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^{2}H and ^{14}N NMR Studies of Amphiphilic Liquid Crystals: Effect of Solubilisation, Electrolyte and Temperature on Water Orientation

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^{2}H and ^{14}N NMR Studies of Amphiphilic Liquid Crystals

Effect of Solubilisation, Electrolyte and Temperature on Water Orientation

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Deuteron NMR on hexagonal and lamellar amphiphile —D_2O mesophases was employed to study the partial orientation of the water molecules and how the degree of orientation is influenced by solubilisation of organic compounds, by addition of simple electrolytes and by temperature changes. Solubilisation effects follow roughly the polarity of the solubilisate, a more polar solubilisate producing a greater reduction in the degree of water orientation, but important differences exist between —CO_2^- and —OSO_3^- end-groups of the surfactant. These results are discussed in terms of changes in amphiphile hydration and altered packing conditions in the aggregates. The effect of electrolyte addition depends markedly on both counter-ion and co-ion and is discussed on the basis of ion hydration. For the tetramethylammonium octanoate —D_2O system the degree of water orientation increases with increasing water content and this is suggested to arise from a particular counter-ion binding mechanism in this case. The counter-ion binding in this system as well as the ammonium octanoate —D_2O system was further studied by means of ^{14}N quadrupole splittings.

INTRODUCTION

The self-association of ionic amphiphile compounds in aqueous systems into micelles or extended aggregates building up liquid crystalline structures of different types[1,2] is governed not only by hydrophobic interactions[3] but also by interactions involving the polar end-groups. Thus head-group repulsions, hydration of head-groups and counter-ions as well as interactions between counter-ions and polar heads are critical for aggregate shape. The ionic interactions are characterized by a marked degree of specificity,[4] a specificity which in many instances involves counter-ion hydration phenomena. The counter-ion binding specificity is often displayed also in macroscopic properties of surfactant systems and is therefore of practical interest. The analogies between surfactant systems and biological lipid systems[5] have greatly stimulated the interest in amphiphilic systems. So, for example, an understanding of the general features of ion binding and hydration phenomena of lamellar mesophases may be of relevance in discussions of processes occuring in biological membrane systems.

Water in amphiphilic systems is thus far from playing the role of an inert solvent in which amphiphile self-association takes place. Instead the water molecules through specific interactions with both amphiphile polar heads and counter-ions play a key role in the association. It is significant to note that water molecules have been postulated to act as bridges both between a counter-ion and an amphiphile ion and between two amphiphile compounds one of which may be non-ionic.[4,6] The importance of these interactions has been thoroughly discussed in connection with studies of phase equilibria[2] and ion binding phenomena.[4]

These considerations point to the importance of elucidating the binding conditions of water molecules in amphiphile systems. It is thereby of interest to investigate how water binding changes with counter-ion, with amphiphile polar head and with temperature and also to investigate the relation between hydration and solubilisation and the effect of electrolyte addition on hydration. NMR studies of the interactions between water and various amphiphiles have been performed using both proton[7–9] and deuteron[7,10–12] NMR. The deuteron quadrupole splitting technique first used by Lawson and Flautt[11] offers a very sensitive probe of water orientation effects relative to an amphiphile aggregate surface. Also the counter-ion binding may be conveniently studied by the quadrupole splitting method.[13,14] Hitherto most studies have been performed with ^{23}Na as the resonant nucleus[15,16] but many other ions have also been considered.[17–19] (Although the quadrupole splitting method is only applicable to anisotropic phases it may be expected that many general features exist among different phases; with due caution information of the type obtained in the present study may be used to discuss hydration in micellar solutions, where NMR is much less informative.)

In a previous study[12] we have discussed the variation of water and amphiphile orientation with water content and counter-ion for a number of anionic surfactant systems. The present work is a report on the effect for some anionic amphiphile systems of the solubilisation of various organic compounds and of the addition of simple electrolytes on the water orientation. Furthermore, we discuss the variation of the degree of water orientation with temperature. Preliminary ^{14}N quadrupole splitting results of the ammonium and tetramethylammonium ions are used as to complement the ^{2}H measurements for certain systems to study the relation between hydration and counter-ion binding.

NUCLEAR QUADRUPOLE SPLITTINGS

The theory of static quadrupole effects in amphiphilic systems has recently been reviewed.[20,21] As these treatments are directly applicable to the present investigation only a brief account of the NMR background will be given here.

All nuclei with spin quantum numbers $I \geq 1$ have electric quadrupole moments. The interactions of these with inhomogeneous electric fields displace the Zeeman energy levels and thereby split the single Larmor frequency signal obtained in the absence of quadrupole interactions into $2I$ components. Both the nuclei considered in this study, ^{2}H and ^{14}N, have $I = 1$ and thus their NMR signals are split into two components. The quadrupole splitting, taken as the frequency separation between the two components, is large for rigid solids while for liquid crystals it is reduced as a result of rapid molecular motion. The resulting splitting depends on the degree of anisotropy imposed on the orientation of the field gradients by the liquid crystalline structure. The following expression of the quadrupole splitting applies

$$\Delta = |\nu_Q \cdot S(3\cos^2\theta_{\mathrm{LD}} - 1)| \tag{1}$$

Here $\nu_Q = \frac{3}{4} \cdot e^2qQ/h$, eq being twice the largest component of the electric field gradient tensor and eQ the nuclear electric quadrupole moment. (e^2qQ/h is conventionally termed the quadrupole coupling constant). θ_{LD} is the angle between the magnetic field (laboratory, L) and the director (D) i.e. the symmetry axis of the liquid crystal. The order parameter, S, characterizes the partial orientation of the field gradients relative to the director and is given by the following expression

$$S = \tfrac{1}{2}\{\overline{(3\cos^2\theta_{\mathrm{DM}} - 1)} + \eta\,\overline{\sin^2\theta_{\mathrm{DM}}\cos 2\phi_{\mathrm{DM}}}\} \tag{2}$$

θ_{DM} and ϕ_{DM} denote the eulerian angles β and γ, respectively, in the coordinate transformation from the director to the molecular (M) coordinate system. η is the asymmetry parameter describing the deviation from cylindrical symmetry of the field gradient tensor.

These considerations apply for a macroscopically oriented sample where the director axes have uniform orientation over the whole sample. Often so-called powder samples with randomly oriented director axes are considered and then a powder spectrum with a broad absorption results. The distance between the two major maxima will be referred to as the powder splitting and is given by

$$\Delta = |\nu_Q S| \tag{3}$$

In the present study only powder samples have been investigated. Representative ^{2}H and ^{14}N spectra obtained either by Fourier-transform or continuous-wave techniques are shown in Figure 1.

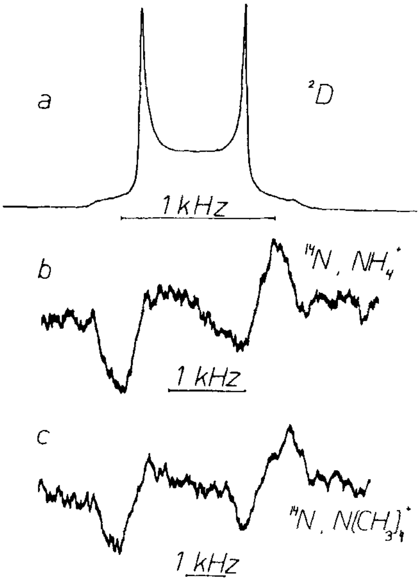

FIGURE 1 Examples of experimental NMR spectra. a) Pulsed-Fourier-transform ^2H spectrum of a hexagonal mesophase sample in the D_2O—C_7COONH_4 system. Molar fraction of water: 0.89. b) Continuous-wave wide-line ^{14}N spectrum of a lamellar mesophase sample in the D_2O—C_7COONH_4 system; molar fraction of water: 0.83. c) Spectrum as in b) of a hexagonal mesophase sample in the D_2O—$C_7COON(CH_3)_4$ system. Molar fraction of water: 0.80.

The quadrupole coupling constant of the deuteron in liquid D_2O has been estimated to be 220 kHz.[22] As the field gradients are of an intramolecular origin they can be assumed to be approximately unaffected by changes in composition, temperature etc. An observed ^2H quadrupole splitting of D_2O in a liquid crystal of 1 kHz, for example, therefore directly gives an order parameter of about $6 \cdot 10^{-3}$.

The situation will be quite different for ^{14}N in the ammonium or tetramethylammonium ions. Here the nucleus in the unperturbed free ion resides at a site of tetrahedral symmetry and, therefore, of vanishing net field gradients. The appearance of a ^{14}N quadrupole splitting therefore reflects a disturbance of the symmetrical situation. For monoatomic ions, the intermolecular field gradients arising from surrounding ionic charges and molecular dipoles explain the quadrupole splittings[14,20] and this mechanism will also be operative for the NH_4^+ and $(CH_3)_4N^+$ ions as well as for the BF_4^- ion which has been studied by ^{11}B NMR by Fujiwara *et al.*[23] Another mechanism by which field gradients may be created for symmetric polyatomic ions is by distortion from the symmetry due to bending or stretching of the bonds. The large intrinsic field gradients of the bonds will then no longer cancel and an effective quadrupole interaction results. This case has recently been examined theoretically by Bailey *et al.*[24] These authors considered ^1H dipolar and ^2H quadrupolar interactions of the NH_4^+ and ND_4^+ ions. From a typical value of the distortional increase in angle between two bonds of 0.026° a ^{14}N quadrupole splitting of ca. 9 kHz is predicted.[24] As will be seen below this is of the same order of magnitude as the splittings obtained in the present work. It is difficult to distinguish between the two interaction mechanisms but as the observed ^{14}N splittings are measures of the interactions between NH_4^+ or $N(CH_3)_4^+$ ions and the surfaces of the amphiphile aggregates, significant qualitative ion binding information may be obtained. We may also note that, as for monoatomic ions,[14,20] a separation of the factors ν_Q and S in Eq. (3) is difficult to achieve.

When discussing quadrupole splittings of either D_2O or counter-ions in lyotropic liquid crystals we must take into account the presence of different binding sites characterized by different intrinsic quadrupole splittings and chemical exchange between the different environments. Generally the fast exchange condition, where the residence time in a site is much smaller than the inverse splitting, may be assumed to apply and then

$$\Delta = |\textstyle\sum p_i \nu_Q^i S_i| \tag{4}$$

Here p_i is the fraction of nuclei in site i having an intrinsic quadrupole splitting $\nu_Q^i \cdot S_i$. For both counter-ions and water a reasonable first approximation is to assume the presence of only two sites, i.e. of free or bound ions and molecules.[11,12,20,25] In certain cases, a distinction between differently bound water molecules may be necessary.[12,26] The "free" water molecules and counter-ions are assumed to have $S_i \simeq 0$, i.e. no net orientation of the field gradients. The applicability of the fast exchange approximation for both counter-ions[14] and water molecules[12,21] has been established in a number of cases and will be assumed to apply also here. The presence of slow exchange either between different binding sites in a single phase or between different phases leads to broadening of the peaks in the spectrum and/or to the appearance of additional peaks. These aspects have been dealt with in previous publications.[21,27,28]

EXPERIMENTAL

Chemical and Sample Preparation D_2O was purchased from CIBA-Geigy, Switzerland and had an isotopic enrichment of 99.7 %. C_7COONa (>97 %)† was purchased from The British Drug Houses, United Kingdom, C_8SO_4Na

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† C_n denotes a normal saturated hydrocarbon chain containing n carbon atoms. Figures in parentheses give the purities.

from Merck, West Germany, and Aerosol OT, sodium di(2-ethylhexyl) sulfosuccinate (denoted AOT in the following, >97%) from Fluka, Switzerland. C_7CN (>97%), C_7CHO (>98%) and C_7COOCH_3 (>99%) were all obtained from Fluka, and CCl_4 (analytical grade), *n*-octane ($= C_8H$, 99.5%) and glycerol (analytical grade) were bought from BDH. NaCl, LiCl and NaI were analytical reagents.

Ammonium *n*-octanoate was prepared by bubbling NH_3 gas (Benzon & Co., Sweden) through a solution of octanoic acid (BDH, 99%) in diethyl ether. The precipitate was separated by filtering and was then dried under reduced pressure. The molecular weight was checked by titration with perchloric acid in acetic acid solution and was obtained to be ~168 (theoretical value 161.3). High-resolution ^1H NMR on a D_2O solution of the salt was employed to test for residual ether in the salt and none was found.

Tetramethylammonium *n*-octanoate was prepared by neutralizing octanoic acid in ethanol solution with a 25% $(CH_3)_4NOH$ aqueous solution. The point of neutralization was checked by adding drops of the solution to phenolphtalein crystals on a hot porcelain plate. After complete neutralization the solvent was distilled off with rotavapor and the salt dried under vacuum at 70–80°C for some hours. The molecular weight was checked as described for ammonium octanoate and was found to be correct within 0.5%. No inappropriate signals could be detected in high-resolution ^1H NMR spectra of D_2O solutions of the salt.

Samples were prepared by weighing the appropriate amounts of the compounds with an accuracy of 0.001 g into glass ampoules which were then sealed off. Sample weight was ca. 1 g in the case of ^2H resonance studies and 2–3 g for ^{14}N measurements.

Phase diagrams for many of the ternary systems investigated (with H_2O instead of D_2O) at 20°C have been determined by Ekwall and co-workers[2] and, except for the variable temperature investigations, measurements were performed at this temperature. For those cases where phase diagrams were not found in the literature, the phase extensions were estimated from visual observations of samples and examinations of NMR spectra. For the $C_7COONH_4{-}D_2O$ and $C_7COON(CH_3)_4{-}D_2O$ systems, the structure of the mesophases was investigated by means of polarization microscope and X-ray techniques.[2] The phase structure studies were most kindly performed for us by Docent Krister Fontell at this laboratory.

Equilibration of the samples was achieved by heating to the point where a clear isotropic liquid is obtained and then cooling slowly. As certain of the chemicals used may decompose on heating, alternatively equilibration was achieved by repeated centrifugation up and down in the ampoule for 1–3 days. A 5 mm glass bead was inserted in the ampoule to facilitate mixing.

After the equilibration procedure, the samples were in both cases left 3–7 days at the experimental temperature before recording the spectra. A number of samples were re-measured after 1–2 months. No sign of ageing effects on the samples neither on their gross appearance nor on spectral lineshape was observed.

NMR Measurements The deuteron NMR measurements were performed with a modified Varian XL-100 spectrometer operating in the pulse-Fourier transform mode. The pulse width was mostly 30 μs, the number of transients 200–500 and the Fourier transformation of the decay was calculated by means of a Varian 620 computer. The delay time between pulses was chosen so that no distortive influence on spectral lineshape resulted. Deuteron NMR studies were performed at 20 ± 1°C except where otherwise stated. The temperature was controlled by means of a Varian temperature controller, and was checked by means of a copper-constantan thermocouple or in some cases a mercury thermometer. The ^{2}H quadrupole splitting was obtained directly as the distance between maxima in the spectrum.

^{14}N NMR measurements were performed by means of a Varian V-4200 wide-line spectrometer equipped with a 12 in. V-3603 magnet. The magnetic field was 1.403 T and was stabilized with a Varian Mark II Fieldial unit. The resonance frequency (4.321 MHz) was stabilized by a crystal oscillator circuit. Spectra were recorded as derivatives of the absorption mode signals using a field modulation frequency of 40 or 80 Hz. The amplitudes of the radiofrequency field and the modulation field were chosen low enough not to cause any appreciable distortion of the lineshape. Owing to the low inherent NMR sensitivity of ^{14}N, maximal sample tube diameter (17 mm) had to be used and this precluded work at other temperatures than the probe temperature which was 29 ± 2°C. The splittings were obtained from spectral shape according to an empirical procedure.[25]

EXPERIMENTAL RESULTS

Effect of Solubilisation on ^{2}H Splittings The effect on the water deuteron quadrupole splitting of adding different organic compounds to binary amphiphile-water mesophases is shown in Figure 2. The systems chosen were the hexagonal mesophases of the systems $C_7COONa—D_2O$ and $C_8SO_4Na—D_2O$ and the effect of solubilisate addition was investigated up to the stability limit of the hexagonal phase. The entrance into the two-phase zone was immediately apparent from the presence of a central peak in the spectrum. (In the case of continuous-wave spectra a central peak arising from double quantum transitions may also appear.)[29] From Figure 2 it may be noted that the effect of solubilisation is highly variable, being markedly dependent on both solubilisate and surfactant end-group. In most cases a

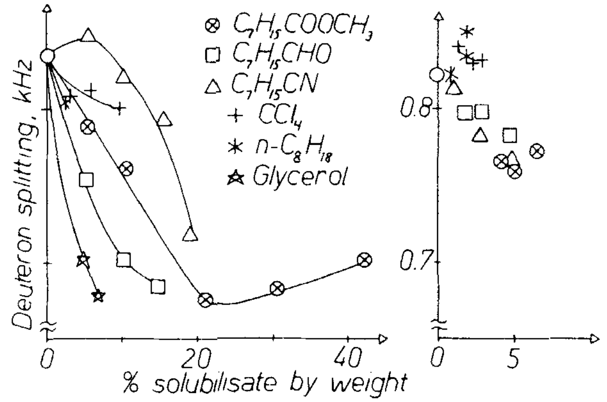

FIGURE 2 Effects on the ^2H water splitting of adding n-octane, carbon tetrachloride, octanonitrile, methyl octanoate, octanal and glycerol to hexagonal mesophase samples of a) D_2O + C_7COONa and b) D_2O + C_8SO_4Na. The molar ratios of soap to water were 0.108 and 0.109, respectively, and these ratios were kept constant throughout the sample series. Temperature 20°C.

decreased quadrupole splitting is obtained in spite of a decreased mole fraction of water in the sample.

Effect of Added Electrolyte on ^2H Splittings The effect of inorganic salt on the water deuteron quadrupole splitting is shown in Figure 3. The addition of NaCl to lamellar mesophase samples composed of AOT and D_2O and to hexagonal mesophase samples composed of C_7COONa and D_2O and of C_8SO_4Na and D_2O was investigated. Furthermore, the addition of NaI and LiCl to samples in the systems $C_7COONa—D_2O$ and $C_8SO_4Na—D_2O$ was studied. These samples were prepared to have the same volume ratios of amphiphile to aqueous electrolyte solution with varying inorganic salt concentration. The change in water-to-amphiphile molar ratio was small enough not to influence the results. NaCl can be seen to induce a markedly reduced water orientation while this is not observed with LiCl. The AOT—D_2O system has a small tolerance to electrolyte addition which makes the studies more difficult.

Temperature Dependence of the ^2H Splitting The effect of temperature variation on the water deuteron quadrupole splitting was investigated for the hexagonal mesophases of the systems $C_7COONa—D_2O$ and $C_8SO_4Na—D_2O$ and the lamellar phase of the system AOT—D_2O. As can be seen from the results in Figure 4, the effect of temperature may be very different for different systems. (To facilitate comparison the same molar ratios water-to-amphiphile apply for the results given in Figure 4.) The decrease in water

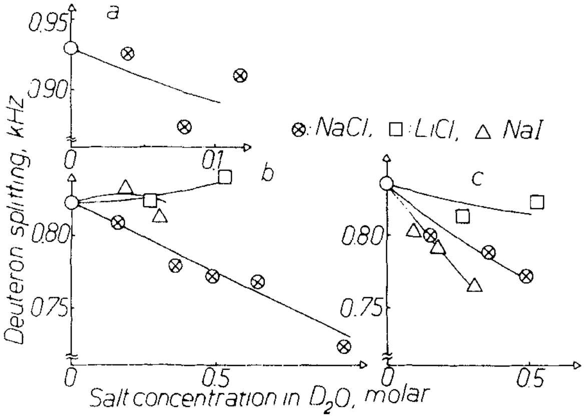

FIGURE 3 Effect on the water deuteron quadrupole splitting of addition of NaCl, LiCl and NaI to a) a lamellar mesophase sample of D_2O and Aerosol OT with 96 mole-% D_2O, b) a hexagonal mesophase sample of D_2O and C_8SO_4Na with 90.2 mole-% D_2O, and c) a hexagonal mesophase sample of D_2O and C_7COONa with 90.2 mole-% D_2O. In each case the D_2O was replaced by the same volume of the appropriate electrolyte solution (in D_2O). Temperature 20°C.

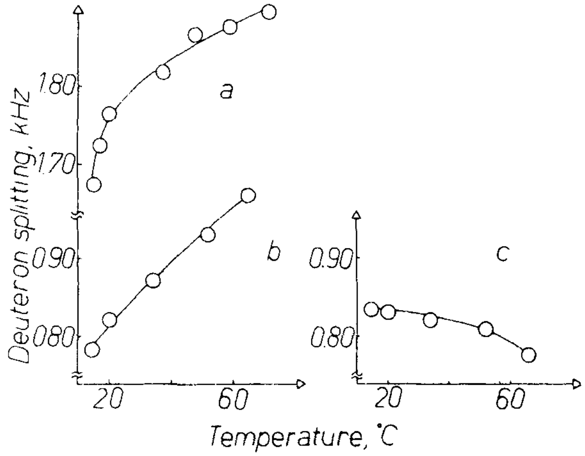

FIGURE 4 Deuteron quadrupole splittings as a function of temperature for a) a lamellar phase composed of D_2O and Aerosol OT, b) a normal hexagonal phase composed of D_2O and C_8SO_4Na and c) a normal hexagonal phase composed of D_2O and C_7COONa. The molar fraction of D_2O was 0.90 in all cases.

orientation with increasing temperature for the $C_7COONa—D_2O$ system is in interesting contrast to the findings with sulfate and sulfonate end-groups.

^2H and ^{14}N Quadrupole Splittings of the Systems $C_7COONH_4—D_2O$ and $C_7COON(CH_3)_4—D_2O$ No phase diagrams have hitherto been published for the two-component systems ammonium octanoate-water and tetramethylammonium octanoate-water. The X-ray and polarisation microscope studies performed in this laboratory in combination with visual inspection of samples revealed the following sequence of phases with increasing surfactant concentration at 20°C for the system $C_7COONH_4—D_2O$: isotropic aqueous solution, normal hexagonal mesophase, isotropic aqueous solution (transforming into hexagonal mesophase on cooling a few degrees), and lamellar mesophase. For the system $C_7COON(CH_3)_4—D_2O$, an isotropic solution phase and a hexagonal mesophase were obtained. The methods of investigation permitted no unambiguous answer to the question whether this mesophase is normal or reversed but its appearance next to an aqueous solution makes the first alternative more probable.

The mesophases in these systems were studied with both ^2H and ^{14}N magnetic resonance. The composition dependences of the deuteron quadrupole splitting shown in Figure 5 deviate markedly from those observed with alkali counter-ions.[12] Thus the ^2H splitting of the system $C_7COON(CH_3)_4—D_2O$ increases with increasing water content and the ^2H splitting of the $C_7COONH_4—D_2O$ system is larger for the hexagonal than for the lamellar mesophase. The ^{14}N quadrupole splittings of these

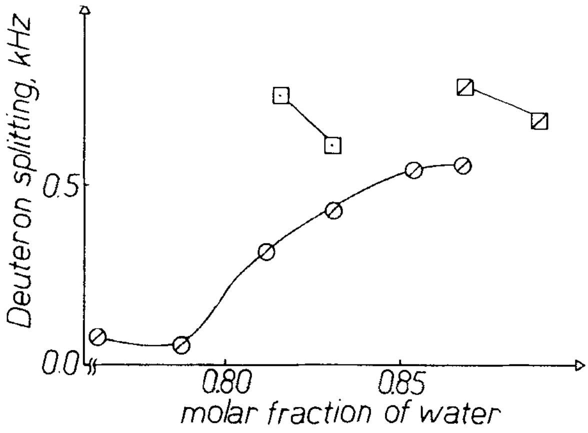

FIGURE 5 Deuteron quadrupole splittings at 20°C as a function of the molar fraction of water for samples in the $D_2O—C_7COONH_4$ (□) and $D_2O—C_7COON(CH_3)_4$ (○) systems. A diagonal line in the symbol indicates a hexagonal and a dot a lamellar phase.

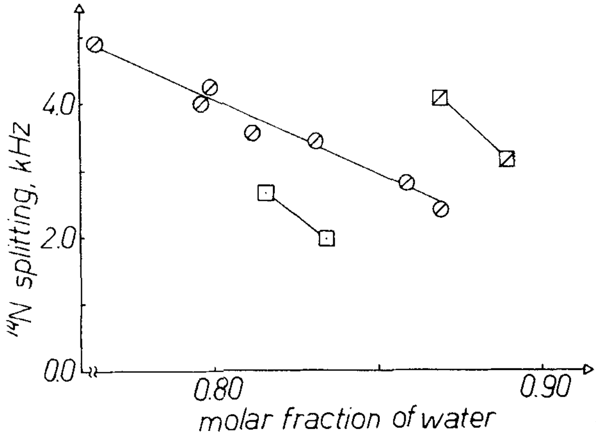

FIGURE 6 ^{14}N quadrupole splittings as a function of molar fraction of water at 29 ± 2°C for the systems C_7COONH_4—D_2O and $C_7COON(CH_3)_4$—D_2O. Symbols as in Figure 5.

systems shown in Figure 6 give a markedly larger value for the hexagonal than for the lamellar phase of the C_7COONH_4—D_2O system while for the $C_7COON(CH_3)_4$—D_2O system the splitting decreases regularly with increasing water content.

The temperature dependences of the ^2H splittings in these systems are depicted in Figure 7. The samples in the C_7COONH_4—D_2O system follow

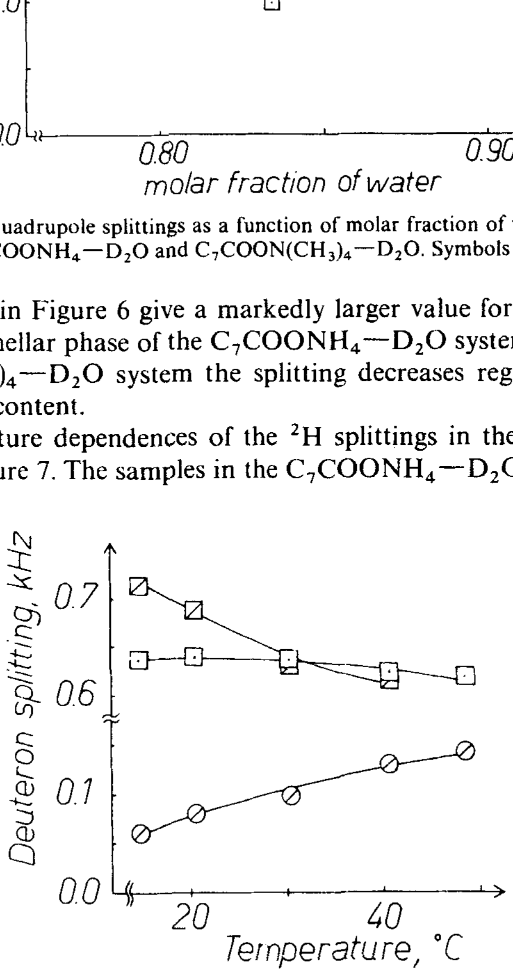

FIGURE 7 Temperature dependence of the ^2H quadrupole splitting for (i) a hexagonal mesophase sample with the molar fraction of D_2O = 0.890 in the C_7COONH_4—D_2O system (⧄), (ii) a lamellar mesophase sample with molar fraction of D_2O = 0.831 (⊡) in the C_7COONH_4—D_2O system and (iii) a hexagonal mesophase sample of the $C_7COON(CH_3)_4$—D_2O system with the molar fraction of water = 0.788 (⊘).

mainly the same trend as observed for the $C_7COONa—D_2O$ system (Figure 4), while an increase in splitting with increasing temperature is obtained for the $C_7COON(CH_3)_4—D_2O$ system.

DISCUSSION

General Aspects of Water ^2H Splittings Before going into a discussion of the present results it is useful to delineate briefly some results obtained in previous studies[10–12,25,26,30,31] regarding the factors determining the water deuteron quadrupole splittings.

The water content influences the splitting via changes in the distribution of water molecules over different sites and via changes in the intrinsic quadrupole splittings. If we assume the simple model discriminating only between free and bound water molecules which have concentration independent splittings and which are under rapid exchange conditions, then a plot of the deuteron quadrupole splitting versus the molar ratio amphiphile-to-water should be linear if the amphiphile hydration number is constant. Such a behaviour has been experimentally observed for the water-rich parts of the lamellar mesophase regions for a number of systems.[12] Furthermore it could be deduced that the quadrupole splitting of the free water molecules is close to zero.[12] In other systems, and in the water poor parts of the phase regions, the simple model is inapplicable. This occurs, inter alia, when the water content is too low for a complete hydration of amphiphile ions and counterions; the hydration numbers are then no longer constant.

The presence of exchangeable deuterons in the amphiphile, for example in $—OD$, $—COOD$, $—ND_2$ and $—ND_3^+$ groups, affects spectral appearance and will, unless deuteron exchange is very slow, make the experimental determination of water deuteron splittings more difficult. Our previous studies[12,27,30] have shown that C_7COOD deuterons in the alkali octanoate–octanoic acid-water systems are under fast exchange conditions while the $C_{10}OD$ deuterons of the systems alkali octanoate–decanol–water may conform to rapid, slow or intermediate exchange depending on temperature. Addition of acid or base may, depending on the components present, accelerate[12,27] or retard[25,32] deuteron exchange. The amphiphile deuterons are generally characterized by large splittings but it may be worth mentioning that an enhanced exchange rate is not necessarily accompanied by an increased observable ^2H splitting as the amphiphile and water deuterons may have different signs of $\nu_Q^i \cdot S_i$.[12,20]

The liquid crystalline structure also affects the degree of anisotropy of the molecular motion. Thus if the translational diffusion around the rods of the hexagonal mesophase is rapid compared to the splitting, and if the molecular interactions are locally the same in the lamellar and hexagonal phases, the quadrupole splitting of the lamellar phase should be twice that of the hexagonal phase.[20,21] For the amphiphile, the assumption of constant molecular interactions is generally reasonable while it may fail completely for the water molecules[12] (cf. below).

The hydration requirement of the counter-ions is of great importance for the binding state of water in amphiphilic mesophases and it has been demonstrated by Ekwall and Mandell[33] that the hydration numbers of the counter-ions govern the minimal water contents of the alkali soap–decanol–water systems. In water-poor samples, the water molecules will not suffice to fully hydrate both the counter-ion and the amphiphile polar group, thus resulting in increased counter-ion binding.[30,34] The effect of the counter-ion hydration on the water ^2H splitting will depend very much on whether the water molecules of counter-ion hydration are oriented with respect to the amphiphilic aggregates or not. In this regard, Li^+ was found to behave differently to the other alkali ions.[12]

The nature of the amphiphile polar head will evidently have a direct influence on the water deuteron splitting through mainly hydrogen-bond, ion-dipole and dipole-dipole interactions and in an indirect way through counter-ion binding phenomena.

Effect of Solubilisation on Water Orientation For the hexagonal mesophase of the C_7COONa—D_2O system, it is evident from Figure 2 that addition of C_8H, CCl_4, C_7CN, C_7COOCH_3, C_7CHO and glycerol causes a reduction in the degree of water orientation with respect to the amphiphile aggregates. In turn, this can result either from a partial liberation of water molecules from the amphiphile aggregates or from a more isotropic motion of the amphiphile hydration water. The location of the solubilized molecules in the aggregates may be thought to be primarily determined by the polarity of the molecules, a non-polar molecule being located in the interior of the rods and a polar one in the vicinity of the amphiphile polar heads; the highly water-soluble glycerol is probably to be found in the water layers though in interaction with the amphiphile polar heads. Roughly, the solubilisation effects follow the polarity sequence, a polar solubilisate reducing the ^2H splitting more than a non-polar one. Location of solubilized molecules in the polar regions of the aggregates is expected to lead to some liberation of water molecules, and this is in line with the observations. It is, on the other hand, difficult to understand the reduced degree of water orientation on solubilisation of octane, for example. Thus solubilisation in the non-polar parts may be assumed firstly not to be in direct competition with hydration and secondly for sterical reasons to cause an increased area per polar group of the aggregates. In turn, this is expected to favour the binding of water molecules to the aggregates. Such behaviour is observed for the hexagonal phase of the

$C_8SO_4Na—D_2O$ system where solubilisation of C_8H and CCl_4 induces an increased degree of water orientation while a reduced degree of water orientation is observed with C_7CHO, C_7CN and C_7COOCH_3.

It is of interest to compare the different behaviour displayed by the two surfactants with other observations. First, we may note that in spite of the much smaller cross-sectional area of the COO^- group than of the OSO_3^- group,[35] the area per polar group of their lamellar mesophases is very similar.[36] This implies larger gaps between polar groups of the $C_7COONa—D_2O$ system and consequently more water molecules in these gaps. These water molecules may be hydrogen-bound to the $—COO^-$ groups and also act as counter-ion hydration water; a further consequence is a difference between the two head groups in the tendency to lateral expansion on solubilisation. Second, several observations point to a markedly different counter-ion binding in the two cases[4] and it has been suggested on the basis of ^{23}Na quadrupole splittings that there is a partial penetration of Na^+ counter-ions between $—COO^-$ end-groups.[16] We note also that hydrogen-bonding most probably occurring via water molecules between adjacent $—COO^-$ groups will give a resistance towards lateral expansion along the aggregate surface in the case of the $C_7COONa—D_2O$ system. Corresponding mechanisms are not operative in the other system.

Effect of Electrolyte on Water Orientation From Figure 3 it can be inferred that the degree of water orientation can both increase and decrease on addition of a simple electrolyte. If we ignore major changes in the packing conditions of the aggregates, salt addition is expected always to lead to an increased total amount of bound counter-ions and such effects have been studied recently for similar systems as those considered here.[34,37] The change in water orientation will then depend on counter-ion competition, if two different counter-ions are present, and on whether the water of counter-ion hydration is oriented with respect to the amphiphilic surfaces or not. (It is now well established that the counter-ions retain their inner hydration sheaths for the conditions studied here).[4] In the light of these considerations and the previous deductions[12] that the Li^+ hydration layer is oriented with respect to the amphiphile aggregates, while that of Na^+ is not, the observations of Figure 3 may be schematically rationalized.

What is more difficult to interpret is the differing behaviour of NaCl and NaI. Apparently the co-ion has a marked influence on the amphiphile hydration, but more systematic studies are required to disclose the mechanism behind this effect. It may only be noted that as the co-ion's hydration water is certainly negligibly oriented, the degree of water orientation is expected to decrease with increasing co-ion-water interaction; this is in qualitative agreement with the present observations.

Effect of Temperature on Water Orientation The degree of water orientation can be seen to increase markedly with increasing temperature for the lamellar phase of the AOT—D_2O system and the hexagonal phase of the C_8SO_4Na—D_2O system, while a weak decrease is observed for the C_7COONa—D_2O hexagonal mesophase (Figure 4). Here we have another marked difference in behaviour between different amphiphile head-groups, and the same considerations as given above in connection with the discussion of the solubilization effects may be used to rationalize the variable temperature effects. Thus a thermal expansion leads to an increased area per amphiphile polar end and to the orientation of an increased number of water molecules. This would explain the results obtained with the —SO_3^- and —OSO_3^- end-groups, while the above noted resistance towards expansion resulting from intermolecular interactions is in agreement with the findings with the —CO_2^- end-group. The decreased water orientation observed at high temperatures probably reflects an enlarged angular range of fluctuation of the field gradients.

For the C_8SO_4Na—D_2O and AOT—D_2O systems, it was important to consider in detail the possibility of an influence from hydrolysis, in the former case into C_8OD and DSO_4^- which might lead to an increased splitting due to the contribution from the C_8OD deuteron. However, considerations of spectral lineshape and estimates based on $C_{10}OD^2H$ splittings[12] as well as studies of time effects indicated the insignificance of this effect.

Water Orientation and Counter-Ion Binding in the C_7COONH_4—D_2O and $C_7COON(CH_3)_4$—D_2O Systems In contrast to the systems discussed above, the mesophases composed of ammonium octanoate and water or of tetramethylammonium octanoate and water provide a complex picture making a well-founded interpretation difficult to obtain. Within the lamellar and normal hexagonal mesophase regions of the system C_7COONH_4—D_2O, the degree of water orientation shows the normal decrease with increasing water content (Figure 5). The slightly higher degree of water orientation in the hexagonal phase than in the lamellar phase is unexpected in view of the above-mentioned effect of phase anisotropy, as is also the higher ^{14}N splitting of the hexagonal phase. The latter points to a higher amphiphile hydration number for the hexagonal phase. Similar trends, in hydration, although not at all so marked, are expected on purely geometrical grounds and have been noted for other amphiphilic systems.[12] X-ray crystallographic studies have also given considerably larger areas per amphiphile polar head for normal hexagonal than for lamellar phases.[38,39]

In discussing the deuteron splittings of the C_7COONH_4—D_2O system it is necessary to take into account the contributions from the ND_4^+ deuterons. Bailey *et al.*,[24] in their study of ND_4^+ in an oriented "nematic" mesophase, obtained a value for this ^2H splitting of 0.035 kHz by acidifying the sample and thus slowing down the deuteron exchange. At the water-poor extreme of our lamellar mesophase samples, about $\frac{1}{3}$ of the deuterons present occur in ND_4^+ ions. Assuming in this case the ND_4^+ deuteron splitting to be 0.070 kHz, and to have the same sign as the D_2O deuteron splitting, we obtain the corrected splitting of D_2O to be ca. 1.0 kHz if fast exchange conditions apply. A similar result, which is also obtained for the hexagonal phase has been obtained previously for hexagonal $C_7COOK—D_2O$ and $C_7COORb—D_2O$ samples.[12] This correlates well with the similarity in the ionic radii of the K^+, Rb^+ and NH_4^+ ions. Attempts to separate out the contribution from the ND_4^+ ions in our systems by acidification were unsuccessful because of the limited stability range of the mesophases.

For the hexagonal phase of the $C_7COON(CH_3)_4—D_2O$ system it is most interesting to note that the order parameter shows a strong increase with increasing water content (Figure 5). Such a behaviour has not been observed in the corresponding phase regions for any other system and the interpretation is not obvious. However, it should be noted that, in comparison with the alkali ions, the tetramethylammonium ion is much bigger (an ionic radius of 0.35 nm[40]) and that tetraalkylammonium salts show peculiar interactions with water molecules, leading to a strong structure-stabilizing effect on the water lattice and to the formation of stable crystalline hydrates of high hydration numbers where the water molecules form cages around the cations.[41-44] (For the present systems complete hydration is not possible.) For the interaction of the $N(CH_3)_4^+$ ions with the amphiphilic aggregates, hydrophobic effects may probably come into play and such a direct ion-ion contact may partially block the water binding sites. On the basis of these considerations a possible interpretation of the results would be in terms of a counter-ion binding involving hydrophobic interactions which are loosened to transform into a normal counter-ion binding at higher water contents, thus making hydration sites on the amphiphile accessible. Such a change in counter-ion binding is consistent with the marked decrease in ^{14}N quadrupole splitting with increasing water content. A fruitful way of testing this hypothesis would probably be by investigating the ^2H splitting of deuterated $N(CH_4)_4^+$ ions.

The increasing water ^2H splitting with increasing temperature of the $C_7COON(CH_3)_4—D_2O$ system (Figure 7) is consistent with this interpretation if increasing temperature can be assumed to weaken the counter-ion-amphiphile hydrophobic interaction. For the $C_7COONH_4—D_2O$ system, in contrast, the degree of water orientation is observed to decrease with increasing temperature, which is the same behaviour as observed with the $C_7COONa—D_2O$ system.

The ^{14}N quadrupole splittings (Figure 6) and their interpretation have already been discussed in some places above. We may only add that within a single phase the ^{14}N splitting decreases with the water content which corresponds to a weakened counter-ion binding. Whether this results from a reduced distortion or a reduced order parameter characterizing intermolecular field gradients is not possible to deduce presently.

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