, the sample temperature was controlled by means of a Varian V-4540 instrument for the powdered samples and by a water thermostat (by circulating water around the sample) for the oriented samples. The actual temperature of the powdered samples was measured with a copper–constantan thermocouple before and after the recording of each series of spectra at a given temperature and was found to be accurate within ± 0.3 °C. The temperature of the oriented samples was estimated as the mean value of the temperature measured at the inlet and outlet of water circulating around the sample and was found to be accurate within ± 0.7 °C.

MATERIALS AND SAMPLE PREPARATION

Sodium *n*-octylsulphate and sodium *n*-octylsulphonate were obtained from Schuchardt, München, Germany and Aldrich, New Jersey, U.S.A., respectively. Sodium *n*-octanoate, *n*-octanoic acid, cholesterol and *n*-decanol were purchased from the British Drug Houses Ltd., Poole, England. The other alkali octanoates were prepared by adding the appropriate alkali ethoxide (Li, K) or hydroxide (Rb, Cs) to a solution of octanoic acid in ethanol. The soaps were then filtered off and dried under vacuum in the presence of P_2O_5. The molecular weights of the products were determined by titration in glacial acetic acid with perchloric acid and with crystal violet as indicator. The molar weights of the salts were found to be accurate within ±1%. The samples were prepared by mixing the appropriate amounts of the components in sealed test tubes above the transition to the amorphous liquid state. The macroscopical alignment of the mesophases was accomplished as described in Ref. 11.

The phosphatidyl choline (lecithin) was extracted from hen egg yolk as described by Singleton *et al.*(12) The purity of the prepared lecithin was kindly determined by Docent Gösta Arvidsson, Dept. of Medical Chemistry, University of Lund, to be better than 99%. The mesophase samples were prepared by adding an aqueous alkali chloride solution to a mixture of lecithin and cholesterol kept under nitrogen atmosphere. The samples were then heated to about 40 °C and homogeneity was attained by stirring from time to time. X-ray photographs, confirming the lamellar structure of some of the samples, were generously made by Dr. Krister Fontell, The Swedish Institute for Surface Chemistry, Stockholm.

3. Static Quadrupolar Effects

All the alkali nuclei have nuclear spin quantum numbers greater than $\frac{1}{2}$ and consequently possess electric quadrupole moments. In certain cases their NMR spectra show quadrupole interactions which are not totally averaged to zero by the molecular motion. A necessary condition for the observation of quadrupole splittings is that the nucleus resides in an environment which is anisotropic on a sufficiently long time-scale. For the case that the quadrupole interaction is much smaller than the Zeeman interaction the quadrupole hamiltonian can be treated as a perturbation to the Zeeman term. A thorough treatment of this situation has been given by Cohen and Reif(13) for solids. By introducing the order parameter, S, which reflects the degree of orientation of the electric field gradient tensor we may modify their results to apply for liquid crystals.(9) For nuclei with spin quantum numbers $I = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, etc., the first-order perturbation term corresponds to a splitting of the NMR signal into an unshifted central peak and $I - \frac{1}{2}$ satellites on each side of the central resonance. The distance between the satellites being closest to the central signal will be denoted the first-order splitting and is given by$^{(11,13)}$

$$\Delta_{\Omega}^{(1)} = \left| p \cdot \nu_Q \cdot S \cdot (3\cos^2 \Omega - 1) \right| \tag{1}$$

Here p is the fraction of the alkali nuclei in a site with static quadrupolar interactions and thus a measure of the degree of counter-ion association with the amphiphilic surfaces. Ω is the angle between the direction of the applied magnetic field and the director, i.e., the direction of preferred orientation in the microcrystallites. $\nu_Q = 3e^2qQ/2I(2I-1)h$ where eq is the largest of the components of the electric field gradient tensor in the principal axes system and eQ the nuclear electric quadrupole moment. As has been reported previously,$^{(11)}$ the angular dependence of the ^{23}Na splitting for samples from the lamellar mesophase composed of sodium octanoate–octanoic acid–water oriented between glass plates is in accordance with Eq. (1). It was also shown that the order parameter may be written as

$$S = \overline{D_{0,0}^{(2)}} + (1/\sqrt{6})\eta(\overline{D_{0,2}^{(2)}} + \overline{D_{0,-2}^{(2)}}),$$

where the $\overline{D^{(2)}}$'s are the second rank Wigner rotation matrix elements averaged over the molecular motion and η is the asymmetry parameter defined in the principal axes system. It should be noted that the value of η does not have any influence on the NMR line shape but that η affects the magnitude of the quadrupole splitting.$^{(11)}$ Thus no assumptions about η have to be made to explain the angular dependence of the quadrupole splitting for an oriented sample.

The NMR spectrum from an unoriented sample is given by a superposition of resonance signals from randomly oriented microcrystallites. For a powder pattern the magnitude of the splitting is given by (cf. Refs. 11 and 13)

$$\Delta_{p}^{(1)} = \left| p \cdot \nu_Q \cdot S \right| \tag{2}$$

If the quadrupole interaction becomes strong enough the second-order perturbation term also affects the spectral shape. Second-order effects cause a shift of the central component in the NMR spectrum. This shift, relative to the location of the resonance signal at the

Larmor precession frequency, ν_L, is governed by the expression(9, 13)

$$\Delta_{\Omega}^{(2)} = \frac{25}{48\nu_L}(p\cdot\nu_Q\cdot S)^2\,|(1-\cos^2\Omega)(9\cos^2\Omega-1)| \tag{3}$$

For a powdered sample, where the line shape of the central resonance signal is more complicated (cf. Ref. 9), we denote the distance between the points of maximum and minimum slope in the central NMR absorption curve as the " second-order quadrupole splitting ", $\Delta_p^{(2)}$. This is given by Eq. (4) if the line width may be neglected.

$$\Delta_p^{(2)} = \frac{25}{48\nu_L}(p\cdot\nu_Q\cdot S)^2 \tag{4}$$

The presence of second-order effects can be established from the spectral shape, from the frequency dependence of the splitting and from the isotopic effect. A brief account of $^{35}Cl^-$ and $^{37}Cl^-$ second-order quadrupolar effects for a lamellar mesophase has been given.(9)

4. Results and Discussion

First-order quadrupole splittings were observed with lamellar mesophases for all the alkali ions. In Fig. 1 are given NMR spectra for ^{7}Li, ^{23}Na, ^{39}K, ^{87}Rb and ^{133}Cs for powdered mesophase samples of lamellar structure composed of alkali octanoate, decanol and water. All these nuclei, except ^{133}Cs, are spin $\frac{3}{2}$-particles and consequently, for first-order static quadrupolar effects, give rise to spectra composed of a central peak symmetrically surrounded by two satellites. In the case of ^{133}Cs with $I=\frac{7}{2}$, as expected, three satellites on each side of the central component are shown.

In the case of sodium and potassium the region of stability of the lamellar phase has been given by Ekwall *et al.*(14) With the other counter-ions the lamellar phase region was estimated from these phase diagrams. Support for a lamellar structure was given by the sample texture and by deuteron NMR spectra (on samples containing heavy water) which were generously recorded for us by Mr. N.-O. Persson.

As can be seen from Fig. 1 the signal-to-noise ratio is largest for ^{23}Na, making this nucleus most suitable in studies of this type. For ^{39}K the signal-to-noise ratio is very low and although a splitting may

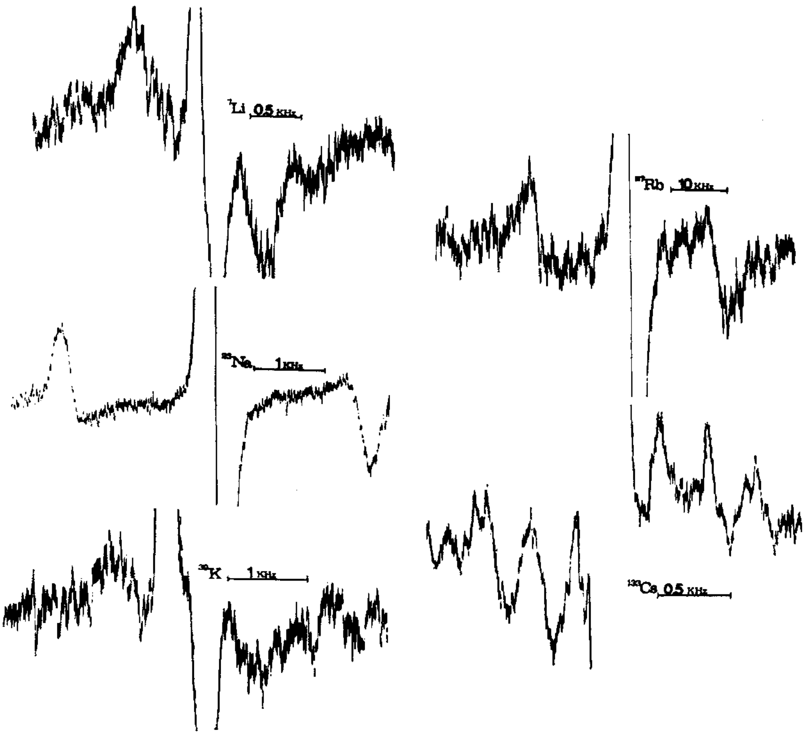

Figure 1. NMR spectra of $^{7}Li^{+}$, $^{23}Na^{+}$, $^{39}K^{+}$, $^{87}Rb^{+}$ and $^{133}Cs^{+}$ for powdered lamellar mesophase samples of the systems alkali octanoate–decanol–water. The sample composition (in mole-%) was 7.5% alkali octanoate, 8.5% decanol and 83.0% heavy water. Temperature 27 °C.

readily be observed its magnitude cannot be measured accurately. Furthermore, at present it is impossible for us to observe the ^{39}K NMR signal for oriented samples. In order to study the binding of K^{+} with the present method, spectra accumulation would be necessary.

Effect of Temperature and Alignment

In order to get some insight into the factors determining the magnitude of the splittings we have investigated the temperature dependence. In Fig. 2 are given ^{23}Na splittings for some powdered lamellar mesophase samples of the ternary systems sodium octanoate–

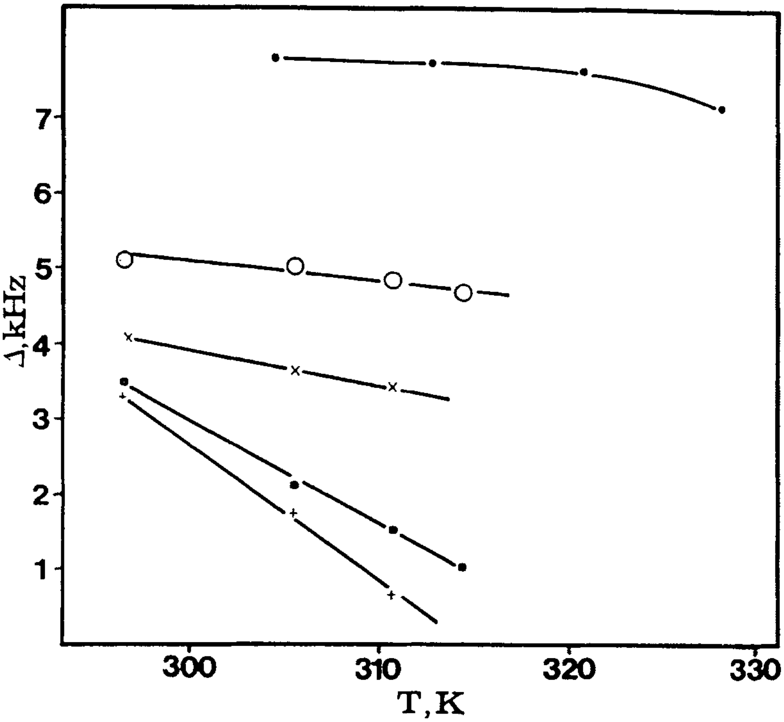

Figure 2. ^{23}Na quadrupole splittings, Δ, as a function of temperature for powdered samples of the lamellar mesophases of the systems sodium octanoate-decanol-water and sodium octanoate-octanoic acid-water. Sample composition (concentrations in mole-%):

Sodium octanoate	:	decanol	:	heavy water	points denoted by
10.8	:	11.7	:	77.5	□
5.1	:	11.9	:	83.0	+
Sodium octanoate	:	octanoic acid	:	heavy water	points denoted by
10.0	:	13.2	:	76.8	●
7.1	:	9.8	:	83.1	○
13.3	:	8.8	:	77.9	×

decanol–water and sodium octanoate–octanoic acid–water. (Phase diagram given in Ref. 14.) Previously, we reported that the splitting for ^{35}Cl in the lamellar mesophase composed of octylammonium chloride, decanol and water is independent of sample temperature.(9) As can be inferred from Fig. 2 the situation is quite different for sodium counter-ions, especially with the sodium octanoate–decanol–

water system. The origin of the drastic decrease in splitting with increasing temperature could be established by studying macroscopically oriented samples of the same composition as for the powdered samples.

The orientation was achieved by applying thin layers of the samples between glass plates. It has previously been shown$^{(11)}$ that the ^{23}Na splitting varies with the angle, Ω, between the normal to the glass plates and the magnetic field as $(3\cos^2\Omega - 1)$ and this dependence was verified also for the samples studied in this work. According to Eqs. (1) and (2) we would expect to obtain identical splittings with oriented samples having $\Omega = 90°$ and with powdered samples. This is normally not observed with ^{23}Na NMR for the sodium octanoate–decanol–water system; instead, in most cases $\Delta_{90}^{(1)}$ is significantly larger than $\Delta_p^{(1)}$ for $^{23}\mathrm{Na}^+$. The temperature variation of the splitting for oriented samples is much weaker than for powdered ones as can be seen in Fig. 3 where the ratio $\Delta_{90}^{(1)}/\Delta_p^{(1)}$ is given as a function of the temperature. The most likely explanation to this fact is that for powdered samples there is an exchange of sodium ions between regions with different Ω. This exchange could be an exchange between randomly oriented microcrystallites. Exchange between microcrystallites having approximately equal orientations of their lamellae with respect to the external magnetic field, as is the case for aligned samples, would not lead to a corresponding elimination of the static quadrupolar effects. Alternatively, if the lamellae are sufficiently curved, the effect is explainable solely in terms of translational diffusion of the counterions along the lamellar surfaces.

For the discussions of the ionic quadrupole splitting experiments it is convenient to introduce specifically the effect of this exchange process in Eq. (2). Obviously, for the powdered samples the order parameter can be considered as arising from two effects, one due to molecular motion within the microcrystallites (denoted S') and one due to molecular motion between microcrystallites (denoted $S_{e\,x}$) We may then formally rewrite Eq. (2) as

$$\Delta_p^{(1)} = \left| p \cdot \nu_Q \cdot S' \cdot S_{\mathrm{ex}} \right| \tag{5}$$

Evidently, since exchange between different Ω's does not occur for macroscopically aligned samples S_{ex} equals the ratio $\Delta_p^{(1}/\Delta_{90}^{(1)}$. In

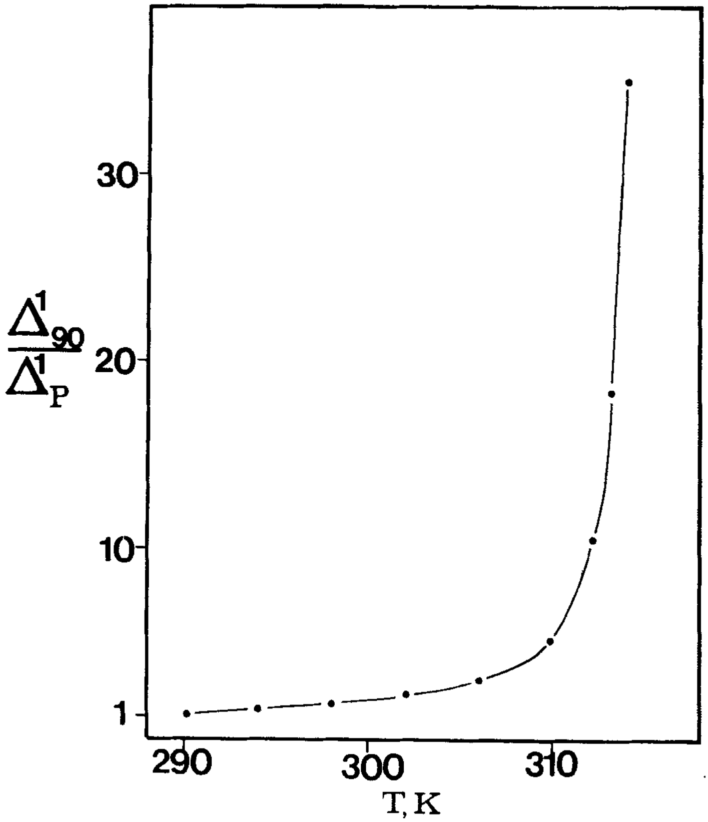

Figure 3. The ratio between the ^{23}Na quadrupole splittings for a macroscopically aligned sample with $\Omega = 90°$, Δ^1_{90}, and the corresponding powder sample, Δ^1_p as a function of temperature. (Ω is the angle between the normal to the glass plates and the external magnetic field.) The sample composition (in mole-%) was 5.1% sodium octanoate, 11.9% decanol and 83.0% heavy water.

principle S_{ex} gives information on the rate of counter-ion translational motion, but this would require knowledge of microcrystallite size and/or lamellar curvature which is not available. In order to probe further into the detailed mechanism of the elimination of the splitting a study of the translational self-diffusion coefficients of counter-ions in lamellar mesophases will be undertaken.

For some of the samples the deuteron splittings were also determined.⁽¹⁵⁾ In this case the decrease of the static quadrupolar interactions due to the exchange process considered above is much less significant. Thus the deuteron splitting is still observable at 90 °C for a sample where the ^{23}Na static quadrupolar effects are completely averaged out at about 40 °C. Furthermore the ratio between the deuteron 90°-splitting and the powder-splitting is much smaller. These observations suggest that the counter-ion translational motion is considerably more rapid than the water motion. This observation should be of great importance in connection with discussions of interactions between small ions and biological membranes.

Comparison between Different Counter-Ions

It would be of great significance, if the quadrupole splitting method could be used to extract information on how the counter-ion interaction with the charged amphiphilic surfaces depends on the ionic radius. This would be one possibility to elucidate the mechanism of ion binding in lyotropic liquid crystals as well as in biological membrane systems. We will now consider this problem and describe experiments relevant in this connection.

Information on relative ion binding can be obtained either by comparing the magnitudes of the splittings observed with different counter-ions or by studying the effect on the splittings of ion competition.

In order to investigate if the splittings can directly give some insight into the mode of amphiphile-counter-ion interaction, NMR spectra for the different counter-ions were recorded at the same molar ratio between alkali octanoate, decanol and water. The magnitudes of the observed first-order splittings for powder samples are given in Table 1. In order to be able to compare the different nuclei it is of course necessary to account for the differences in quadrupole moments. Furthermore, the difference in atomic number along the alkali series has the consequence that the electron density is differently distorted for the different ions by electric charges located outside the ions. Accordingly, we must take the Sternheimer antishielding factor into account. A quantity which should be meaningful when one wants to compare splittings from different ions is the

TABLE 1 Quadrupole splittings of alkali ions for powdered lamellar mesophase samples with the composition (in mole-%) alkali octanoate : decanol : heavy water = 7.5 : 9.5 : 83.0. Temperature 27 °C. For notations see text.

Ion	I	$Q \cdot 10^{20}$ (m^2)[a]	$1-\gamma_\infty$[b]	$\Delta_p^{(1)}$ (kHz)	$\Delta_{red}^{(1)} \cdot 10^{-17}$ (V/m^2)
$^7Li^+$	3/2	−0.04	0.737	1.2	35 (38)[c]
$^{23}Na^+$	3/2	0.11	5.56	4.4	6 (7.7)[c]
$^{39}K^+$	3/2	0.09	18.32	1.9	1
$^{87}Rb^+$	3/2	0.14	48.2	36.4	4
$^{133}Cs^+$	7/2	−0.003	145	7.2	96

[a] *International Handbook of Chemistry and Physics*, 51st ed., Chemical Rubber Co., 1970–71.

[b] Deverell, C., in *Progress in NMR Spectroscopy*, Vol. IV, p. 235, Pergamon Press, Oxford, 1969, and Hertz, H. G., " Magnetische Kernresonanzuntersuchungen zur Struktur von Elektrolytlösungen ", in *Theorie der Elektrolyte*, Falkenhagen, H., ed., S. Hirzel, Leipzig, 1971.

[c] Macroscopically aligned samples.

" reduced first-order quadrupole splitting ", $\Delta_{red,}^{(1)}$ defined by Eq. (6).

$$\Delta_{red}^{(1)} = \left| \frac{\Delta_p^{(1)} 2I(2I-1)h}{3eQ(1-\gamma_\infty)} \right| = \left| p \cdot S' \cdot S_{ex} \cdot eq_e \right| \qquad (6)$$

Here γ_∞ is the antishielding factor and eq_e the electric field gradient acting on the ion with its electron cloud included. Reduced quadrupole splittings for the different counter-ions are given in Table 1. It can be seen that $\Delta_{red}^{(1)}$ varies considerably and in a complex manner with the radius of the counter-ion, which suggests that at least two of the factors in Eq. (6) are strongly dependent on the size of the counter-ion. Obviously, it is not possible from these data alone to identify these factors. A better way should be to compare $\Delta_\Omega^{(1)}$-values but, unfortunately, sensitivity limitations prevent us at present from obtaining the data corresponding to those in Table 1 for macroscopically aligned samples (except for ^{7}Li and ^{23}Na).

With the hope of resolving the problem of interpretation we studied the competitive binding of the alkali ions for samples

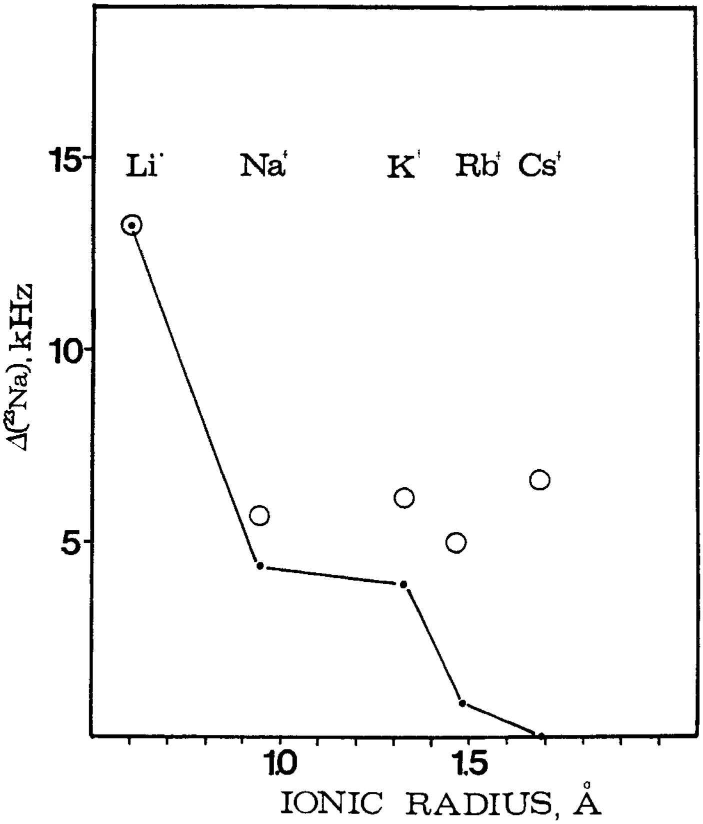

Figure 4. ^{23}Na quadrupole splittings of some lamellar mesophase samples. The sample composition (in mole-%) was 7.5% sodium octanoate, 9.5% decanol and 83.0% heavy water for the samples denoted Na$^+$. In the other cases another alkali ion was substituted for half of the sodium ions. The points are denoted thus;

● powdered samples

○ macroscopically aligned samples.

Temperature 27 °C. For reasons of presentation the quadrupole splittings are given, somewhat ambiguously, as a function of the ionic radius.[a]

[a] Robinson, R. A., and Stokes, R. H., in *Electrolyte Solutions*, Butterworths Scientific Publications, London, 1965.

composed of alkali octanoate, decanol and water. In Fig. 4 are given some results obtained with ^{23}Na NMR as a function of the crystallographic radii of the ions. The total alkali ion concentration was the same throughout these experiments. Except for the points denoted sodium, equal concentrations of sodium and another alkali ion are present. It is apparent that substitution of lithium for part of the sodium ions leads to an enforced ^{23}Na static quadrupolar interaction both for powdered and macroscopically aligned samples. On the other hand, when instead of half of the sodium ions cesium ions are introduced the ^{23}Na powder splitting is eliminated, whereas partial elimination of the static quadrupole interaction occurs on introduction of potassium or rubidium ions. For oriented samples, substitution of potassium, rubidium or cesium ions for half of the sodium ions has a small effect on the splitting.

It is quite apparent that these findings may not be interpreted simply in terms of competitive ion binding in an invariant medium and this is further substantiated by the results for powdered samples given in Table 2. Thus it can be seen in this table that for a sample containing equimolar quantities of sodium and lithium octanoate both the ^{7}Li and the ^{23}Na splittings are larger than for the corresponding samples containing only the lithium or the sodium salt. The opposite effect is observed when the surfactant is an equimolar mixture of cesium and sodium octanoate (Table 2). Thus in the mixture sample the cesium splitting is the same as that obtained with only cesium octanoate as surfactant, whereas the sodium splitting of the mixture sample is unobservable but quite large with only sodium octanoate as surfactant.

TABLE 2 Quadrupole splittings of different ions in powdered samples, $\Delta_p^{(1)}$, and in macroscopically aligned samples, $\Delta_{90}^{(1)}$. (The angle between the normal to the glass plates and the applied magnetic field was 90°.) Sample composition (in mole-%) was total content of alkali octanoate: decanol : heavy water = 7.5 : 9.5 : 83.0. Equal concentrations of sodium and another alkali ion are present in the cases with mixture of alkali ions. Temperature 27 °C

Alkali ion in the sample	$\Delta_p^{(1)}(^7\mathrm{Li})$ (kHz)	$\Delta_{90}^{(1)}\Delta(^7\mathrm{Li})$ (kHz)	$^{(1)}_{p}(^{23}\mathrm{Na})$ (kHz)	$\Delta_{90}^{(1)}(\mathrm{Na})$ (kHz)	$\Delta_p^{(1)}(^{133}\mathrm{Cs})$ (kHz)
Li	1.2	1.3			
Li + Na	2.0	2.0	13.2	13.2	
Na			4.4	5.6	
Cs + Na			[a]	6.6	7.1
Cs					7.2

[a] No splitting observed.

Using Eq. (5), some information about the factors determining the magnitude of the splitting and their variation with the nature of the counter-ion may be obtained. Firstly, we note from Fig. 4 that for $^{23}Na^+$, introduction of Li^+ ions instead of Na^+ ions leads to an increase in S_{ex} whereas this quantity is progressively decreased on substitution for Na^+ of K^+, Rb^+ or Cs^+. In analogy with this, we conclude from Table 2 that S_{ex} is close to unity for $^7Li^+$ but markedly lower for $^{23}Na^+$. These observations show that for sodium counter-ions the rate of exchange between the microcrystallites strongly depends on the presence of other alkali ions. Definite statements about the other factors S', p and eq_e are more difficult to make. However, a comparison between $\Delta_{90}^{(1)}$ for $^{23}Na^+$ and $\Delta_p^{(1)}$ for $^{133}Cs^+$ performed utilizing Eq. (6) and the fact that $\Delta_p^{(1)}$ never can exceed $\Delta_{90}^{(1)}$ implies that the quantity $S' \cdot p \cdot eq_e$ is at least 12 times as large for cesium as for sodium. A difference in $S' \cdot p$ to this extent between the two ions seems to be unlikely (cf. Ref. 16) and, therefore, this observation indicates that eq_e is larger for Cs^+ than for Na^+. Concerning S' and p, at present, we are unable to obtain any information. However, assuming, in analogy with the conclusion drawn above, that eq_e increases with the size of the naked ion (cf. also below), the observation that the reduced splitting for oriented samples is larger for $^7Li^+$ than for $^{23}Na^+$ (cf. Table 1) would indicate that $S' \cdot p$ is larger for $^7Li^+$ than for $^{23}Na^+$. However, in view of the puzzling observation (Table 2) that for a sample containing equal concentrations of sodium and lithium ions the splittings (both $\Delta_p^{(1)}$ and $\Delta_{90}^{(1)}$) for both $^7Li^+$ and $^{23}Na^+$ are greater than for the corresponding samples containing only Li^+ or Na^+, respectively, this interpretation can only be regarded as a speculation. By performing a similar study as the present one by the quadrupole relaxation method and by exploring the effect of counter-ion size on amphiphile proton NMR spectra and on ESR spectra of incorporated spin labels we hope to shed further light on these problems.

It is of interest to consider what can be inferred from other types of studies on the quantities determining the quadrupole splittings.

The increase in c.m.c. of aqueous alkali octanoate solutions with increasing counter-ion size(17, 18) indicates that counter-ion association to carboxylate groups is decreased in going from Li^+ to Cs^+. It has also been shown(19) that the Krafft points for some alkali carboxylate soaps decrease from lithium to rubidium and Gallot and Skoulios(20) found from X-ray diffraction experiments that the specific area per carboxylate group increases from sodium to cesium for alkali alkanoate–water lamellar mesophases. An increased amphiphile charge density of the lamellar surfaces can be anticipated to directly affect two of the factors in Eq. (5). Thus we expect an increasing molecular organization, or an increase in S', as the specific area per polar group decreases. Furthermore, a high charge density will tend to affect the counter-ion distribution in such a way as to increase p. It is interesting that studies(21, 22) of force-area and surface-area curves on monolayers of alkali salts of carboxylic acids lead to the conclusion that the interaction decreases with increasing crystallographic radii of the alkali ions. It can also be seen that for samples containing heavy water the deuteron splitting(15) is anomalously high with Li^+ as counter-ion, which can probably be explained by a high degree of amphiphile organization in this case.

The quantity eq_e is expected to depend strongly on the hydration properties of the counter-ion. For an ion being strongly hydrated the charged lamellar surfaces are expected to cause smaller field gradients, eq_e, than for unhydrated ions. Our suggestion that eq_e increases from Li^+ to Cs^+ is in analogy with the hydration properties of the alkali ions (cf. Ref. 23).

For ^7Li, ^{23}Na, ^{39}K, ^{87}Rb and ^{133}Cs, in the lamellar mesophases we have studied, the static quadrupole interaction can be calculated from Eq. (4) to give second-order effects much smaller than the line-broadening caused by quadrupole relaxation. Therefore shifts due to second-order quadrupole interactions are unobservable in these cases. For ^{85}Rb with lamellar mesophase samples in the rubidium octanoate–decanol–water system we observed a broadening of the central peak which was too large to be due to relaxation effects. Thus in the case of quadrupole relaxation the line width should increase by a factor of 3.5 on going from ^{87}Rb to ^{85}Rb (cf. Ref. 7) whereas we have observed factors surpassing 10. If the line width were determined by relaxation it should decrease rapidly with increasing temperature. However, in this case ^{85}Rb line width is insensitive to temperature changes.(24) Since the line-broadening varies approximately inversely with the resonance frequency we could attribute these effects to second-order quadrupole interactions. Further evidence for this is provided by the fact that the second-order ^{85}Rb quadrupole splitting calculated from the first-order ^{87}Rb quadrupole splitting by Eq. (4) is close to the observed line-broadening.

EFFECTS OF COMPOSITION AND PHASE STRUCTURE

In order to employ the quadrupole splitting method to get information on mesophase structure and on interactions between counter-ions and amphiphiles and between counter-ions and water we have performed detailed investigations of several systems on how the ^{23}Na splitting depends on sample composition and on how it changes at phase transitions. The following observations were made:

TABLE 3 ^{23}Na quadrupole splitting in different lyotropic liquid crystalline systems. The different mesophase structures have been proposed by Ekwall *et al.*(14) to be lamellar, mucous woven type (B), two-dimensional tetragonal (C), lamellar, neat phase type (D), two-dimensional, middle phase type (E) and reversed two-dimensional hexagonal (F). Concentrations are given in mole-%. Temperature 27 °C. All observations concern powder samples.

Sample composition	phase	$\Delta_p^{(1)}$ (kHz)
sodium octanoate : decanol : water		
5.1 : 12.1 : 82.8	D	3.9
10.1 : 12.6 : 77.3	D	5.0
4.2 : 10.2 : 85.6	D	1.7
9.5 : 27.5 : 63.0	F	13.1
7.5 : 26.3 : 66.2	F	8.5
9.5 : — : 90.5	E	3.7
9.1 : 1.5 : 89.4	E	2.9
1.2 : 1.6 : 97.2	B	[a]
2.7 : 4.3 : 93.0	C	16.9
6.0 : 7.5 : 86.5	C	12.6
sodium octanoate : octanoic acid : water		
14.7 : 7.8 : 77.5	D	2.1
11.9 : 10.7 : 77.4	D	7.4
sodium octylsulphate : decanol : water		
9.8 : 13.3 : 76.9	D	32.0
5.1 : 11.9 : 83.0	D	21.0
sodium octylsulphonate : decanol : water		
4.4 : 9.7 : 85.9	D	19.7
5.9 : 13.4 : 80.7	D	20.1

[a] No splitting observed.

(i) The powder splitting is strongly dependent on phase structure and discontinuous changes are observed at phase transitions (Table 3).

(ii) For lamellar phases, in most cases the splitting increases as the water content is decreased (Table 3).

(iii) The splitting is strongly dependent on soap end-group at comparable sample compositions. Thus with sodium octylsulphate or sodium octylsulphonate as surfactant the ^{23}Na powder splitting is an order of magnitude larger than with sodium octanoate (see Table 3).

(iv) For cubic mesophases no splittings are observed (cf. Ref. 25) and consequently in this case the field gradient tensor may occupy all directions with respect to the external magnetic field in a time short compared to the inverse quadrupole interaction.

(v) For lamellar phases, substitution of heavy water for ordinary water leads to a marked increase in ^{23}Na powder splitting (Table 4). Since sample alignment almost eliminates this isotope effect (Table 4) we may attribute the difference between D_2O- and H_2O-samples to differences in rate of exchange between the microcrystallites (i.e., caused by a change in S_{ex}). This exchange is thus slowed down considerably on introduction of D_2O instead of H_2O. It can be observed in this connection that the translational motion(26) of sodium ions in aqueous solution is markedly retarded on substitution of D_2O for H_2O.

In light of the exchange phenomena described above the data on the concentration dependences of the powder splittings cannot be interpreted solely in terms of molecular interactions; and, therefore, these data will be given at a later date when more detailed

TABLE 4 ^{23}Na quadrupole splittings for H_2O- and D_2O-containing powdered, $\Delta_p^{(1)}$, and oriented, $\Delta_{90}^{(1)}$, lamellar mesophase samples for the sodium octanoate–decanol–water system

	Sample composition sodium octanoate : decanol : water (mole-%)	
	7.6 : 9.5 : 83.0	10.8 : 11.7 : 77.5
$\Delta_p^{(1)}$ (H_2O)(kHz)	2.7	2.9
$\Delta_p^{(1)}$ (D_2O)(kHz)	4.4	3.5
$\Delta_{90}^{(1)}$ (H_2O)(kHz)	5.0	—
$\Delta_{90}^{(1)}$ (D_2O)(kHz)	5.6	—

information on the splittings of oriented samples has been collected.

Pertinent information on mesophase structure could be obtained on the phase in the ternary system sodium octanoate–decanol–water denoted *C* by Ekwall *et al.*(14) For this phase large ^{23}Na splittings were observed (Table 3) whereas at almost the same sample composition lamellar mesophase samples showed no resolved splittings. Thus the structure of the *C* phase must deviate considerably from the lamellar arrangement and it appears not to be possible to reconcile the proposal(27) that the *C* phase is a " flocculated emulsion of lamellar *D* in a small amount of micellar solution " with our findings. In contrast with lamellar phases, for the *C* phase the ^{23}Na splitting increases with increasing water content, a behaviour which was found also for some hexagonal phases.(25) This is consistent with the proposal of Ekwall *et al.*(14) that the *C* phase is built up of long aggregates constituted of amphiphilic molecules.

Model Membrane Systems

The information on the interactions between small ions and biological membranes is rather limited and this fact can largely be attributed to a lack of suitable experimental methods. Nuclear magnetic resonance, giving a negligible perturbation of the system, is a promising possibility in this respect. One of our reasons for studying quadrupole splittings is to investigate the potential use of this method for the study of ion binding in biological systems. As a first step in this direction we have studied quadrupole splittings of ionic nuclei for phospholipid-containing lamellar mesophases. Such phases can serve as models,(28) although primitive, of biological membranes.

Observed ^{23}Na quadrupole splittings of powdered lamellar mesophase samples composed of egg yolk lecithin, cholesterol, aqueous alkali chloride(s) solutions and of egg yolk lecithin, alkali chloride and water are given in Table 5. (Preliminary experiments have shown that the temperature dependence of the splitting is small and, therefore, S_{ex} can be assumed to be close to unity in this case.) For the cholesterol-containing samples an increase in ^{23}Na quadrupole interaction with increasing cholesterol content was observed. This observation may be rationalized in terms of a decrease in the distance between the lecithin head-groups (cf. the discussion on the octanoate

TABLE 5 Observed ^{23}Na quadrupole splittings for some phospholipid containing powdered lamellar mesophase samples. Concentration in per cent by weight. Temperature 27 °C.

Sample composition lecithin : cholesterol : alkali chloride solution	(composition)	$\Delta_p^{(1)}$ (kHz)
55.9 : 24.7 : 19.4	(0.8 M NaCl)	25
63.6 : 16.4 : 20.0	(0.8 M NaCl)	21
80.0 : — : 20.0	(0.8 M NaCl)	18
72 : 8.0 : 20.0	(0.4 M LiCl + 0.4 M NaCl)	21
72 : 8.0 : 20.0	(0.4 M KCl + 0.4 M NaCl)	19
72 : 8.0 : 20.0	(0.4 M CsCl + 0.4 M NaCl)	20

lamellar system given above). This is compatible with the results obtained with other methods. Thus calculations from X-ray data(29) have shown that the partial area of lecithin, on the lamellar surface, diminishes when cholesterol is added. One of the inferences following from electron spin resonance spin label studies,(30, 31) was that the distance in the lamellar plane between particular points on adjacent phospholipids, e.g., the phosphorus atoms, may decrease with increasing cholesterol content. ^{13}C nuclear magnetic relaxation data,(32) high resolution proton NMR(33) and other types of NMR measurements(34) are also consistent with this conclusion. As can be seen from the competition experiments (see Table 5) no pronounced difference between the binding of the different alkali ions can be inferred. This observation pertains both to the lecithin–alkali cholate–water system and the lecithin–alkali chloride–cholesterol–water system. In order to obtain results of biological significance we will undertake studies on different types of phospholipids as well as on samples where proteins are present.

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REFERENCES

1. Bryant, R. G., *Biochem. Biophys. Res. Commun.* **40,** 1162 (1970).
2. Andrasko, J., Lindqvist, I. and Bull, T. E., *Chemica Scripta* **2,** 93 (1972).
3. James, T. L. and Noggle, J. H., *Proc. Nat. Acad. Sci. U.S.* **62,** 644 (1969).
4. Lindman, B. and Lindqvist, I., *Chemica Scripta* **1,** 195 (1971).
5. Lindman, B. and Ekwall, P., *Mol. Cryst.* **5,** 79 (1968).
6. Robb, I. D., *J. Colloid Interface Sci.* **37,** 521 (1971).
7. Lindman, B. and Danielsson, I., *J. Colloid Interface Sci.* **39,** 349 (1972).
8. Lindblom, G. and Lindman, B., *Mol. Cryst. and Liq. Cryst.* **14,** 49 (1971).
9. Lindblom, G., Wennerström, H. and Lindman, B., *Chem. Phys. Lett.* **8,** 849 (1971).
10. Lindblom, G., *Acta Chem. Scand.* **25,** 2767 (1971).
11. Lindblom, G., *Acta Chem. Scand.* **26,** 1745 (1972).
12. Singleton, W. S., Gray, M. S., Brown, M. L. and White, J. L., *J. Amer. Oil Chem. Soc.* **42,** 53 (1965).
13. Cohen, M. H. and Reif, F., *Sol. State Phys.* **5,** 321 (1957).
14. Ekwall, P., Mandell, L. and Fontell, K., *Mol. Cryst. and Liq. Cryst.* **8,** 157 (1969).
15. Persson, N.-O., Wennerström, H. and Lindman, B., *Acta Chem. Scand.*, in the press.
16. Butler, K. W., Dugas, H., Smith, I. C. P. and Schneider, H., *Biochem. Biophys. Res. Commun.* **40,** 770 (1970); Seelig, J., *J. Amer. Chem. Soc.* **92,** 3881 (1970).
17. Graber, E., Lang, J. and Zana, R., *Kolloid-Z. Z. Polym.* **238,** 470 (1970).
18. Gustavsson, H. and Lindman, B., *J.C.S. Chem. Commun.* **1973,** 93.
19. Démareq, M. and Dervichian, D., *Bull. Soc. Chim.* **12,** 939 (1945).
20. Gallot, B. and Skoulios, A., *Kolloid-Z. Z. Polym.* **208,** 37 (1966).
21. Sears, D. F. and Schulman, J. H., *J. Phys. Chem.* **68,** 3529 (1964).
22. Goddard, E. D., *Croatica Chem. Acta* **42,** 143 (1970).
23. Hertz, H. G., *Progress in NMR Spectroscopy*, Vol. III, Pergamon Press, Oxford, 1967, p. 159.
24. Lindblom, G. and Lindman, B., *Proc. Intern. Congr. Surface Active Agents, 6th, Zürich, 1972,* in the press.
25. Lindblom, G., Persson, N.-O. and Lindman, B., *Proc. Intern. Congr. Surface Active Agents, 6th Zürich, 1972,* in the press.
26. Swain, C. G. and Evans, D. F., *J. Amer. Chem. Soc.* **88,** 383 (1966).
27. Tiddy, G. J. T., *J.C.S. Faraday I* **68,** 379 (1972).
28. See, *e.g.* Williams, R. M. and Chapman, D., *Progr. Chem. Fats Other Lipids* **11,** 1 (1970).
29. Lecuyer, H. and Dervichian, D. G., *J. Mol. Biol.* **45,** 39 (1969).
30. Hubell, W. L. and McConnell, H. M., *J. Amer. Chem. Soc.* **93,** 314 (1971).
31. Hsia, J.-C., Schneider, H. and Smith, I. C. P., *Can. J. Biochem.* **49,** 614 (1971).
32. Levine, Y. K., Partington, P., Roberts, G. C. K., Birdsall, N. J. M., Lee, A. G. and Metcalfe, J. C., *FEBS Letters* **23,** 203 (1972).
33. Darke, A., Finer, E. G., Flook, A. G. and Phillips, M. C., *J. Mol. Biol.* **63,** 265 (1972).
34. Oldfield, E. and Chapman, D., *FEBS Letters* **23,** 285 (1972).