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Ion Binding in Liquid Crystals Studied by NMR.: I. The Cetyltrimethylammonium Bromide/Hexanol/Water System

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Ion Binding in Liquid Crystals Studied by NMR.
I. The Cetyltrimethylammonium Bromide/Hexanol/Water System†

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Abstract—The nuclear magnetic relaxation of ^{81}Br in the liquid crystalline phases in the ternary system cetyltrimethylammonium bromide (CTAB)/hexanol/water was investigated. The dependence of the nuclear magnetic resonance line width on the composition of the samples is discussed. In the lamellar mesophase the ^{81}Br NMR line width decreases when either the hexanol or the water concentration is increased. This is interpreted as a release of counter-ions from the charged surfaces by hexanol, and as a reinforced hydration of the bromide ions, respectively. Below a molar ratio of about one between hexanol and CTAB the binding of the bromide ions is strongly dependent on this ratio. A comparison is made between the line width in the mesomorphous phases with lamellar and hexagonal structure and the line width in the proximate isotropic solution phases. It appears that the binding of the ions is stronger in the hexanol-deficient part of the lamellar mesophase than in the isotropic water-rich solution phase. In the hexanol-rich part of the lamellar mesophase with high water content the line widths are the same as in the isotropic hexanol-rich solution phase with high water concentration. The binding of the ions in the hexagonal mesophase is similar to that in concentrated aqueous solutions of CTAB.

Introduction

In the last few years there has been a number of applications of nuclear magnetic relaxation techniques to the study of ion binding in systems containing association colloids. The studies by this method have dealt with counter-ion binding in systems containing

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micelles of the normal type(1–3) or of the reversed type.(4–6) It seems clear at present that this technique offers a convenient way of obtaining rather detailed information on the interaction between ions and other species in a solution. The purpose of the present work is to determine the degree to which this method is capable of providing enlightenment about the binding of ions in amphiphilic mesomorphous phases. Ekwall *et al.*(7) carried out a thorough investigation of the phase equilibria in the three-component system cetyltrimethylammonium bromide (CTAB)-hexanol-water at 25 °C. Their study demonstrates that two liquid crystalline phases exist in the ternary system, one with a lamellar structure (denoted D) and one with two-dimensional hexagonal structure (denoted *E*). (Fig. 1). The present paper is concerned with ^{81}Br NMR studies of these mesophases.

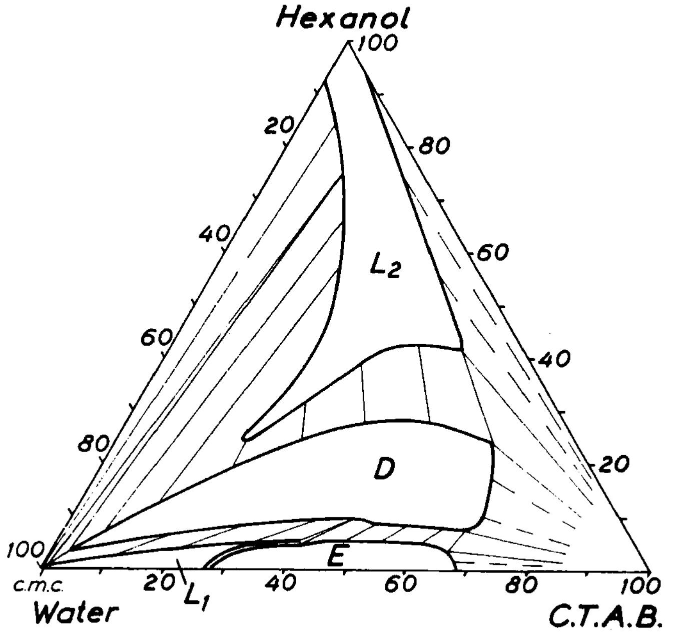

Figure 1. Ternary phase diagram for the system cetyltrimethylammonium bromide/*n*-hexanol/water at 25 °C according to Ekwall *et al.*(7) Compositions are given in per cent by weight. *D* and *E* denote regions with lamellar and hexagonal mesomorphous phases, respectively, L_1 and L_2 are regions with isotropic solution phases.

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Experimental

NMR MEASUREMENTS

The ^{79}Br and ^{81}Br NMR measurements were performed with a Varian V–4200 NMR spectrometer equipped with a 12 inch V–3603 magnet and a Varian Mark II Fieldial as described previously.(6) The sample temperature was 29 ± 2 °C. In the determinations of the frequency dependence, the sample temperature was kept constant (at about 34 °C) by means of a Varian V–4540 temperature controller. This instrument was also used in the investigations of the temperature dependence. The actual temperature in the sample was measured with a thermocouple before and after the recording of each series of spectra at a given temperature, and is accurate within ± 0.5 °C.

The reported line widths are the arithmetical means of 2–4 spectra, and the individual measurements are usually within 5% of the average.

MATERIALS

CTAB and *n*-hexanol were obtained from the British Drug Houses Ltd. Poole, England. CTAB was recrystallized twice from ethanol and hexanol was distilled once. The preparation of the samples was as described by Ekwall and co-workers.(7)

Results and Discussion

Atomic nuclei with spin quantum numbers (I) greater than 1/2 generally have electric quadrupole moments. The predominant nuclear magnetic relaxation mechanism in fluid systems is in this case usually the interaction between the nuclear electric quadrupole and fluctuating electric field gradients at the nucleus. Abragam and Pound(8,9) have given an expression for the longitudinal relaxation rate ($1/T_1$) due to the quadrupole interactions for a nucleus of spin I:

$$\frac{1}{T_1}=\frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \qquad (1)$$

Here eQ is the nuclear electric quadrupole moment, eq is the principal component of the electric field gradient tensor, $\hbar = h/2\pi$ where h is Planck's constant and τ_c is the correlation time of the field gradient

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components. The asymmetry parameter, η, has been neglected in Eq. (1). Eq. (1) is valid for the case in which the motion is rapid enough to give $\omega_0\tau_c \ll 1$, where ω_0 is the nuclear Larmor frequency. In this case the transverse relaxation time T_2 equals T_1, the longitudinal relaxation time. The inverse value of T_2 is proportional to the resonance line width, ΔB, which implies that the following equation is valid when $T_1 = T_2$:

$$\Delta B = Kq^2\tau_c \tag{2}$$

In Eq. (2) K is a constant for a given nucleus. Thus line width measurements yield the product of q^2 and τ_c. These quantities are of great interest since they are determined by the bonding properties of the ions and by the microdynamic properties of the system studied. Unfortunately a separation of q^2 and τ_c is difficult, but a comparison of data for different systems is nevertheless informative.

If all of the ions under consideration are bound in the same way in the solution, *i.e.* only one site exists, Eq. (2) gives the line width. When the ions are exchanging between several sites with different bonding properties and the residence times in the different sites are much smaller than the relaxation times, the line width is given by(10):

$$\Delta B_{\text{obs}} = \textstyle\sum_i p_i \Delta B_i \tag{3}$$

ΔB_{obs} is the observed line width and ΔB_i is the line width for the ions in site i. The mole fraction of the total number of ^{81}Br nuclei situated in site i is denoted by p_i.

The applicability of Eqs. (2) and (3) to the interpretation of our findings will now be examined. It should be noted that we have failed to observe any splittings of the ^{81}Br resonance signals. (Of course this does not necessarily exclude the presence of a splitting, it may be due to insufficient intensity of the outer peaks. By improved experimentation we are currently studying this problem in more detail.) If quadrupole splitting is actually absent we may then interpret our results in terms of relaxation. Even if a first-order quadrupole splitting is present the line width of the central peak will, for nuclei having half integer spin quantum numbers, be determined by relaxation if the splitting is great enough to make overlap between the central peak and the outer peaks insignificant. Measurements (at 33.5 °C) showed no frequency dependence of the line width for a sample with the composition 62.3% CTAB, 17.7% hexanol and 20.0%

water and it was concluded that this was a case of extreme narrowing, *i.e.* $T_1 = T_2$, and thus Eq. (2) is applicable. That Eq. (3) (*i.e.* a case of fast exchange) is valid in the present situation can be concluded from measurements of the ratio between ΔB (^{79}Br) and ΔB (^{81}Br) which is 1.55 for a sample with the above composition. This value is in good agreement with the value calculated from the expression

$$\frac{\Delta B(^{79}\mathrm{Br})}{\Delta B(^{81}\mathrm{Br})} = \frac{Q^2(^{79}\mathrm{Br})}{Q^2(^{81}\mathrm{Br})} \cdot \frac{\gamma(^{81}\mathrm{Br})}{\gamma(^{79}\mathrm{Br})} = 1.545$$

where γ is the magnetogyric ratio. Thus we may assume that Eq. (3) is applicable (*cf.* Ref. (3)), and the marked line narrowing with increasing temperature (Fig. 2) provides further support for the

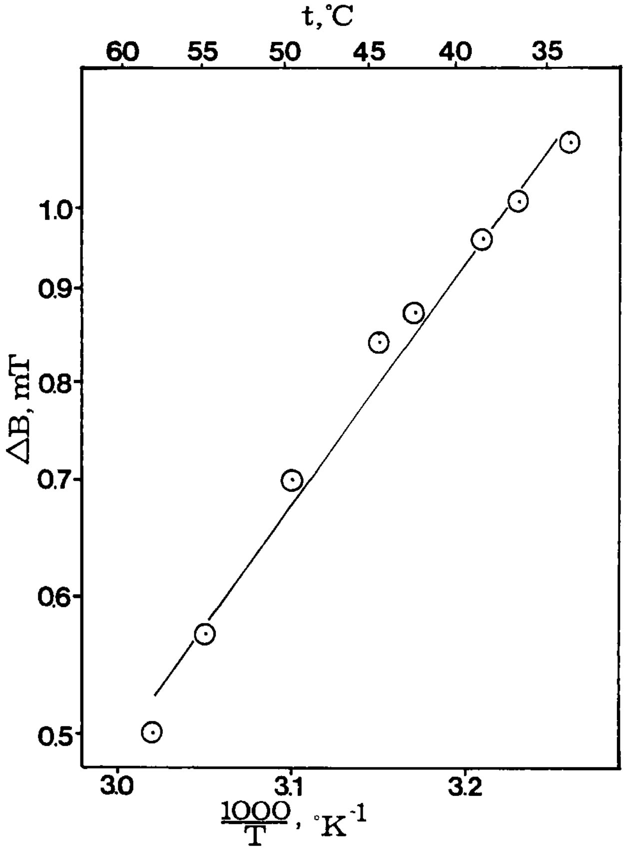

Figure 2. The logarithm of the ^{81}Br line width plotted against the inverse absolute temperature for a sample with the composition 20.0% water, 17.7% hexanol and 62.3% CTAB. Temperature range 33.5°–57.7 °C.

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validity of Eq. (3). The observed ratio $\Delta B(^{79}\mathrm{Br})/\Delta B(^{81}\mathrm{Br})$ furthermore supports our assumption that the observed NMR signal is not affected by first-order quadrupole splittings. The contribution from second-order quadrupole interactions is small since the line widths are independent of the magnetic field strength. (For $^{35}\mathrm{Cl}$ second-order quadrupole splittings have been observed in a similar system).(11)

The results presented in Fig. 3 are concerned with the variation of the line width with the water content at a constant ratio of 2.3 w/w between CTAB and hexanol. (All concentrations are given in per

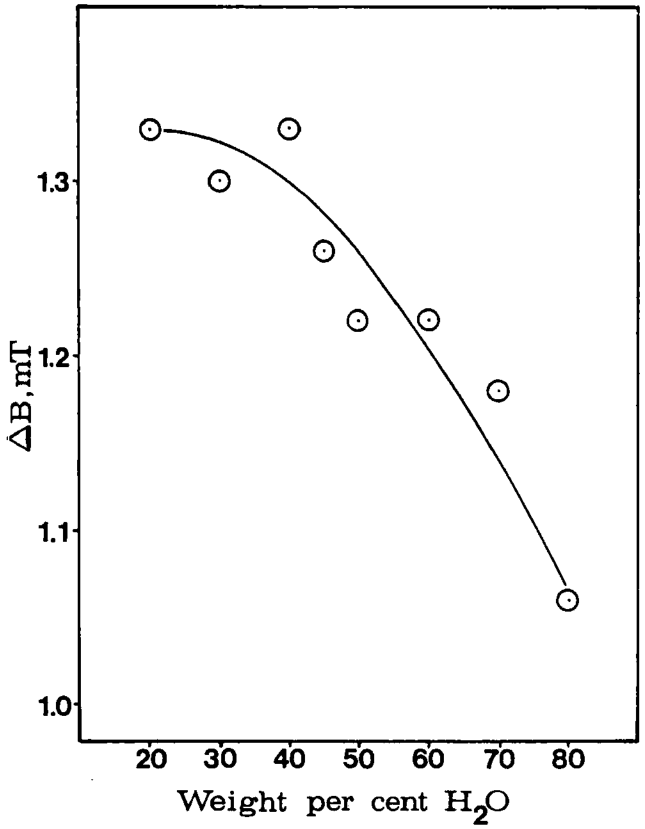

Figure 3. The $^{81}\mathrm{Br}$ line width, ΔB (in millitesla), as a function of water concentration (in per cent by weight) in the lamellar phase (D) in the ternary system CTAB–hexanol–water. The ratio between the content of CTAB and hexanol was kept at a constant value, 2.3 w/w. Temperature 29 °C.

cent by weight.) It is obvious from the figure that the line width increases with decreasing water concentration, the changes being most marked at high water content.

This observation is also valid when the water content is varied at constant hexanol concentration (Fig. 4). The line width changes from 1.2 to 0.8 mT (T = tesla, $1T = 10^4$ gauss) for a variation in the water content from 20 to 50 per cent by weight. In Fig. 5 the line width is given as a function of the CTAB concentration at a constant

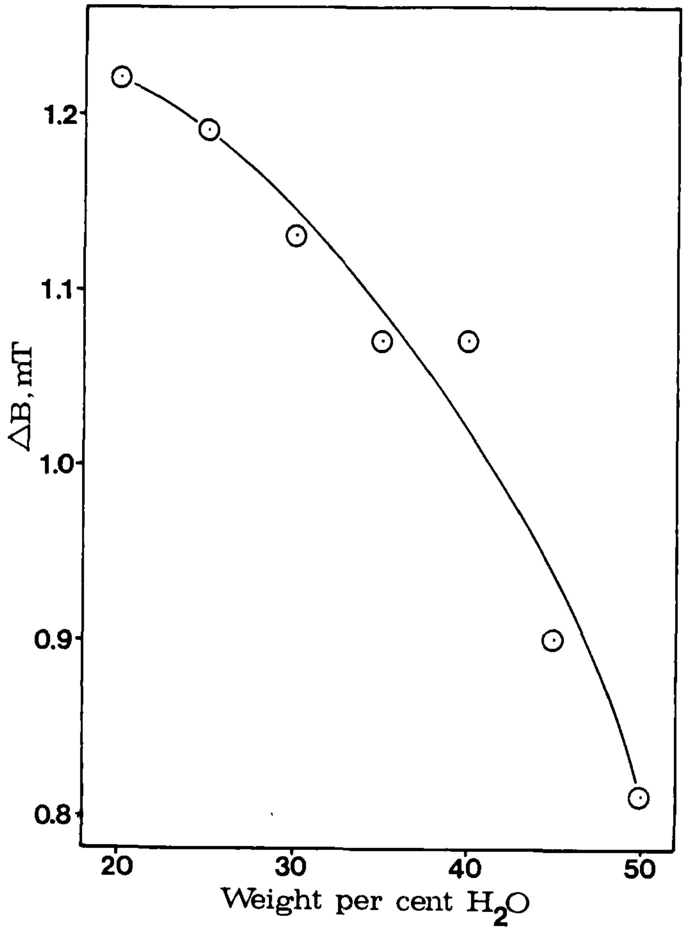

Figure 4. The observed line width, ΔB (in millitesla), for ^{81}Br as a function of the water concentration at constant hexanol concentration, 17.7%, in the lamellar phase (D) in the CTAB–hexanol–water system. Temperature 29 °C.

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ratio of 2.3 w/w between water and hexanol. It is clear that the line width increases immensely with increasing CTAB content in the entire concentration range investigated.

An increasing NMR line width can normally be assumed to indicate an enhanced binding of the ion under consideration (see *e.g.* Refs. (1), (6), (12) and (13)). Thus it may be inferred from Fig. 3 that decreasing the water concentration leads to a firmer binding of the bromide ions. It is known from X-ray diffraction measurements$^{(7)}$ that the thickness of the water layer between the amphiphilic

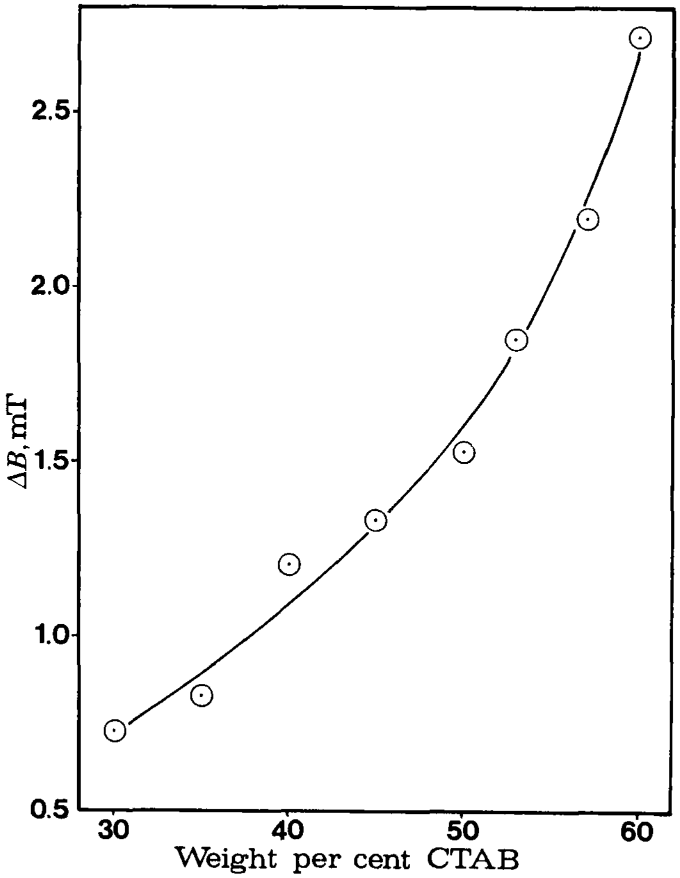

Figure 5. The ^{81}Br line width, ΔB (in millitesla), as a function of the CTAB concentration at a constant ratio of 2.3 w/w between water and hexanol in the lamellar phase (*D*) in the ternary system CTAB–hexanol–water. Temperature 29 °C.

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layers decreases with decreasing water content. Hence it seems probable that an increasing part of the bromide ions may be adsorbed at the amphiphilic surface when the water content decreases. The changes in line width on variation of the water content is however moderate (Figs. 3 and 4) and consequently the water concentration alone can not account for the very large line widths observed in the CTAB-rich part of the mesophase (Fig. 5).

In almost the entire mesomorphic phase *D* the line width decreases with increasing hexanol concentration if the ratio between surfactant and water is constant. Thus at a constant ratio of 0.7 w/w between CTAB and water the line width decreases from 1.3 to 0.9 m*T* for changes in hexanol concentration between 15 and 20%. When the ratio in question is 2.3 w/w the line width decreases from 2.7 to 1.3 m*T* if the hexanol content varies between 12 and 24%. On the other hand, on addition of hexanol to lamellar mesophase with a high hexanol concentration, the line width does not change appreciably.

It may be postulated that an increasing hexanol content and/or an increasing water content results in a decreasing binding of the bromide ions in the lamellar mesophase. Predominantly, the line width is determined by the molar ratio between hexanol and CTAB (Fig. 6). Thus it may be seen from Fig. 6 that when this molar ratio is less than about unity the line width increases strongly with decreasing hexanol concentration. It is also clear that when the number of hexanol molecules per CTAB molecule is larger than one, the variation in line width is considerably less. (It is interesting to note that an alteration in the mechanism of water uptake in this mesophase occurs at roughly the same molar ratio between hexanol and CTAB.)(7)

In the hexagonal phase (*E*) the ^{81}Br line width is practically independent of sample composition (Table 1) and only a slight increase in line width on increasing the CTAB concentration can be observed. These observations indicate that the counter-ion binding is very similar in different parts of this phase. In spite of considerable variations in the macroscopic viscosity over the region *E* the microdynamic properties, as sensed by the bromide ions, are practically constant. Our observations of a constant counter-ion binding correlate with the observed large areas per hydrophilic

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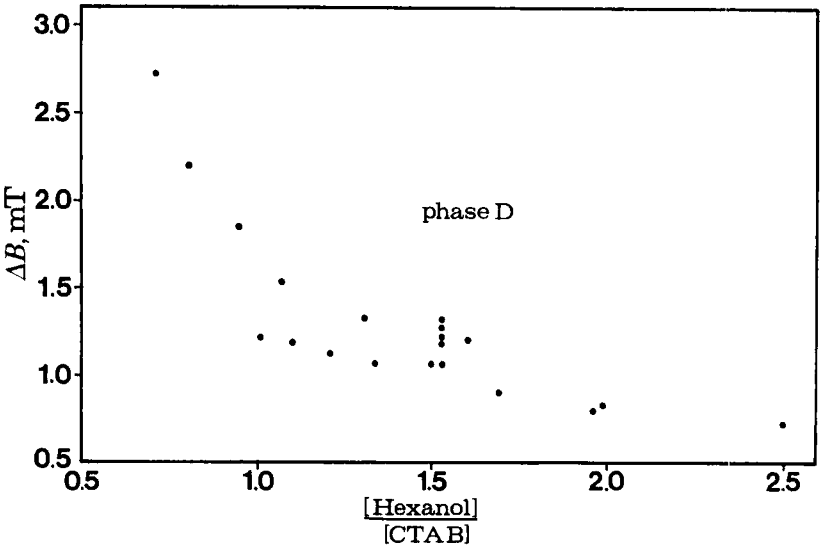

Figure 6. The observed ^{81}Br line width, ΔB (in millitesla), as a function of the molar ratio hexanol to CTAB in the lamellar phase (D) in the CTAB–hexanol–water system at various water concentrations. Temperature 29 °C.

group at the amphiphile/water interface.(7) The ^{81}Br line width is independent of the hexanol concentration in the E phase (Table 1). This also holds true for the distance between the amphiphilic cylinders.(7)

The lamellar mesophase D can be in equilibrium with both the isotropic phases L_1 (water-rich) and L_2 (hexanol-rich) and the hexagonal mesophase E can be in equilibrium with the L_1 phase.

Table 1 ^{81}Br nuclear magnetic resonance line widths in the mesomorphic hexagonal phase E in the cetyltrimethylammonium bromide/hexanol/water system. Concentrations in per cent by weight. Temperature 29 °C.

CTAB (%)	H_2O (%)	Hexanol (%)	ΔB (mT)
30.0	70.0	0.0	0.73
40.0	60.0	0.0	0.74
50.0	50.0	0.0	0.75
60.0	40.0	0.0	0.76
65.0	35.0	0.0	0.80
38.5	59.0	2.5	0.73
48.5	49.0	2.5	0.78
58.5	39.0	2.5	0.81

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Thus it is of interest to compare the bromide ion binding in the different phases. Firstly it may be noted that the line width at the highest water content in the D phase is larger than that of the broadest signal observed in the L_1 phase (about 0.8 mT, Ref. (14)). Hence, in spite of a high water content, the counter-ions are more firmly bound than anywhere in the L_1 phase. In the upper left hand region of the D phase with a high content of hexanol the line width has a value comparable with that determined in the water-rich part of the L_2 phase(6) which consists of so-called reversed micelles.(15) This implies that the binding of the counter-ions is not very much altered on going from this part of the mesophase to the water-rich part of the isotropic solution phase L_2. A similar result is found for the other mesophase denoted E: the binding in the right hand part of the L_1 phase(14) is of the same strength as in the water-rich part of the mesophase (Table 1). It should be noted that although the line widths in the mesophases are usually large, they are of the same order of magnitude as in the micellar solutions. This indicates that the microdynamic properties of the mesophases, in the vicinity or the bromide ions, are not very different from those of the isotropic micellar solutions.

After this qualitative discussion we will now try to rationalize our findings in terms of electric field gradients and correlation times. Unfortunately a separation of these factors is not directly possible and can only be achieved when more extensive relaxation data are available. It is known that in the L_1 solutions the field gradients are important.(16) Since the line widths are of comparable magnitude in the mesophases it seems reasonable to assume that the field gradients are important for determining the line widths also in the present case. The field gradients may either be due to binding of the counter-ions at the amphiphilic surface, or by location of the ions in a stabilized water lattice (*cf.* Refs. (3) and (17)).

A simple model assuming only two sites for the bromide ions, (*i.e.* either they are extensively solvated by water, or they are associated with the cations) seems to be useful for the discussion. The factors now determining the line width were previously stated in connection with Eq. (3). Even at as high a water content as 80% the line width in the D phase is 1.06 mT (Fig. 3), while in an aqueous solution of an alkali bromide the width of the ^{81}Br nuclear magnetic resonance signal is 0.02–0.03 mT even at relatively high concentrations.(18,19)

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This line width corresponds to a bromide ion which is nearly symmetrically surrounded by water molecules. Thus it may be presumed that the bromide ions in the present case experience field gradients, which are orders of magnitude larger than in a normal aqueous solution. This strongly implies that a large part of the bromide ions are adsorbed at the amphiphilic surface even at high water contents. On solubilization of hexanol in the liquid crystal it seems reasonable to assume that the hexanol molecules orient themselves with their hydrophobic part within the hydrocarbon layer and their hydrophilic OH-groups towards the water. Measurements of ^{81}Br relaxation rates in the upper part of the lamellar mesophase (rich in hexanol) give lower relaxation rates than samples deficient in hexanol at the lower boundary in the same phase. This may be interpreted as a displacement of the equilibrium between bound counter-ions and solvated ions for the benefit of the bromide ions in the water layer. A similar course is shown in the right hand part of the L_1 phase containing hexanol.(14) Such a mechanism is also indicated from conductivity studies of soap solutions when an organic amphiphile is added.(20–22) At least two mechanisms may explain the release of counter-ions as the hexanol content is increased: Firstly the hydration of the lamellar surfaces will depend on the molar ratio of hexanol to CTAB in the lamellae; this will in turn affect the hydration of the counter-ions. Secondly the charge density on the lamellar surfaces will vary with the molar ratio of non-ionic to ionic amphiphile.(7)

Thus far we have discussed our data in terms of electric field gradients with the only justification that the quadrupole relaxation in the corresponding micellar solutions seems to be determined by the field gradients.(16) The contribution to the line widths from changes in the correlation times may not be deduced at the present stage of our investigation. It may, nevertheless be assumed that an increase in line width in most cases is paralleled by an increase in correlation time. Thus the change in the binding of the counter-ions will at the same time cause a change in electric field gradients and reduce the mobility of the bromide ions. At least at high water contents the motion of the bromide ions seems to depend on the motion of the water molecules and consequently one possible way of obtaining a deeper understanding of the line broadening mechanisms would be to study the water nuclear magnetic relaxation.

The value of the apparent energy of activation for the relaxation process obtained from a least-squares treatment for a sample with the composition 62.3% CTAB, 20.0% water and 17.7% hexanol (Fig. 2) is very high (26.7 ± 0.8 kJ/mole) compared with the value of 8–11 kJ/mole[23,24] normally found in aqueous solutions of alkali bromides. Several workers (see Refs. (3), (4), (17), (24) and (25)) have discussed the activation energies of the relaxation process for ions in solution. It may be concluded that the high value of the energy compared to for example an aqueous alkali bromide solution indicates that the bromide ions are much more firmly bound in the present case. (Of course in liquid crystalline systems one also has to consider the possibility of structural changes when the temperature is altered.)

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