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Magnesium and calcium surfactants
Ternary phase diagrams of magnesium and calcium dodecylsulphate with decanol and water

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Abstract: The isothermal ternary phase diagrams for the systems magnesium dodecylsulphate-decanol-water at 40 °C and calcium dodecylsulphate-decanol-water at 50 °C are determined by water deuteron NMR and polarizing microscopic studies. In the magnesium system, three liquid crystalline phases (lamellar and normal and reverse hexagonal) and two isotropic (normal and reverse) solution phases are characterized and their ranges of existence are obtained. The calcium system yields the same liquid crystalline phases, but only the lamellar liquid crystalline phase is investigated in detail. The important observations made are: (i) The lamellar liquid crystalline phase for the magnesium and calcium systems can incorporate, respectively, a maximum of 22.5 and 14.3 mole water per mole surfactant ion against 139 mole water for the corresponding sodium system. (ii) The reverse hexagonal liquid crystalline phase is formed for both the magnesium and calcium systems while no such liquid crystalline phase exists for the corresponding sodium system. (iii) The ^{2}H NMR quadrupole splittings obtained in the liquid crystalline phases for $C_8SO_4^-$ and $C_{12}SO_4^-$ surfactant systems with different counterions (Ca^{2+}, Mg^{2+}, Be^{2+}, Na^+) reveal that surfactant hydration is almost independent of alkyl chain length and counterions.

Key words: Magnesium and calcium dodecylsulphate, liquid crystals, phase diagram, ^{2}H NMR, surfactant hydration.

Introduction

Recently we have observed very important differences in the phase diagrams (binary and ternary) between ionic surfactants with monovalent and those with divalent counterions [1–7]. The phase equilibria of ionic surfactants with monovalent counterions have been studied extensively [8–9], but those with divalent ions are limited to octyl sulphate ($C_8SO_4^-$) and Aerosol OT (AOT) type surfactant systems. One important observation made in these surfactant systems with different divalent counterions (Ca^{2+}, Mg^{2+}, Ba^{2+}) is that the lamellar liquid crystalline phase (*D*) has very limited swelling capability.

Friberg and Osborne [10] studied the solubility of calcium dodecylsulphate (CDS) in the lamellar liquid crystalline phase formed by the system sodium dodecylsulphate (SDS) – decanol – ^2H_2O at 300 K and concluded that the *D* phase formed by the calcium system is stable at high water contents. This is a four-component system which contains both mono- and divalent counterions. Recently it has been demonstrated that a three-component aqueous surfactant system with both mono- and divalent counterions can yield two lamellar liquid crystalline phases in equilibrium, one stable at very high and the other at low water contents [7]. In a study of the stability of a *D* phase formed by a surfactant system with divalent counterion, the presence of a monovalent counterion in the system is, therefore, a complicating factor.

We report here the complete ternary phase diagram for the system $(C_{12}H_{25}OSO_3)_2Mg$-decanol-^2H_2O at 313 K and a partial phase diagram of the system $(C_{12}H_{25}OSO_3)_2Ca$-decanol-^2H_2O at 323 K. The partial isothermal phase diagram [8] reported for the sys-

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tem $C_{12}H_{25}OSO_3Na$-decanol-water contains the determined lamellar liquid crystalline phase region incompletely. We have therefore determined the range of existence of the *D* phase for the sodium system. The phase diagrams are determined by water deuteron NMR in combination with polarizing microscopic studies. ^2H NMR quadrupole splittings (Δ) in the liquid crystalline phases are used to obtain the hydration of amphiphiles and we will compare and discuss ^2H NMR results for different alkyl chain lengths and counterions (both mono- and divalent ions).

The study of the phase eqilibria and phase structure of divalent surfactant systems has both theoretical and applied interest. The important application is to develop surfactants for hard water [11]. The experimental findings and theoretical studies, which include the solutions of Poisson-Boltzmann (PB) [12–113] and Modified Poisson-Boltzmann (MPB) [14] equations and Monte Carlo simulations [15], all lead to very big differences in the behaviour between monovalent and divalent counterion systems.

Experimental

Materials

Sodium dodecylsulphate (SDS) was recrystallized in absolute ethanol. Magnesium dodecylsulphate (MDS) was prepared by adding aqueous $MgCl_2$ solution (20 % excess of stoichiometric) to a SDS solution. The precipitate (MDS) was washed with water till it was free from $MgCl_2$. The precipitate was either lyophilized or dried under vacuum at 40 °C. Calcium dodecylsulphate (CDS) was prepared by the same method as MDS. ^{23}Na NMR spectra of MDS and CDS solutions did not show the presence of Na^+ in MDS or CDS samples. ^2H_2O (99.7 at % ^2H) was supplied by Ciba-Geigy, Switzerland and decanol, specially pure, was obtained from BDH, England.

Sample preparation

The samples were prepared by weighing appropriate amounts of substances in glass tubes which were flame-sealed (freshly dried MDS under vacuum at 40 °C was used). Samples were shaken and mixed by repeated centrifugation. The samples were subsequently kept in a thermostat at appropriate temperature for two weeks before the first NMR measurement was made. The procedure was repeated and the second NMR measurement was made after another four weeks with no significant change in the ^2H NMR noticed. It was observed that the samples of magnesium and calcium surfactants could be kept at 40–50 °C for 8 weeks without any noticeable chemical degradation provided they were handled carefully; the samples were found to attain equilibrium within two weeks at these temperatures.

^2H NMR measurements

The water deuteron (^2H) NMR studies were carried out at a resonance frequency of 15.351 MHz with a modified Varian XL-100-15 pulsed spectrometer working in the Fourier-transform mode using ^1H external lock. ^2H NMR spectra were recorded at 30°, 40° and 50 °C for sodium, magnesium and calcium samples respectively. The samples were thermostated many days at the appropriate temperature and were quickly transferred to the NMR probe for measurements. The NMR probe was also thermostated at the required temperature by passing air and the temperature was correct to ± 1 K. The samples were kept for a sufficient period in the probe to avoid a temperature gradient before the spectra were recorded.

The total amount of sample used for the NMR measurements was normally 0.2–0.5 g and in a 10 mm (i.d.) NMR tube, the volume of the sample is covered by the r. f. coil of the spectrometer. In the case of large sample volumes spectra were recorded at different vertical positions of the NMR tube so that the total volume of the sample was recorded.

In isotropic (e. g. micellar) solutions, the water yields a narrow signal in the ^2H NMR spectrum, while in an anisotropic medium such as lamellar or hexagonal liquid crystalline phases the interaction between the quadrupole moment of deuterium ($I = 1$) and the electric field gradients at the nucleus does not average to zero and the deuterium signal splits into a symmetrical doublet. For symmetry reasons $\Delta_{lam} = 2\Delta_{hex}$ if local conditions are alike. Deuteron exchange between phases in heterogeneous surfactant systems is generally slow on the NMR time-scale and the recorded ^2H NMR spectrum in a multiphase sample is the superposition of spectra of individual phases (see e. g. Fig. 1). This simple and efficient technique has primarily been used to construct the phase diagrams. All the samples were first examined against crossed polaroids in order to ascertain the sample homogeneity and the occurrence of birefringency. The texture of the samples was studied in a polarizing microscope.

Results and discussion

Phase diagrams: general

^2H NMR spectra were used to identify phases in homogeneous and heterogeneous samples. Some representative spectra obtained in the calcium system are shown in Figure 1. The boundaries between phases were obtained by systematic variations of sample compositions and analysis of the ^2H NMR spectra. The presence of hydrated surfactant crystals was not revealed in the ^2H NMR spectra but the microscopy texture of the hydrated surfactant crystals was easy to identify. The polarizing microscope was found more useful in this part (low water content) of the phase diagram to establish the phase boundaries. A detailed treatment to determine phase boundaries and phase diagrams by ^2H NMR and polarizing light microscopy was given previously [1]. The borderlines between the homogeneous L_1 aqueous phase and the heterogene-

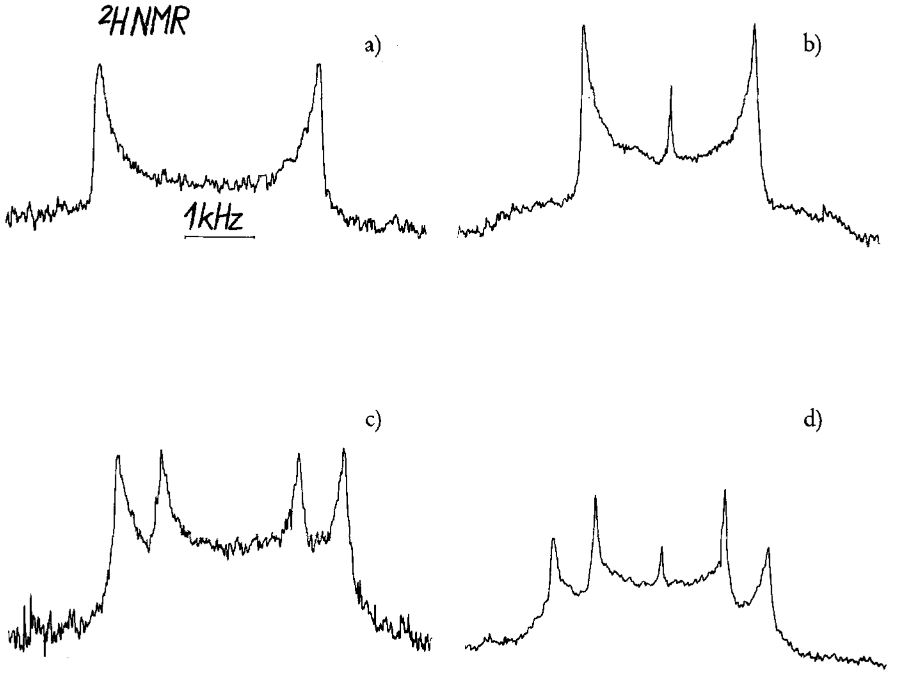


Fig. 1. A few representative ^2H NMR spectra obtained for the system calcium dodecylsulphate – decanol-^2H_2O at 50 °C. Sample compositions are given as wt % surfactant/decanol/water. a) *D* liquid crystalline phase, 52.3/28.9/18.8; b) $D + L_1$, 35.7/34.4/29.9; c) $D + F$, 46.3/36.9/16.8 and; d) $D + F + L_2$, 42.1/40.8/17.1

ous regions and between the homogeneous L_2 decanolic phase and the heterogeneous regions were determined by ocular inspection. The ternary phase diagrams obtained for the magnesium, calcium and sodium systems are shown in Figure 2.

About 400 samples were used to construct the phase diagram of the magnesium system and about 60 samples to obtain the area of the lamellar liquid crystalline phase for the calcium and sodium systems. The accuracy of boundaries for single phases is within ± 2 % and is slightly less for the heterogeneous regions.

Phase diagram of magnesium system

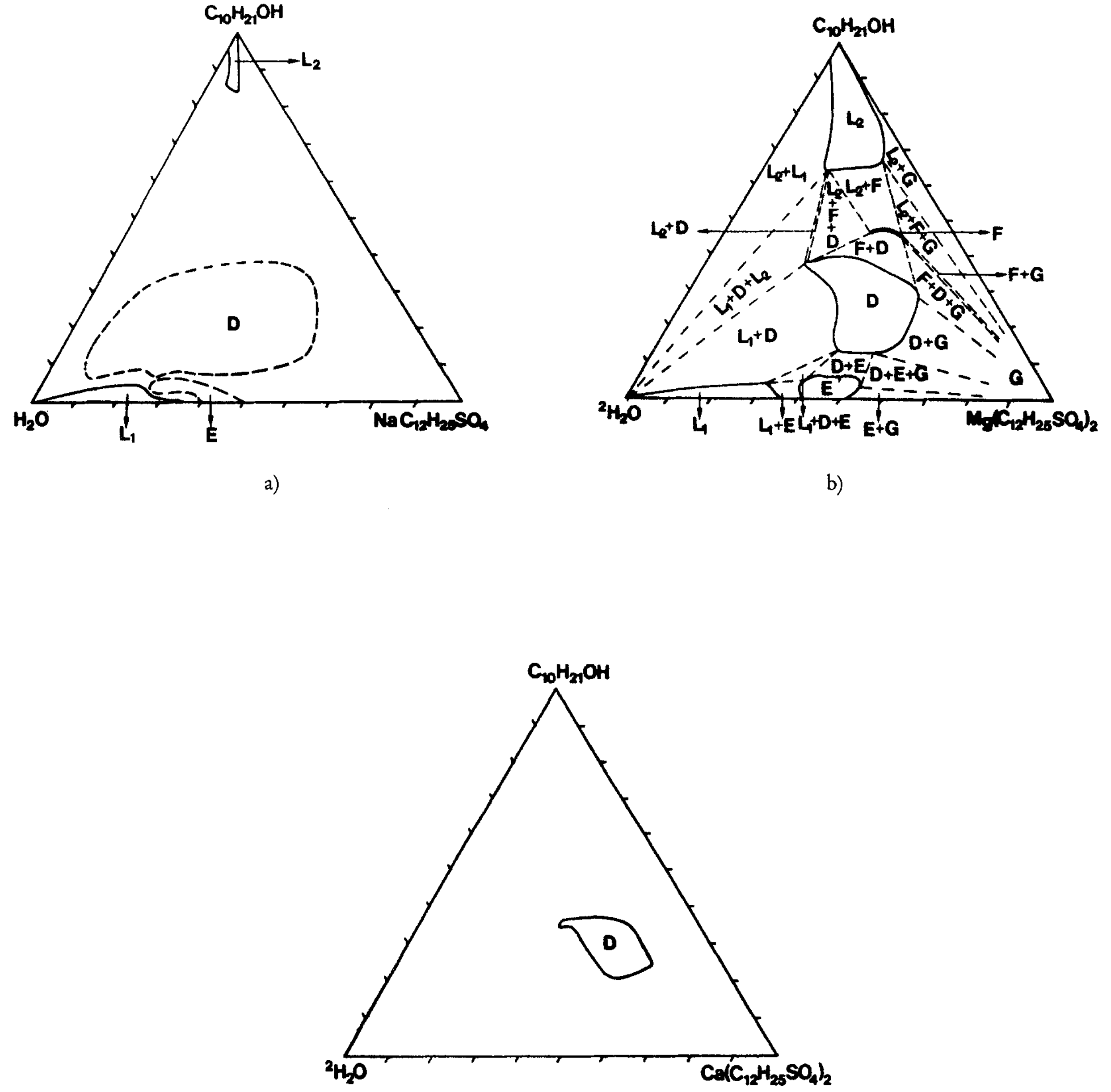
Aqueous solution phase (L_1)

The Krafft point of MDS is about 35 °C and the CMC in water is 8.8×10^{-4} m (0.047 wt % MDS) [16–17] while the solubility is 1.06 m (36.04 wt % MDS) at 40 °C. ^1H NMR of MDS solutions produces narrow signals and there is little increase in their line-widths even at the solubility limit of MDS. This result, as well as the observed low viscosity of the solutions, indicates that the micelles are small and globular in shape in the entire concentration range.

A maximum amount of 0.23 mole decanol per mole surfactant ion can be solubilized in the aqueous MDS solutions. Addition of decanol increases the viscosity and leads to a broadening of the ^1H NMR signals. The viscosity and ^1H NMR line-width effects are bigger in the magnesium system than in the corresponding sodium system and give evidence for growth into non-spherical micelles. The micellar structure is under study by the NMR self-diffusion technique.

Decanolic solution phase (L_2)

In this solution phase there is a maximum of 0.23 mole surfactant ion and 2.6 mole ^2H_2O per mole decanol. One unusual feature of this phase in comparison with other metal alkylsulphate systems is that the L_2 phase extends to very near the decanol-surfactant axis. The solubility of freshly dried MDS in decanol is about 0.5 %, but as much as 24 wt % MDS could be dissolved



a)

b)

c)

Fig. 2. Isothermal ternary phase diagrams. a) Sodium dodecylsulphate – decanol – water at 27 °C; b) magnesium dodecylsulphate – decanol – water at 40 °C; c) calcium dodecylsulphate – decanol – water at 50 °C. *D*, *E*, *F* are, respectively, lamellar, normal hexagonal and reverse hexagonal liquid crystals; L_1 and L_2 are isotropic solution phases; $L_1 + D$, $D + F$ and $L_1 + F + L_2$, $D + F + L_2$ etc. are, respectively, two- and three-phase regions

in decanol if the surfactant contained a small quantity (< 1 wt %) of water. It was very important to use freshly dried (under vacuum at 40 °C) MDS to determine the area of L_2 phase.

The lamellar liquid crystalline phase (D)

The stability of the lamellar liquid crystalline phase extends to 22.5 mole ^2H_2O (39 wt %) & 2.7 mole (37 wt %) decanol per mole surfactant ion toward the water corner and the minimum amounts of ^2H_2O and decanol at maximum surfactant content necessary to form *D* phase are, respectively, 4.2 (16.5 wt %) and 1.0 (29.5 wt %) (dry side). The samples in this region have a mosaic microscopic texture typical of lamellar liquid crystalline phases [18–19]. The ^2H splitting values vary between 1.4 kHz at high water contents and 3.2 kHz at low water contents. These values are much larger (about 2 times) than those obtained in the *E* or *F* liquid crystalline phase (after correcting for water contents). One special feature of this liquid crystalline phase is that the samples with low water and high surfactant contents (dry side) do not show the stiffness observed in the corresponding systems with other counterions.

Hexagonal liquid crystalline phases (E and F)

Both the normal, *E*, and reverse, *F*, hexagonal liquid crystalline phases are stiff and have angular microscopic texture [18–19]. *E* phase forms when MDS is added to ^2H_2O between 59.0 and 48.5 wt % ^2H_2O (19.9–13.0 mole ^2H_2O per mole surfactant ion) and in this phase can be solubilized up to 0.14 mole decanol per mole surfactant ion. The *F* phase, on the other hand, occupies a very small area in the triangular phase diagram and appears near to the decanol-surfactant axis. This liquid crystalline phase is very sensitive to temperature and its equilibrium boundary was not determined in detail.

The liquid crystalline samples in both *E* and *F* phases produce a single splitting in the ^2H NMR spectra. The ^2H NMR splitting-values (Table 2) in the *E* phase vary little (± 10 %) with composition while trends within the *F* phase were not explored.

The heterogeneous regions

All heterogeneous regions (two and three phase regions) as required to satisfy the phase rule have been identified and their boundaries were determined as shown in Figure 2. The two phase regions, $D + F$, and $F + G$, are very narrow and their boundaries were not determined with any accuracy. In general, the accuracy in the determination of region boundaries is better on the left hand side of the phase diagram than in the right hand side of the triangle.

Calcium surfactant system

Calcium dodecylsulphate (CDS) in water has a Krafft point of about 50 °C. In order to document further how general the observation of the extension of the lamellar liquid crystalline phase is for divalent counterion surfactant systems the stability range of the *D* phase was established also for the calcium dodecylsulphate - decanol - water at 50 °C. It is to be mentioned that the addition of decanol to the aqueous mixture of CDS lowers the Krafft point considerably below 50 °C.

As shown in Figure 2 the lamellar phase occupies a small region and has limited swelling capability (32.5 wt % ^2H_2O) in comparison with sodium dodecyl system (82.5 wt % ^2H_2O). The *D* phase has mosaic microscopic texture [18–19] and the samples in this region yield single splittings in the ^2H NMR spectrum. The Δ^2H values (Table 2) are approximately of the same magnitude as those obtained in the MDS or SDS systems. The ^2H NMR was run for a few samples in the region which corresponds approximately to the $D + F$ region in the MDS system (Fig. 1). Here we obtained double ^2H NMR splittings, one splitting corresponding to *D* phase and the other to *F* phase. The sample has two microscopic textures, one of *D* phase and the other of *F* phase. The calcium system thus like the MDS system, but unlike the SDS system, forms reverse hexagonal liquid crystalline phase with low water and high surfactant and decanol contents.

Sodium surfactant system

Certain aspects of the phase diagram for the system sodium dodecylsulphate (SDS) – decanol – water have been studied previously [8]. Two liquid crystalline (lamellar and normal hexagonal) phases and two isotropic (normal and reverse micellar) solution phases were reported to form for this system. The ranges of existence of all phases but the lamellar were determined. Here, we have determined the stability range of the lamellar liquid crystalline phase as shown in Figure 2. We have used ^2H_2O to prepare samples for NMR measurements and the compositions in the phase diagram in Figure 2 for the SDS system are given in normal water with reconversion on a molar basis.

The ^2H NMR yields quadrupole splittings for samples in this region except for water contents above 80 % where a single broad signal in the ^2H NMR spectrum is obtained. The boundary for the *D* phase at high water contents (> 80 %) is determined by polarizing microscopy and by examining the presence of any solution phase in the sample after prolonged centrifugation. The swelling capability of the *D* phase extends to 139 moles of water per mole of surfactant and the minimum amount of water necessary to form lamellar liquid crystalline phase is about 4 moles per surfactant mole. No reverse hexagonal liquid crystalline phase appears to form in the SDS surfactant system.

A comparison between phase diagrams

The ternary phase diagrams presented here (Fig. 2) give the concentration of each component in wt %. In a comparison of different phase diagrams, a better understanding may be realized by expressing concentrations on a molar basis. We have computed some important data on molal concentration for C_8 and C_{12} alkyl sulphates with Na^+, Mg^{2+} and Ca^{2+} as counterions and presented them in Table 1. Data for C_8 alkyl sulphate systems are taken from previous studies [1, 4].

Table 1. Stability range of various homogeneous phases in the binary and ternary metal alkylsulphate surfactant systems

Surfactant	Counterion	Phase	n_{max}	n_{min}
$C_{12}H_{25}OSO_3^-$	Na^+	*D*	139 (1.5)	4.2 (0.99)
	Mg^{2+}	*D*	22.5 (2.7)	4.2 (0.96)
	Ca^{2+}	*D*	14.3 (1.9)	3.9 (0.76)
	Na^+	*E*	24.8 (0)	16.0 (0)
	Mg^{2+}	*E*	19.9 (0)	13.0 (0)
	Na^+	*E*	44.8 (0.36)	–
	Mg^{2+}	*E*	21.1 (0.14)	–
	Na^+	L_1	–	29.6 (0)
	Mg^{2+}	L_1	–	24.6 (0)
	Na^+	L_1	52.5 (0.41)a)	–
	Mg^{2+}	L_1	29.1 (0.23)a)	–
$C_8H_{17}OSO_3^-$	Na^+	*D*	232 (1.5)	9.3 (0.55)
	Mg^{2+}	*D*	29.1 (2.9)	4.2 (0.56)
	Ca^{2+}	*D*	17.1 (2.3)	4.7 (0.69)
	Na^+	*E*	11.4 (0)	7.6 (0)
	Mg^{2+}	*E*	11.7 (0)	8.5 (0)
	Ca^{2+}	*E*	9.2 (0)	7.8 (0)
	Mg^{2+}	*E*	15.1 (0.34)	–
	Ca^{2+}	*E*	11.0 (0.25)	–
	Na^+	L_1	–	14.4 (0)
	Mg^{2+}	L_1	–	15.3 (0)
	Ca^{2+}	L_1	–	13.2 (0)
	Na^+	L_1	13.3 (0.25)a)	–
	Mg^{2+}	L_1	16.3 (0.32)a)	–
	Ca^{2+}	L_1	12.5 (0.26)a)	–

n_{max} and n_{min} are, respectively, the maximum and minimum number of moles of ^2H_2O per mole surfactant ion and the values within brackets are the moles of decanol.

a) indicates maximum solubilization of decanol.

The results regarding the swelling capability of the lamellar liquid crystalline phase confirm our previous findings [1, 4], namely that the *D* phase incorporates substantially smaller amounts of water for a divalent than for a monovalent counterion. Electrostatic calculations [12–13] and Monte Carlo simulations [15] have been used to explain the experimental observations. The results further show that the *D* phase is able to take more water with Mg^{2+} than with Ca^{2+} ion. A similar observation has been made with other systems [3, 4] (Table 1). This result has been explained in terms of the difference of hydrated ion radii.

The alkyl chain length (C_8 and C_{12}) also effects the swelling capability of the *D* phase, the longer the chain length, the lesser is the swelling. This effect is present both with mono- and divalent counterion systems. The solubilization of decanol into the *D* phase at its maximum swelling is found to be affected very little by counterion substitution or length of the alkyl chain.

The minimum amount of water necessary at maximum surfactant content to form *D* phase for the magnesium and calcium systems is about 4–5 molecules per molecule surfactant irrespective of alkyl chain length. The ratio between decanol and surfactant at this composition is about 0.5 for C_8 and 1 for C_{12} systems.

The range of existence of the hexagonal liquid crystalline phase is almost identical for the two-component SDS and MDS systems. Both the systems solubilize small quantities of decanol. The incorporation of decanol increases the ability of the E phase of the SDS system to be stable at high water contents. This effect is absent in the MDS system and in the calcium (COS), magnesium (MOS) and sodium (SOS) octylsulphate systems [4]. From the observations for the C_8 and C_{12} alkyl sulphate systems, it appears that the longer the alkyl chain, the smaller is the quantity of surfactant necessary to form *E* phase in water.

In the MDS and CDS systems, there is a formation of reversed hexagonal liquid crystalline phase. The *F* phase has previously been observed in the MOS system [4] but is absent in the SDS (Fig. 2), COS or SOS [1] systems.

A cubic liquid crystalline phase, occupying a very narrow range, forms in the system MOS–^2H_2O [4] while no such phase has been observed with the other C_8 and C_{12} alkyl sulphate systems.

Both SDS and MDS dissolve easily in water above their respective Krafft point. The aqueous solution phase, L_1, determined at 25 °C for the SDS system is not expected to be markedly different at 40 °C at which temperature the phase diagram of the MDS system was obtained. The results in Table 1 and Figure 2 show that the L_1 phases for the two systems are almost identical except that the solubility of decanol at high SDS contents decreases slowly whereas for the MDS system, the decrease is rapid.

The decanolic solution phase, L_2, for the SDS system occupies a small area in the phase diagram whereas for the MDS system, the L_2 phase extends much more towards the water surfactant and decanol-surfactant axes. It has been observed that decanol can dissolve as much as 24 wt % MDS if the surfactant contains a small amount (< 1 %) of water.

Water (^2H) quadrupole splittings and surfactant hydration

A large number of ^{2}H NMR quadrupole splittings have been obtained for the lamellar liquid crystalline phases in the MDS (at 40 °C) and CDS (at 50 °C) systems and a few representative Δ^2H values are given in Table 2. The splittings are found to depend primarily on the water content and to a lesser extent on the surfactant-to-decanol ratio. Thus all samples with high water contents give small Δ^2H values irrespective of surfactant and decanol concentrations while those at low water contents give large splittings.

Table 2. Some representative water deuteron NMR quadrupolar splitting values (Δ^2H) obtained in the liquid crystalline phases of surfactant systems.

Surfactant system	Surfactant (wt %)	^2H_2O (wt %)	Decanol (wt %)	Phase	Δ^2H (kHz)
MDS (40 °C)	44.9	55.1	–	*E*	0.59
	50.0	50.0	–	*E*	0.68
	50.0	45.2	4.8	*E*	0.74
	47.2	46.8	6.0	*E*	0.68
	24.7	38.2	37.1	*D*	1.34
	24.5	36.3	39.2	*D*	1.44
	43.7	43.2	13.1	*D*	1.38
	35.7	25.9	38.9	*D*	1.57
	56.3	26.7	17.0	*D*	2.64
	46.7	20.6	32.7	*D*	3.21
	37.7	17.1	45.2	*F*	1.76 (~ 4.6)
	37.9	14.9	47.2	*F*	2.46 (~ 5.4)
CDS (50 °C)	33.0	32.2	34.8	*D*	2.19
	44.7	28.2	27.1	*D*	2.42
	59.1	15.8	25.1	*D*	3.23
	51.8	15.8	32.4	*D*	3.58
SDS (30 °C)	44.4	55.6	–	*E*	0.50
	20.1	44.7	35.2	*D*	1.65
	18.0	50.3	31.7	*D*	1.36
BDS (30 °C)	45.0	55.0	–	*E*	0.50
	18.0	49.5	32.5	*D*	1.40
	20.1	44.8	35.1	*D*	1.63

MDS, CDS, SDS, BDS are, respectively, magnesium, calcium, sodium and beryllium dodecylsulphate. Δ^2H-values within brackets are calculated for the *D* phase according to Equation (2).

Table 2 also contains Δ^2H values for the corresponding system with Be^{2+} and Na^+ as counterions. Examination of results (Table 2) shows that Δ^2H values in the *E* and *D* phases of the sodium system are close to those of the beryllium system at identical compositions while the values of the *E* phase in the magnesium system are about 15 % higher. Comparison of Δ^2H values in the *D* phases of these systems is made difficult because of difficulties in preparing samples with identical compositions. However, it appears that Δ^2H values differ by a few percent for samples having almost identical compositions in the order Ca (50 °C) > Mg (40 °C) > Be (30 °C) ≅ Na (30 °C). Previously, it has been shown [20–21] that Δ^2H values in the liquid crystalline phases of alkali alkylsulphates increase slightly (10–15 %) with increasing temperature in this range. The slight differences in Δ^2H values between different systems is consequently attributed mainly to differences in experimental temperature. Thus a counterion substitution has a negligible effect on Δ^2H values. As Δ^2H values are directly related to surfactant aggregate hydration the difference in swelling capacity between *D* phases with different counterions cannot be referred to differences in hydration (cf. Ref. [6]).

The Δ^2H values of the dodecylsulphate systems are very close to those previously obtained for octylsulphate systems with Na^+, Ca^{2+} and Mg^{2+} as counterions [1, 4] taking into account in the comparison differences in temperature and concentration. Thus the surfactant alkyl chain length does not affect hydration appreciably.

In order to rationalize the deuteron quadrupole splittings in more detail we use the conventional two-site model with a division into "free" and "bound" water molecules. Assuming the degree of orientation of the free water molecules to be negligible we may express the splitting as

$$\Delta^2\mathrm{H} = n \cdot \nu_Q \cdot S \cdot (1 - X_W)/X_W \qquad (1)$$

where ν_Q is the water ^{2}H quadrupole coupling constant (independent of composition, temperature and system with excellent approximation), S is the average order parameter of bound water molecules, n is the (average) number of bound water molecules per nonaqueous component and X_W is the mole fraction of water. If n and S are constant in the composition range discussed, then

$$\Delta^2\mathrm{H} = K(1 - X_W)/X_W \qquad (2)$$

where K is a constant. For symmetry reasons, $K_{\mathrm{hex}} = 2K_{\mathrm{lam}}$. As we indeed find the reduced splitting to be roughly twice as large for the lamellar as for the hexagonal phases (E & F) we infer that the local conditions of water binding and orientation are similar in the different phases.

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