

## Studies of Lyotropic Mesophases Containing Ionic Amphiphiles by Means of $^2\text{H}$ and $^{23}\text{Na}$ Resonance

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Liquid crystalline phases, mainly of the lamellar type, formed in ternary amphiphile-water systems, have been studied by means of deuterium and  $^{23}\text{Na}$  resonance. The following systems have been investigated: sodium caprylate-caprylic acid-water, sodium caprylate-decanol-water, sodium octylsulphate-decanol-water, sodium octylsulphonate-decanol-water, and cetyltrimethylammonium bromide-hexanol-water.

The deuterium resonance from  $\text{D}_2\text{O}$  exhibits quadrupole splittings in the approximate range 0–4 kHz. This effect is partly due to partial orientation of water molecules, and partly due to deuterium exchange between water and amphiphilic molecules. The dependence of the quadrupole splitting on sample composition and temperature has been investigated. An increase in the degree of counter-ion binding, as evidenced by an increase in the  $^{23}\text{Na}$  resonance linewidth, is often accompanied by a decrease in the deuterium quadrupole splitting. In systems containing aliphatic alcohols, the quadrupole splitting strongly increases at increasing temperature, and this is attributed to deuterium exchange between hydroxyl groups and water molecules.

Liquid crystalline phases, formed by amphiphilic compounds and water, have been a subject of investigation by various experimental techniques.<sup>1</sup> An important method for the structural investigation of these systems is X-ray diffraction, which has led to the characterization of various mesophase structures on the basis of the geometrical arrangement of the amphiphilic molecules.<sup>2-5</sup> NMR methods have also been applied to the study of lyotropic mesophases.<sup>6,7</sup> A particular application of NMR, which has been used in the present investigation and which was first discovered by Flautt and Lawson,<sup>8</sup> is the measurement of the deuterium quadrupole splitting in water molecules, situated in anisotropic mesophases. This method has been subsequently used by several authors,<sup>9-13</sup> and the quadrupole splitting is shown to originate from partial orientation of water molecules,<sup>9</sup> and, in some cases, also from rapid deuterium exchange between water and amphiphilic molecules.<sup>13</sup> The origin of the quadrupole splitting and different mechanisms of water orienta-

tion have been discussed by Johansson and Drakenberg.<sup>13</sup> With the purpose of obtaining more extensive experimental data about these phenomena we have measured the deuteron quadrupole splitting in various anisotropic mesophases built up from ionic and nonionic amphiphiles and water. Most phases were of the lamellar type,<sup>2-5</sup> *i.e.* they consisted of alternating amphiphilic and water layers. However, we have also studied a few hexagonal phases, which are built up from a hexagonal array of rod-shaped micelles of indefinite length.<sup>2-5</sup> The lamellar mesophase is particularly interesting as a model system for biological membranes.<sup>3</sup>

### EXPERIMENTAL

*Sample preparation.* Mesophases in the following systems have been investigated (the notation  $C_x$  is used for an n-aliphatic chain containing  $x$  carbon atoms):  $C_7\text{COONa}-D_2O$ ,<sup>14</sup>  $C_7\text{COONa}-C_{10}\text{OH}-D_2O$ ,<sup>15</sup>  $C_8\text{OSO}_2\text{Na}-C_{10}\text{OH}-D_2O$ ,<sup>4</sup>  $C_8\text{OSO}_2\text{Na}-C_{10}\text{OH}-D_2O$ ,<sup>4</sup> and  $C_{16}\text{NMe}_3\text{Br}$  (CTAB)- $C_8\text{OH}-D_2O$ .<sup>16</sup> The phase diagrams for the various systems are given in the references cited.  $C_7\text{COONa}$ ,  $C_{10}\text{OH}$ ,  $C_8\text{OH}$  and CTAB were purchased from British Drug Houses Ltd., Poole, England, and  $C_8\text{OSO}_2\text{Na}$  and  $C_8\text{OSO}_2\text{Na}$  were obtained from Schuchardt, Switzerland, and Aldrich, U.S., respectively. The purity was better than 99 % for all chemicals, except  $C_8\text{OH}$  (> 95 %). The CTAB was recrystallized once from ethanol. Deuterium oxide was purchased from Norsk Hydro, Norway, and the enrichment was 99.8 %.

The samples were prepared by weight in 9 mm tubes which were immediately sealed off. A *ca.* 5 mm glass bead was also present in each tube, which facilitated the mixing of the samples. In most cases, the mixing was performed by shaking at a temperature above the mesomorphic - isotropic transition, but in the samples containing sodium octylsulfate and sodium octylsulfonate, hydrolysis probably occurred at this temperature. These systems were therefore mixed by shaking at *ca.* 70°C. After careful mixing, the temperature was slowly decreased to room temperature.

*NMR measurements.* A Varian V-4200 wide-line spectrometer, equipped with a 12 inch V-3603 magnet, was used for the measurements. The magnetic field was regulated by a Varian Mark II Fieldial unit, and the sample temperature was controlled by means of a Varian V-4540 Temperature Controller. The actual temperature was measured using a copper-constantan thermocouple, and was found to be accurate within  $\pm 0.3^\circ$ . Unless otherwise specified, all measurements were made at 20°C. In the CTAB- $C_8\text{OH}-D_2O$ , the sample temperature was 25°C in most cases.

The deuteron resonance was studied at the r.f. frequency 9.1786 MHz, and the variable frequency oscillator of the spectrometer was stabilized to within  $\pm 1$  Hz by means of an external crystal oscillator. Appropriate magnitudes of the r.f. power, sweep time and response time were chosen to avoid measurable distortion of the lineshape. For quadrupole splittings larger than *ca.* 0.5 kHz, the derivative of the absorption spectrum was recorded, using a 20 - 40 Hz modulation of the magnetic field, and a small modulation amplitude. For smaller quadrupole splittings, the first sideband of the absorption line was detected, using a modulation frequency of 400 Hz, and a large modulation amplitude. In the first case, the measured values of the quadrupole splitting were evaluated according to a previously described procedure,<sup>13</sup> and the standard deviation was found to be less than 5 %. In the second case, the splitting was measured as the distance between the two inflection points, corresponding to the extreme values of the derivative, and the standard deviation in this case did not exceed *ca.* 8 %. In a few samples, the quadrupole splitting was so small ( $\leq 0.1$  kHz) that it was totally masked by the line broadening, and consequently only an upper limit could be established for the quadrupole splitting, which was taken to be the width of the absorption signal at half maximum. This value was corrected by subtraction of the linewidth measured for pure  $D_2O$ , which is essentially equal to the magnetic field inhomogeneity, usually *ca.* 3  $\mu\text{T}$ .\* (The deuteron relaxation time in  $D_2O$  at 25°C<sup>17</sup> corresponds to a natural linewidth of 0.11  $\mu\text{T}$ .)

\* The magnetic field unit in the SI system is Tesla (T), 1 T = 10<sup>4</sup> gauss.

The  $^{23}\text{Na}$  resonance measurements were carried out at 15.821 MHz (also stabilized to within  $\pm 1$  Hz), and the first sideband of the absorption signal was chosen for the linewidth measurements. The modulation frequency was also in this case 400 Hz. The experimental linewidth was corrected for magnetic field inhomogeneity in the following way. The linewidth of the  $^{23}\text{Na}$  resonance signal in 1 M NaBr water solution was first measured, and from this value, the magnetic field inhomogeneity was calculated by subtracting the natural linewidth of the sample,  $0.51 \mu\text{T}$ , as calculated from relaxation data.<sup>18</sup> The magnetic field inhomogeneity was then subtracted from the measured linewidths.

The procedure used to correct for magnetic field inhomogeneities is only strictly valid if they give rise to Lorentzian lineshapes, and this is only approximately true. Therefore, the estimated errors in the corrected linewidths in the region of  $2 \mu\text{T}$  may be as large as ca. 10 %, while for larger linewidths, the error is less.

A few proton resonance spectra were recorded using a Varian A60-A spectrometer.

### THEORY

The general theory of quadrupole coupling was developed by Cohen and Reif.<sup>19</sup> In polycrystalline samples, the quadrupole coupling gives rise to characteristic powder patterns, from which its magnitude may be evaluated. In liquid crystals, the molecular motion is often restricted, and therefore, in anisotropic phases, the molecules usually have some degree of partial orientation. For nuclei with a non-zero quadrupole moment, *i.e.* nuclei for which  $I > 1$ , this partial orientation can give rise to an observable quadrupole splitting, which is usually considerably smaller than that observed in the solid state. In liquid crystalline "powders", *i.e.* phases in which all crystallite orientations are equally probable, powder patterns may also be observed. This has been demonstrated for the case of  $\text{D}_2\text{O}$  in anisotropic mesomorphic phases of amphiphilic and water molecules.<sup>8-13</sup> The observed splitting has been interpreted as being due to partial orientation of water molecules,<sup>8-11,13</sup> but for systems in which the amphiphilic molecules contain exchangeable protons, rapid exchange between amphiphilic and water deuterons may also contribute to the quadrupole splitting.<sup>12,13</sup>

Partial molecular orientation can generally be described by the method of Saupe,<sup>20</sup> which was subsequently applied to quadrupole interaction by Buckingham and McLauchlan.<sup>21</sup> As previously demonstrated,<sup>13</sup> this leads to the following expression for the quadrupole splitting observed in partially oriented  $\text{D}_2\text{O}$  molecules:

$$\Delta\nu = \left| \frac{3e^2qQ}{2h} S \left\langle \frac{3}{2} \cos^2\Omega - \frac{1}{2} \right\rangle \right| \quad (1)$$

Here,  $\Delta\nu$  is the quadrupole splitting,  $eq$  is the principal tensor component of the electric field gradient (EFG) at the position of the deuterons,  $eQ$  is the deuteron quadrupole moment,  $h$  is Planck's constant,  $S$  is a parameter characterizing the partial orientation of the  $\text{D}_2\text{O}$  molecules, and  $\Omega$  is the angle between the direction of the constraint responsible for the molecular orientation and the applied magnetic field. This expression is valid under the assumptions that the  $\text{D}_2\text{O}$  molecules are rapidly reorienting, and that the EFG is axially symmetric. In a liquid crystalline "powder", a pattern similar to that observed in solids will result, but the width will be reduced by the factor

$S$ . The frequency separation between the absorption maxima in this pattern is given by  $\Delta\nu = 3e^2qQ S/4h$ . (The factor  $e^2qQ/h$  will in the following be denoted by  $E_Q$ .) The influence of the asymmetry of the EFG in the  $D_2O$  molecules on the validity of eqn. 1 has been discussed by Johansson and Drakenberg.<sup>13</sup> Under the further assumption that the principle component of the EFG tensor is directed along the O–D bond, the  $S$  parameter may be expressed in the following way:<sup>13,21</sup>

$$S = S_{11} \cos^2 \beta + S_{22} \sin^2 \beta \quad (2)$$

In this equation,  $S_{11}$  and  $S_{22}$  are two independent orientation matrix elements,<sup>21</sup> which can have any value between 1 and  $-\frac{1}{2}$ , and  $\beta$  is half the D–O–D angle in  $D_2O$  ( $\beta = 52^\circ 16'$ ). In the case of isotropic orientation, all orientation matrix elements equal zero, and consequently the quadrupole splitting will then vanish. Variations in the quadrupole splitting may be attributed to changes in the  $S$  parameter, while the value of  $E_Q$  is expected to be essentially constant in the systems investigated.<sup>13</sup> The value of the  $S$  parameter depends both on the *degree* of partial orientation and on the *direction* of preferred orientation relative to the direction of the constraint,<sup>13</sup> and both these factors must in general be considered in the interpretation of the quadrupole splittings.

The mechanism by which the water molecules become oriented can be thought of as a specific interaction between water and oriented amphiphilic molecules, and in this process, hydrogen bonding, ion-dipole and/or dipole-dipole interaction are probably important.<sup>13</sup> A change in the  $S$  parameter can, according to this description, arise both from a change in the amphiphile-water interaction and from an altered degree of orientation of the amphiphilic molecules, and these effects cannot generally be separated.

In cases where deuterons can exchange between amphiphilic and water molecules, such as in amines, alcohols, and carboxylic acids, the appearance of the spectrum will depend on the rate of exchange.<sup>13</sup> When this rate is slow, compared with the inverse difference in quadrupole splitting between the water and amphiphilic deuterons, separate resonance signals will be observed, as found in the system  $C_8NH_3Cl - D_2O$ .<sup>13</sup> If, on the other hand, the rate of exchange is rapid on the same time scale, an average quadrupole splitting,  $\langle \Delta\nu \rangle$ , will be observed in accordance with the following expression:<sup>13</sup>

$$\langle \Delta\nu \rangle = x_w \Delta\nu_w + \sum_i x_{ai} \Delta\nu_{ai} \quad (3)$$

Here,  $x_w$  and  $x_{ai}$  denote the fractions of deuterons in water and in the  $i$ :th chemically distinguishable position in the amphiphilic molecule, respectively, and  $\Delta\nu_w$  and  $\Delta\nu_{ai}$  are the corresponding quadrupole splittings at slow exchange. Rapid deuteron exchange has been found in amine–water systems, while slow exchange seems to occur in some alcohol–water systems.<sup>13</sup>

Quadrupole splitting can also be expected to be found in the NMR spectra of counter-ions in anisotropic mesophases, and investigations by Lindblom *et al.*<sup>22a</sup> provide evidence for such effects in the  $^{35}Cl$  resonance in lamellar phases of  $C_8NH_3Cl - C_{10}OH - H_2O$ . For nuclei having half-integer spin quantum numbers, such as the stable chlorine, bromine, and sodium

isotopes, a central component of the resonance line will always be observed even in the presence of quadrupole splitting. This central component may only be affected by second order quadrupole coupling<sup>19</sup> (*cf.* also Ref. 22a). If second order effects may be neglected and if the shape of the central component is not affected by first order quadrupole coupling, the linewidth will be proportional to the inverse of the transverse relaxation time,  $T_2$ , irrespective of the possible existence of quadrupole splittings. Under conditions of extreme narrowing,  $T_2$  is equal to the longitudinal relaxation time,  $T_1$ , and under such conditions the linewidth is therefore proportional to  $1/T_1$ , which, for the case of quadrupole relaxation, is given by<sup>23</sup>

$$\frac{1}{T_1} = \frac{3}{40} \frac{4I(I+1)}{I^2(2I-1)^2} \left(\frac{eQ}{\hbar}\right)^2 \langle q^2 \rangle \tau_c \quad (4)$$

where  $I$  is the nuclear spin quantum number,  $\langle q^2 \rangle$  is the mean square of the EFG at the nucleus, and  $\tau_c$  is the correlation time, characterizing the random molecular motion producing the fluctuating EFG's. The linewidth is thus proportional to the product of  $\langle q^2 \rangle$  and the correlation time, and a separation of these contributions is difficult to make. As discussed in several investigations of counter-ion binding in amphiphile-water systems,<sup>24,25</sup> an increase in the linewidth can often be interpreted as a stronger bonding of the counterions to the amphiphile molecules.

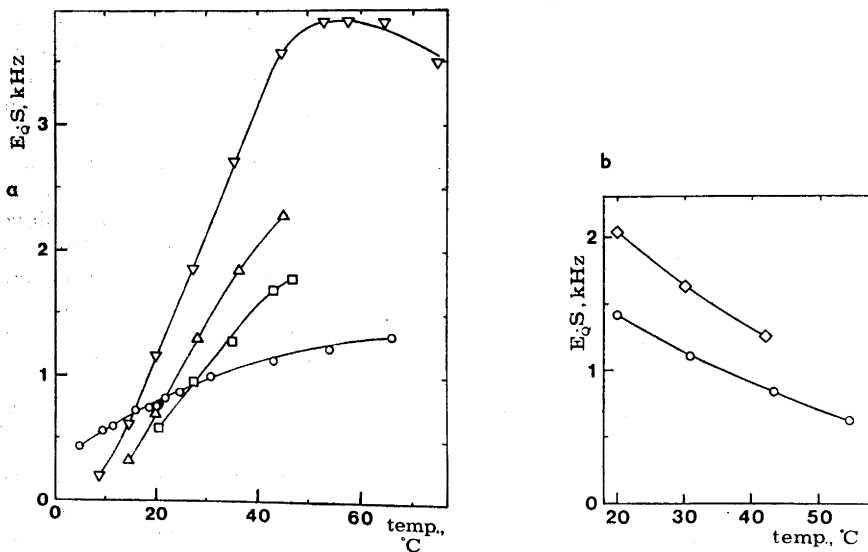


Fig. 1. Temperature dependence of  $E_Q S$  in some lamellar phases. The molar ratio of ionic amphiphile to total amphiphile is denoted by  $R_{ionic}$ .

a.  $\nabla$   $C_7COONa-C_{10}OH-D_2O$ ,  $x_{D_2O}=0.78$ ,  $R_{ionic}=0.48$ ;  $\Delta$   $C_8OSO_3Na-C_{10}OH-D_2O$ ,  $x_{D_2O}=0.77$ ,  $R_{ionic}=0.42$ ;  $\square$   $C_8OSO_2Na-C_{10}OH-D_2O$ ,  $x_{D_2O}=0.77$ ,  $R_{ionic}=0.50$ ;  $\circ$   $CTAB-C_8OH-D_2O$ ,  $x_{D_2O}=0.80$ ,  $R_{ionic}=0.37$ .

b. The system  $C_7COONa-C_7COOH-D_2O$ ,  $x_{D_2O}=0.77$ .  $\diamond$   $R_{ionic}=0.452$ ;  $\circ$   $R_{ionic}=0.606$ .

## RESULTS

The deuteron quadrupole splitting was measured in the following lamellar mesophases:  $C_7COONa-C_7COOH-D_2O$ ,  $C_7COONa-C_{10}OH-D_2O$ ,  $C_8OSO_3Na-C_{10}OH-D_2O$ ,  $C_8OSO_2Na-C_{10}OH-D_2O$ , and  $CTAB-C_6OH-D_2O$ . For the last system, measurements have also been carried out in the hexagonal phase. In Fig. 1 a and b, the temperature dependence of  $E_QS$  in various lamellar phases is illustrated. (Since the value of  $\bar{E}_Q$  is not known, we will use the parameter  $E_QS$  to describe the partial orientation.) Fig. 1a refers to systems containing aliphatic alcohols, whereas Fig. 1b refers to the system  $C_7COONa-C_7COOH-D_2O$ .

The composition of the mesophases was varied within their limits of stability, either by changing the water concentration at a constant ratio between the two amphiphiles, or by changing this ratio at a constant mol fraction of  $D_2O$ . In Fig. 2a,  $E_QS$  is plotted *vs.* the mol fraction of  $D_2O$  in the various systems. Besides the data given in Fig. 2a, the deuteron resonance has also been studied in the hexagonal phase of the system  $CTAB-C_6OH-D_2O$ . Since the linewidths are generally very small (in the region of 0.05 kHz), the significance of  $E_QS$  evaluated from the linewidths is doubtful. We have listed the values in Table 1.

Table 1. Maximum values of  $E_QS$  evaluated from the linewidth of the deuteron resonance in the hexagonal phase of the system  $CTAB-C_6OH-D_2O$  at 25°C ( $x$  denotes mol fraction).

$x_{D_2O}$	$x_{C_6OH}$	$(E_QS)_{max}$ , kHz
0.972	0.000	0.013
0.975	0.003	0.015
0.970	0.008	0.051
0.913	0.015	0.107

In the system  $C_8OSO_3Na-C_{10}OH-D_2O$ , the width of the  $^{23}Na$  resonance line was also measured at various water contents and a constant ratio between the amphiphiles. The results are illustrated in Fig. 2b.

In Fig. 3a, the parameter  $E_QS$  is shown as a function of the ratio ionic amphiphile/total amphiphile\* at a constant mol fraction of  $D_2O$ , and in Fig. 3b, the corresponding  $^{23}Na$  linewidth is shown for the systems  $C_7COONa-C_7COOH-D_2O$  and  $C_8OSO_3Na-C_{10}OH-D_2O$ .

## DISCUSSION

In previous work<sup>13</sup> it was shown that deuteron exchange between water and amphiphile molecules may strongly influence the magnitude of the deu-

\* The term ionic amphiphile refers to salt-like compounds, whereas for example fatty acids will be referred to as non-ionic amphiphiles.

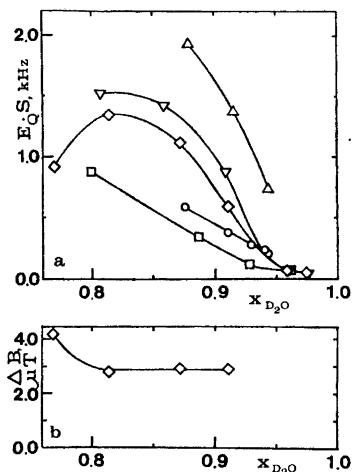


Fig. 2. a.  $E_{QS}$  as a function of mol fraction of  $D_2O$  in various lamellar mesophases. ○  $C_7COONa-C_7COOH-D_2O$ ,  $R_{ionic} = 0.31 \pm 0.02$ ; △  $C_7COONa-C_{10}OH-D_2O$ ,  $R_{ionic} = 0.27$ ; ◇  $C_8OSO_3Na-C_{10}OH-D_2O$ ,  $R_{ionic} = 0.31$ ; ▽  $C_8OSO_3Na-C_{10}OH-D_2O$ ,  $R_{ionic} = 0.31$ ; □ CTAB- $C_8OH-D_2O$ ,  $R_{ionic} = 0.37 \pm 0.01$  (temp.  $\approx 25^\circ C$ ).

b. Linewidth of the  $^{23}Na$  resonance signal as a function of mol fraction of  $D_2O$  for the system  $C_8OSO_3Na-C_{10}OH-D_2O$  (same samples as in a).

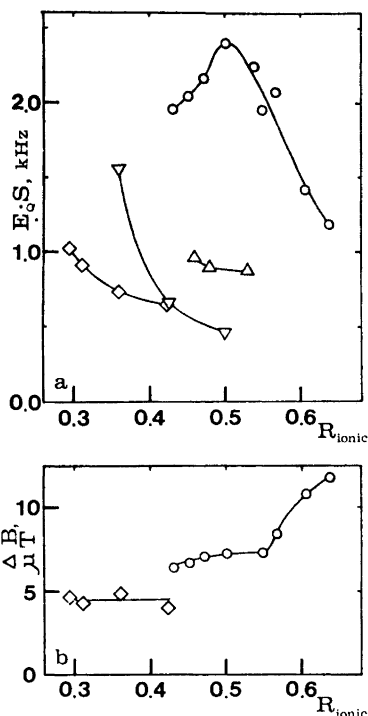


Fig. 3. a.  $E_{QS}$  as a function of  $R_{ionic}$  (defined as in Fig. 1) for various lamellar phases with a constant mol fraction of  $D_2O$  equal to 0.77. Symbols as in Fig. 2a.

b. Linewidth of the  $^{23}Na$  resonance signal as a function of  $R_{ionic}$  for samples in the  $C_8OSO_3Na-C_{10}OH-D_2O$  and  $C_7COONa-C_7COOH-D_2O$  systems. Symbols as in Fig. 2a.

teron quadrupole splitting in anisotropic mesophases containing  $D_2O$ . Therefore, before going into the interpretation of the variation in  $E_{QS}$  at different mesophase compositions, we must establish whether or not such exchange phenomena are operative.

From the temperature dependence of the quadrupole splitting it is evident that in all systems containing amphiphiles with hydroxyl groups, an increase in  $E_{QS}$  is observed with increasing temperature (Fig. 1a). Besides the increased splitting, a variation in the line-broadening is also observed: starting with rather narrow lines at low temperature, the linewidth goes through a maximum

in the intermediate temperature region, and decreases at high temperature. This effect is especially significant in the system  $C_7COONa-C_{10}OH-D_2O$ . The described change in lineshape is that expected from exchange effects,<sup>13</sup> and we therefore conclude that the hydroxyl deuteron exchange is slow at low temperature (under *ca.* 20°C) and increases at higher temperature. In the system  $C_7COONa-C_{10}OH-D_2O$ , a maximum in the quadrupole splitting is observed at *ca.* 50°C, and this may indicate that the rapid exchange limit has been reached. (The meaning of the terms "rapid" and "slow" exchange was explained in the preceding section.)

The deuteron (or proton) exchange between hydroxyl groups and water molecules has preliminarily been studied also by variation of the pH. The hydroxyl proton exchange is known to be both acid- and base-catalyzed.<sup>26</sup> In an isotropic solution of  $H_2O$  in  $C_{10}OH$ , separate *proton* resonance signals are observed at 37°C for hydroxyl and water protons. Addition of a very small amount of  $C_7COONa$  suffices to increase the rate of exchange to the extent that coalescence of these signals occurs. In the lamellar phase of  $C_7COONa-C_{10}OH-D_2O$ , the hydroxyl deuteron exchange rate at 20°C is slow enough to give rise to separate resonance signals from water and hydroxyl deuterons (only the water signal is observable for intensity reasons). Upon addition of small amounts of  $NaOH$ , a drastic increase in the quadrupole splitting is observed, which can be attributed to an increase in the hydroxyl deuteron exchange rate (*cf.* above). The same effect is also observed in the systems  $C_8OSO_3Na-C_{10}OH-D_2O$  and  $C_8OSO_2Na-C_{10}OH-D_2O$ .

However, since the quadrupole splitting is also temperature dependent when the line-broadening is approximately constant, we believe that other factors than chemical exchange are responsible for the temperature dependence of the splitting. As will be discussed later in this section, there is some evidence that the quadrupole splitting decreases with increasing degree of counter-ion binding. This might be an explanation for the continuous decrease in  $E_QS$  with decreasing temperature (Fig. 1a).

At the temperature of measurement used in studying the influence of mesophase composition on  $E_QS$  (usually 20°C), there is a strong temperature dependence of this parameter. However, there is no pronounced line-broadening of the peaks (possibly with the exception of the system  $C_7COONa-C_{10}OH-D_2O$ ) which indicates that exchange phenomena do not primarily influence the value of  $E_QS$  in this temperature region. In the  $C_7COONa-C_{10}OH-D_2O$  system, the comparatively strong basicity of the carboxylate anion may give rise to a greater hydroxyl deuteron exchange rate due to base-catalysis (*cf.* Ref. 26). In the system  $C_8OSO_3Na-C_{10}OH-D_2O$ , a preliminary investigation of the temperature dependence of  $E_QS$  at high water content shows the same qualitative features as in Fig. 1a. We therefore assume that the quadrupole splitting measured at 20–25°C in the presence of hydroxylic amphiphiles is primarily that of the water deuterons (this is only approximately true in the system  $C_7COONa-C_{10}OH-D_2O$ ).

In the system  $C_7COONa-C_7COOH-D_2O$ , a decrease in  $E_QS$  is observed with increasing temperature (Fig. 1b). The same qualitative temperature dependence is observed at two different compositions. In carboxylic groups, the deuteron exchange rate is expected to be orders of magnitude larger than



for hydroxylic deuterons. Therefore, we assume that the deuteron exchange between water and carboxylic groups is rapid in the temperature region investigated. In this system, therefore, the splitting measured is probably the average of the splittings of water and carboxylic deuterons (*cf.* eqn. 3).

Concerning the investigation of the temperature dependence of  $E_QS$  it should be pointed out that the phase structure is in many cases well characterized only at one temperature (usually 20°C). However, in the temperature regions corresponding to the experimental points in Fig. 1 a and b, the line-shape of the deuteron resonance does not undergo any discontinuous changes, and the samples have the texture characteristic of lamellar phases. We therefore assume that the lamellar phase may persist in the temperature regions investigated. In most systems at high temperature, a central component appears in the spectra, which may indicate the presence of small amounts of an isotropic phase (*cf.* Ref. 13).

From Fig. 2a it is evident that an increased water content in the lamellar phase with a constant composition of the amphiphilic part of the system generally gives rise to a decrease in the value of  $E_QS$ . This is in agreement with previous observations.<sup>9,11-13</sup> (The observed minimum in  $E_QS$  on variation of the composition of the system  $C_{11}COOK-D_2O$ , reported in Ref. 11, has later proved to be non-reproducible.<sup>27</sup>) One possible explanation for this effect is based on the assumption of two types of sites for the water molecules: surfactant-associated and self-associated water.<sup>9</sup> Since only one resonance line is observed, the exchange between these two positions must be rapid.<sup>9</sup> At increased water contents, the relative amount of self-associated water is expected to increase, and since the self-associated water is essentially isotropic, the value of  $E_QS$  can be expected to decrease. The possible distinction between different types of water has also been discussed on the basis of X-ray investigations.<sup>15,28,29</sup>

A very simple model for the water layers in lamellar mesophases has been discussed by Johansson and Drakenberg,<sup>13</sup> and it has been shown that under certain assumptions,  $E_QS$  will be proportional to the mol fraction of amphiphile, *i.e.*  $1-x_{D_2O}$ , where  $x_{D_2O}$  is the mol fraction of  $D_2O$ . These assumptions are: (a) the mol fraction of surfactant-associated water is small compared with that of the self-associated water, (b) the mol fraction of surfactant-associated water is directly proportional to the mol fraction of amphiphile, (c) the self-associated water is essentially isotropic, and (d) the degree of orientation of the surfactant-associated water is constant. It is true that many objections can be raised against all these assumptions, but nevertheless, at least at high water contents, approximately linear relationships of the type described are observed in some systems (*cf.* Fig. 2a and Refs. 12 and 13). However, such a model can, of course, not be expected to be generally valid.

The physical state of water close to interfaces has been the subject of a large number of investigations.<sup>30,31</sup> In colloidal systems, various investigations indicate that characteristic changes in the physical properties of water reach a few molecular diameters into the water adjacent to the interface.<sup>30,31</sup> This gives some justification for the mechanism of orientation of water molecules in lamellar mesophases discussed above.

In the case of ionic amphiphiles, the properties of the water layer must be very much dependent on the concentration of counter-ions, which can reach values corresponding to one ionic group per a few water molecules. However, even in this case it is possible to conceive of at least two distinguishable sites for the water molecules, *i.e.* surfactant-associated and counter-ion-associated water, of which the latter, for symmetry reasons, can be assumed to be approximately isotropic with respect to water orientation, at least as long as the counter-ions are rapidly reorienting. That this in fact ordinarily occurs may be inferred from the linewidths of counter-ion resonance signals (*cf.* Figs. 2b, 3b and Refs. 22b and 25). If the counter-ions were undergoing slow reorientation, the absorption signals would be very strongly broadened due to rapid quadrupole relaxation (*cf.* eqn. 4). At high water contents in systems containing ionic amphiphiles, one may also consider a second isotropic site, corresponding to self-associated water.

Variations in the degree of counter-ion binding to the hydrophilic groups will give rise to changes in the amphiphile—water interaction and may consequently also influence the partial orientation of water molecules. The degree of counter-ion binding can be expected to increase at low water contents as well as at high contents of ionic amphiphile, and this is in fact observed in some systems as evidenced by an increased linewidth of the  $^{23}\text{Na}$  resonance signal (Figs. 2b, 3b and Ref. 25). In the systems investigated, an increased  $^{23}\text{Na}$  linewidth, *i.e.* a stronger counter-ion binding, is accompanied by a decrease in the value of  $E_Q S$ . A stronger counter-ion binding may reduce the possibilities for water orientation by means of hydrogen bonding to the hydrophilic groups, whereas a dipolar orientation mechanism seems more plausible. According to the discussion of different mechanisms of orientation given in Ref. 13, this would correspond to a smaller value of  $S$ . The influence of hydrogen bonding on the value of the quadrupole splitting is illustrated by the data in Table 1. In a hexagonal phase of the binary system CTAB— $\text{D}_2\text{O}$ , where there are no possibilities for hydrogen bonding between amphiphile and water molecules, the quadrupole splitting is close to zero. On addition of small amounts of  $\text{C}_6\text{OH}$ , the deuteron resonance linewidth increases significantly. This may be interpreted as an increase in the quadrupole splitting.

The values of  $E_Q S$  in lamellar mesophases with a constant mol fraction of  $\text{D}_2\text{O}$  and various ratios between ionic and non-ionic amphiphiles (Fig. 3a) confirm the previously reported observation<sup>13</sup> that an increased proportion of ionic amphiphile will as a rule give rise to a decrease in  $E_Q S$ . (The system  $\text{C}_7\text{COONa} - \text{C}_7\text{COOH} - \text{D}_2\text{O}$ , which shows exceptional behaviour, will be discussed below.) From a comparison of  $^{23}\text{Na}$  linewidth and the value of  $E_Q S$  in the system  $\text{C}_8\text{OSO}_3\text{Na} - \text{C}_{10}\text{OH} - \text{D}_2\text{O}$  (Fig. 3a and b) it is evident that the value of  $E_Q S$  decreases at higher proportions of ionic amphiphile even at an approximately constant degree of counter-ion binding (as judged from the  $^{23}\text{Na}$  linewidth). This may be attributed to an increased influence of a dipolar orientation mechanism for the surfactant-associated water molecules, since the ionic density on the lamellar surface will increase as the proportion of ionic amphiphile increases (*cf.* Ref. 15). This type of mechanism may also be operative in the systems  $\text{C}_8\text{OSO}_2\text{Na} - \text{C}_{10}\text{OH}$  and  $\text{C}_7\text{COONa} - \text{C}_{10}\text{OH} - \text{D}_2\text{O}$  (Fig. 3a).

The system  $C_7COONa - C_7COOH - D_2O$  behaves differently from the other systems investigated with respect to Fig. 3a. As mentioned above, we assume that deuteron exchange is rapid at  $20^\circ C$ , and that the resonance observed is actually the average of those due to carboxylic and water deuterons. The quadrupole splitting associated with the carboxylic deuterons is most probably larger than that associated with the water deuterons (*cf.* also Ref. 13). An decrease in the proportion of ionic amphiphile at constant water content could therefore be expected to lead to a higher value of  $E_Q S$  (*cf.* eqn. 3). This mechanism may in part be responsible for the observed increase in  $\bar{E}_Q S$ , as the proportion of ionic amphiphile decreases (see the right-hand part of Fig. 3a). It is apparent from Fig. 3b that there is a simultaneous decrease in the  $^{23}Na$  linewidth, and therefore the previously discussed effect of counter-ion binding may also contribute to the increase in  $E_Q S$  in this region of composition.

On further reduction of the proportion of ionic amphiphile, the value of  $E_Q S$  goes through a maximum, and finally decreases. The maximum value corresponds to equimolar amounts of soap and acid. This behaviour is exceptional, and we will only give a tentative and very hypothetical explanation. In a system of carboxylic acid and the corresponding salt, there are several possibilities for complex formation. In a lamellar phase, complex formation between the amphiphilic molecules would probably require geometrical rearrangements, which at first sight seem to be rather improbable. However, if complexes in some way are formed between the amphiphilic molecules in a lamellar mesophase, the interaction between water and amphiphilic molecules will probably be affected. If such complex formation involves hydrogen bonding, one might expect a decrease in the degree of partial orientation of the water molecules. In the isotropic  $L_2$  phase of the system  $C_7COONa - C_7COOH - H_2O$ , a 1:2 complex between soap and acid has been found,<sup>32,33</sup> but on the basis of the results of the present investigation it is not possible to even establish the *existence* of complex formation in the lamellar phase. We therefore refrain from going into any further discussion on this point.

From the  $^{23}Na$  linewidth data for the system  $C_7COONa - C_7COOH - D_2O$  in Fig. 3b, an interesting comparison can be made with X-ray investigations by Ekwall *et al.*<sup>34</sup> From the variation of the Bragg spacing in the lamellar phase with the water content, two different parts of the region of existence of the lamellar phase were distinguished.<sup>34</sup> Similar observations have been made in other lamellar phases.<sup>15,35,36</sup> In one of these regions, the "constantly expanding lamellar phase", no change in area per hydrophilic group occurs on the addition of water, while in the other, the "variably expanding phase", the area per hydrophilic group increases on the addition of water. The last region is only found in systems containing ionic amphiphiles, and the increase in area per hydrophilic group with increasing water content has been explained as an effect of ion hydration.<sup>15,34,35</sup> In the ternary systems containing both ionic and non-ionic amphiphiles it was found that as the proportion of non-ionic amphiphile increases, the lamellar phase is changed from the "variably expanding" to the "constantly expanding". This transition is expected to be accompanied by a release of counter-ions from the lamellar surface.<sup>34</sup> These ideas are supported by the observed decrease of the  $^{23}Na$  resonance linewidth, as the proportion of non-ionic amphiphile in the system  $C_7COONa - C_7COOH -$

D<sub>2</sub>O increases (Fig. 3b). The position of the discontinuity in the slope of the curve roughly corresponds to the composition range in which the limit between the two regions of lamellar phases is found.<sup>34</sup> Similar observations have been made in the system CTAB-C<sub>6</sub>OH-H<sub>2</sub>O, using Br resonance.<sup>22b</sup>

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