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Studies of Specific Adsorption Sites for Sodium Ion and Water on the Interface of Mixed Micelles of Novel Type II Lyomesophases

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Novel aqueous type II lyotropic mesophases that align in magnetic fields have been synthesized for binary and ternary mixtures of amphiphiles. A system in which major components of the micelle bilayer are decyltrimethylammonium and dodecanoate ions is an aligning mesophase from 100% to 35% dodecanoate, but replacement of the cationic amphiphile with hexadecyltrimethylammonium facilitates the extension to aligning mesophases up to 100% replacement of the dodecanoate ions. A study of sodium and deuterium quadrupole splittings observed in their nuclear magnetic resonance spectra, confirms and extends a three site adsorption theory for sodium ion in the mixed head group interface. The first site is associated with more strongly hydrated ions and head groups and involves adjacent dodecanoate head groups, the second is not so strongly hydrated and involves one dodecanoate group while the third is a weakly bound water at $-N(CH_3)_3^+$ groups and a sodium remote from the interface layer in close to average isotropic motion.

Mixed detergent mesophases of type II, which spontaneously align in the field, have also been synthesized from variable mixtures of hexadecyltrimethylammonium bromide and decylammonium chloride and from mixtures of potassium dodecanoate and sodium decylsulphate. In the mixed cationic system the sodium quadrupole splittings are always low but water is tightly bound to the $-NH_3^+$ head group. In the anionic detergent mixture sodium appears about as strongly bound to dodecanoate and decylsulphate head groups. In most of the mixed mesophases some decanol is required (maximum 25% of the bilayer) in order to render the desired type II mesophase stable over a range of mixtures of the charged detergents. Specific site adsorption for sodium and water, peculiar to different head groups renders the effect of the added decanol as primarily a convenient diluent in the bilayer to preserve mesophase integrity.

1 INTRODUCTION

The effects of monatomic ions such as sodium, cesium, chloride, bromide and others within the interfacial regions of lipid and detergent bilayers have been the subject of recent researches.[1–22] These studies have provided considerable insight with respect to the origin of observed quadrupole splittings in anisotropic mesophases, showing experimentally that to a large extent they arise from specific binding interactions to the headgroups of the amphiphilic components of the bilayer rather than overall electric field gradients from more macroscopic electric double layer phenomena. The results strongly suggest that such binding interactions also involve hydrogen bonds between the water of hydration about the monatomic ions and the headgroups. The studies have however been unable to elucidate the specific nature of such binding interactions.

Recent studies of deuterated water, bromide, acetate and sodium ions in lyotropic liquid crystalline materials that align in magnetic fields prepared from mixtures of potassium dodecanoate and decyltrimethylammonium bromide have led to a specific model proposal for the behaviour of sodium ions in those mesophases.[12] Unfortunately with this choice of amphiphiles, after about 65 mole % of the dodecanoate had been replaced with an equimolar amount of decyltrimethylammonium bromide the desired mesophase was not stable and the behaviour of the sodium ion throughout the complete range of bilayer compositions could not be investigated. We have recently discovered that hexadecyltrimethylammonium ion can replace decyltrimethylammonium in the desired region thus extending the interface study to 100 % cationic amphiphile in the bilayer.

From the results of the studies on the dodecanoate/decyltrimethylammonium mesophase it was suggested that the sodium ion could be bound in two distinct ways to the carboxylate group of the dodecanoate amphiphile.[23,24]

The simultaneous study of deuterium and sodium magnetic resonances in the mixed mesophase reveals an association involving both water and sodium ion with the carboxylate head group. A model was suggested in which one site involves sodium and water of hydration bridging two carboxylate groups. This site I lies, in all likelihood, among the carboxylate head moeites near the average interface plane defined by their mean positions. When neighbour positions of two carboxylate groups are successively removed by insertion of trimethylammonium in the average interface plane, a position of short range repulsion occurs for a positive ion and bridging sites of the type envisaged above are step by step eliminated. The experimental evidence leads to the postulate of a second site II in which the sodium is associated with one carboxylate group, such that there is vertical displacement of the sodium along the interface normal. The deuterium quadrupole splittings from water indicate a simultaneous decrease in the stability of the water association at the interface when site I is substituted for site II.

2 THE THREE SITE THEORY FOR SODIUM IONS ON THE MIXED INTERFACE $-N(CH_3)_3^+$ AND $-CO_2^-$

Exchange between all sites is rapid on the NMR time scale and thus the observed sodium quadrupole splitting, $\Delta\gamma_{Na}$, is given by Eq. (1).

$$\Delta\gamma_{Na} = X_I\Delta\gamma_I + X_{II}\Delta\gamma_{II} + X_{III}\Delta\gamma_{III} \tag{1}$$

where the X_i are the mole fractions of sodium ions in site i and $\Delta\gamma_i$ are the characteristic quadrupole splittings for each site.

The third site III is a general average of all sodium environments remote from the interface, where to a good approximation isotropic motion is expected.

From the model proposed it is clear that replacement of one dodecanoate by one decyltrimethylammonium destroys two site I locations for sodium and creates two of site II besides which of course there is one less sodium ion in the total system. Implicit in the model is the assumption that sodium at site III is unaffected by any replacements. The sodium splitting at high dodecanoate mole fraction is given by Eq. (2).

$$\Delta\gamma_{Na} = [\Delta\gamma_I C_D(3x - 2) + 2\Delta\gamma_{II} C_D(1 - x) + \Delta\gamma_{III} C_E]/[xC_D + C_E] \tag{2}$$

where C_D is the total number of moles of amphiphile, cationic plus anionic x is the mole fraction dodecanoate of total detergent and C_E is the number of moles of electrolyte present. From Eq. (2) it is seen that at 66.6 mole% dodecanoate all contributions from site I vanish as they should since there are no longer sodium ions in site I. Continued replacement of carboxylate by trimethylammonium simply removes one site II location. As a consequence from 66.6 to 0 moles percent dodecanoate in the bilayer the sodium splitting is given by Eq. (3).

$$\Delta\gamma_{Na} = [\Delta\gamma_{II} xC_D + \Delta\gamma_{III} C_E]/[xC_D + C_E] \tag{3}$$

With the amphiphilic system previously employed[24] it was not possible to vary the amphiphile ratio through the complete range and thus the experimental verification for the model proposed was limited. We have found that decyltrimethylammonium can be replaced by hexadecyltrimethylammonium in the region previously inaccessible, that is from 35 to 0 mole% potassium dodecanoate. The present study seeks to confirm the earlier model and extend the bilayer composition to complete replacement of anionic by cationic amphiphiles.

We have also prepared mixed mesophases of potassium dodecanoate with sodium decylsulfate and hexadecyltrimethylammonium bromide with decylammonium chloride. Previously the mixed mesophase of hexadecyltrimethylammonium bromide with hexadecylpyridinium chloride was reported[24] so that except for minor variations such as replacing one counter ion with another or variations in hydrocarbon chain lengths we have experimentally linked the behaviour of sodium ion and water in all of these systems. The mesophases reported here, which show type II behaviour[10] in their alignment in the magnetic field, are all novel combinations of amphiphiles in quaternary and quinquiternary systems.

RESULTS AND DISCUSSION

Mixed anionic/cationic mesomorphic materials spanning the range 90 to 0 mole % potassium dodecanoate in total detergent with the same overall amphiphile concentration in mole fraction have been prepared. Decyltrimethylammonium bromide was the cationic component in the 90 to 40 mole % range while hexadecyltrimethylammonium bromide was the second component in the range 40 to 0 mole % dodecanoate.

Table I shows the compositions of the mesophases studied, the deuterium and sodium quadrupole couplings observed and the sense of the corresponding variation with temperature as the samples warmed from room to magnet temperature, 31°C. Throughout the entire concentration range the total number of moles of detergent (C_D in Eqs. (2) and (3)) was kept constant at 1.745 mmoles. The amount of electrolyte, sodium bromide was kept constant at 0.875 mmoles. The small amount of decanol was varied as required for the desired mesophase formation while that of D_20 was constant for the decyltrimethylammonium bromide phases but about 10 % more was utilized in the hexadecyltrimethylammonium mesophases. Various samples containing dodecanoate, 0.4 mole fraction and decyl- plus hexadecyltrimethylammonium, 0.6 mole fraction, were also prepared. No unusual behaviour was observed on going through the concentration range from the extreme of pure decyl to that of hexadecylamphiphiles. There is therefore no phase change in this range.

The sodium quadrupole splitting (Figure 1 and Table I) decreases from a fairly large positive value of 4–5 KHz to become zero at about 73 mole % decanoate in the interface, and then proceeds to change sign reaching a maximum negative sign of −2.0 KHz at a little less than 60 mole % dodecanoate. The algebraic sense of the variation then reverses, the sodium

TABLE I

Results obtained for the mixed mesophases prepared with K Dodec/DTMABr/HDMABr. The magnitude of the quadrupole splittings and their direction of change as the samples warm in the spectrometer are given.

K Dodec, potassium dodecanoate; DTMABr, decyltrimethylammonium bromide; HDTMABr, hexadecyltrimethylammonium bromide.

	Composition mgm of each component					Parameters Quadrupole Splitting (Hz) and Temperature Dependence			
KDodec	DTMABr	HDTMABr	NaBr	D_2O	Decanol	^2H	Temp. Depend.	^{23}Na	Temp. Depend.
—	—	636	90	1098	85	−20	decrease	+896	increase
42	—	572	90	1103	59	−22	decrease	+265	increase
62	—	540	90	1092	48	−24	decrease	−40	decrease
83	—	509	90	1102	40	−23	decrease	−380	decrease
125	—	445	90	1103	17	−4	decrease	−1052	decrease
166	—	381	90	1097	—	+18	increase	−1781	decrease
166	91	263	90	1068	14	+25	increase	−1487	decrease
166	213	104	90	1028	33	+32	increase	−1440	decrease
166	294	—	90	1002	46	+42	increase	−1671	decrease
166	294	—	90	1003	47	—	—	−1532	decrease
209	246	—	90	999	18	+90	increase	−1722	decrease
250	196	—	90	1000	6	+140	increase	−1770	decrease
291	148	—	90	1000	—	+191	increase	−745	decrease
332	90	—	90	998	8	+247	small	+1524	increase
375	49	—	90	1000	27	+284	small	+4250	small

Errors in quadrupole splittings (except for the very small splittings) are estimated to be less than 1 %.

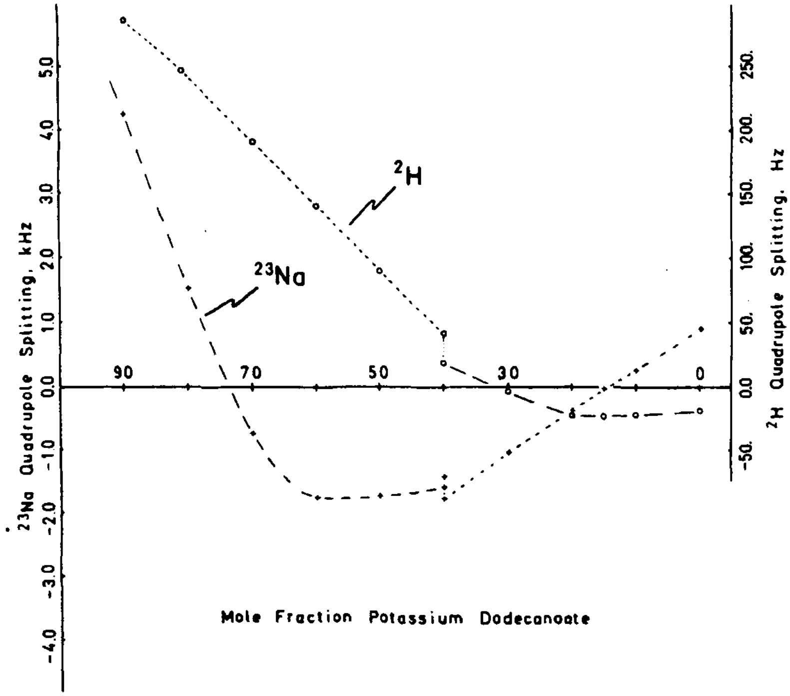

FIGURE 1 Sodium and deuterium quadrupole splittings as a function of mole fraction potassium dodecanoate (K Dodec) in the micelle bilayers. The mesophase compositions corresponding to the experimental points are taken from Table I. DTMABr and HDTMABr represent the decyl- and hexadecyl-trimethylammonium bromides respectively.

quadrupole splitting becoming a small positive quantity at 0 mole % dodecanoate. A view of the corresponding deuterium quadrupole splittings obtained for water, shows a strong decrease in magnitude to 50 % dodecanoate replacement and low values thereon. The model previously proposed and summarised here[24] explains the existence of 3 sites, only one of which requires an involvement of tightly bound water at the interface. Such structures are also indicated by the temperature dependence of the water splitting. At a high proportion of dodecanoate in the bilayer the deuterium quadrupole splitting of the deuterated water is insensitive to temperature, indicating a tightly bonded structure which is thus reasonably stable to small increases of temperature. At low concentrations of anionic amphiphile in the bilayer the temperature dependence of the water splitting is quite marked. This behaviour has previously been discussed.[24] The present results are more extensive in bilayer composition and show that there is a change in sign of the deuteriated water quadrupole splitting. However also rather small changes in mesophase composition are sufficient to change the values from negative to positive.

The sodium splittings in this system behave similarly to those previously reported,[24] there being minor differences doubtless the result of changes in composition between the two systems. The zero sodium splitting at 14 mole % dodecanoate was previously unobserved because this falls within the region that has now become accessible with replacement of decyltrimethylammonium by hexadecyltrimethylammonium in the micelle bilayer. The curve calculated using Eqs. (2) and (3) and the characteristic splittings; $\Delta\gamma_{\mathrm{I}} = +8.5$ KHz, $\Delta\gamma_{\mathrm{II}} = -4.2$ KHz, and $\Delta\gamma_{\mathrm{III}} = +1.0$ KHz and the values $C_D = 1.745$ mmoles of detergent and $C_E = 0.875$ mmoles of added sodium as the bromide follows closely the experimental values. Figure 2 shows the calculted curve with the observed values superimposed on it. The agreement is extremely good especially when one considers that many parameters not taken into account in the simple model proposed are in principle, accountable. For instance, the charge on the bilayer has been neglected. This should be important at high proportions of cationic amphiphile. Specifically a carboxylate surrounded by 4 trimethylammonium ions probably will not bind as efficiently to sodium as it would if the carboxylate were only associated with one trimethylammonium. Coulomb forces between ions are

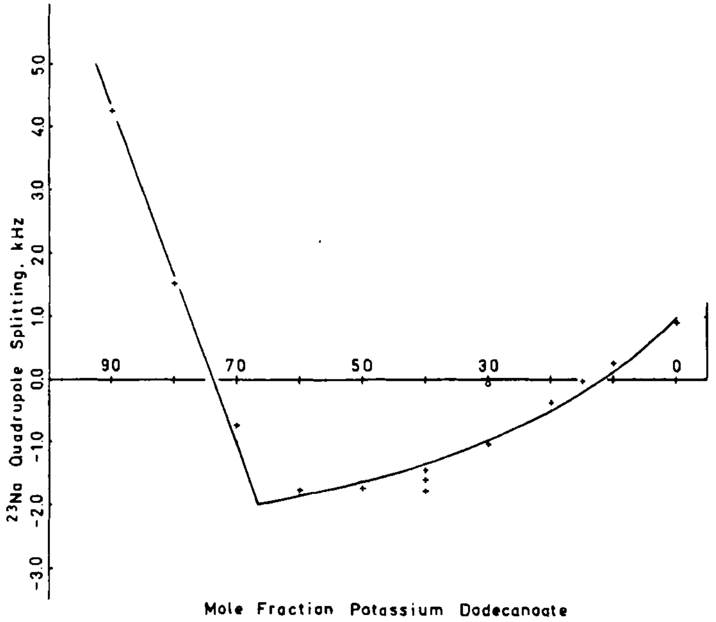

FIGURE 2 The calculated sodium quadrupole splittings as a function of mole percentage potassium dodecanoate in total detergent, + indicates the experimental points.

on the other hand short range and the cationic head group neighbour is well shielded by methyl groups. The effect of decanol has been ignored. It has an indirect affect on the splitting perhaps influencing the characteristic splittings through changes of micelle size.

All of the observed splittings are reduced from some higher value by oscillatory motions of the individual micelles. These amplitude and frequency spectrum of these movements are dependent in some manner on micelle size. Implicit in the proposed model for sodium interactions is the assumption that throughout the entire concentration range the reduction in degree of order of the distortion axis is constant. *Any* change in the composition of the mesophase will, in general, affect the characteristic values and produce a different experimental curve. For instance the experimental values reported here should be compared with those previously measured.[23] Fortunately, if molar proportions of all components are kept as constant as possible the calculated values agree well with experiment. This provides a means by which the various parameters not explicitly taken into account can be investigated.

An important point here is that a very simple mathematical expression has been obtained which predicts the experimental splittings with high accuracy, giving credance to the model. If the proposed chemical nature of the binding site is incorrect we are at least highly limited as to alternate proposals.

We have recently reported type II aligning mesophases prepared from two cationic detergents hexadecylpyridinium chloride and hexadecyltrimethylammonium bromide in any proportion.[23] It was found that throughout the range of mixed amphiphiles from pure pyridinium to pure trimethylammonium the water splitting was always small, although there was a decrease from +29 to +19 Hz. The sign of the water splitting was established by the temperature dependance of the magnitude of the splitting. As we have previously mentioned the sign of this splitting is dependent on the composition of the mesophase; the temperature dependance is not. That the water splitting is small and changes only slightly even with such a large change in chemical properties of the headgroup shows either that water associated with the headgroup is essentially isotropic in nature, or that there is only a small fraction of water in the interface, which could then be tightly bound. The first suggestion seems most reasonable.

The sodium splitting like the water splitting were relatively unaffected by replacement of one amphiphile by the other. The results of the previous study[23] have been reproduced here to contrast and emphasize the role of chemical variations of the interface in ordering aqueous components (Table II). There is a relatively small decrease in sodium splitting with the replacement of hexadecyltrimethylammonium by hexadecylpyridinium. This de-

TABLE II

Sodium quadrupole splittings for the HDTMABr/HDPCl mixed mesophases indicated. The sodium splittings increase in magnitude as the sample warms from room temperature to magnet temperature (32°). HDTMABr, hexadecyltrimethylammonium bromide; HDPCl, hexadecylpyridinium chloride.

	Phase composition mgm of each component				Quadrupole splitting (Hz)
HDTMABr	HDPCl	NaCl	H_2O	Decanol	^{23}Na
595	—	43	1052	114	1078
471	90	43	1050	114	966
446	139	43	1052	113	922
297	277	43	1050	116	897
149	416	43	1050	120	869
—	555	44	1054	114	759

Errors in quadrupole splittings are estimated to be less than 1%.

crease parallels that of the water being about 30% in either case. This small decrease perhaps indicates a difference in micelle size rather than any intrinsic difference between the behaviour at the two extremes of the mesophase. The changes are small and further studies are required.

In contrast to the pyridinium cases, replacement of hexadecyltrimethylammonium bromide with decylammonium chloride causes a large change in the water quadrupole splitting. The results are given in Table III. In this case the mesophase containing constant molar proportions of all com-

TABLE III

Sodium and deuterium quadrupole splittings for the HDTMABr/DACl mixed mesophases indicated. HDTMABr, hexadecyltrimethylammonium bromide; DACl, decylammonium chloride.

HDTMABr (mgm)	DACl (mgm)	NaCl (mgm)	Decanol (mgm)	H_2O (10%D_2O) (mgm)	$\Delta\gamma Na^+$ (KHz)	$\Delta\gamma D_2O^+$ (Hz)
—	300	36	—	503	1.025	180
57	270	37	17	554	1.310	164
113	240	38	24	599	0.885	103
169	210	38	35	650	0.845	78
226	180	39	50	742	0.930	65
282	150	41	54	803	0.710	45
339	120	41	61	865	0.770	37
395	90	42	68	909	0.744	29
451	61	43	73	952	+0.783	+24
509	30	44	78	1,003	+0.694	+16
564	—	43	81	1,015	+0.659	+12

The positive signs were determined from the temperature dependence of the splittings.

ponents was not possible. The signs of the water splittings were determined to be positive at low proportions of decylammonium chloride from their temperature dependance. The splittings at higher concentration must also be positive because the splittings always increase with higher proportions of decylammonium chloride. The temperature dependence cannot be used at high mole percentages of decylammonium chloride because the stability of the mesophase itself is quite temperature sensitive.[11] The large deuterium splittings for the pure decylammonium mesophase indicate a hydrogen bonded water structure built around the unshielded ammonium headgroup. The large value cannot be caused simply by rapid exchange with the highly aligned headgroups because the mesophase is acidified so that resonances from the water and ammonium group are seen separately the water splitting is still large.[11]

The sodium splittings, shown in Table III, cannot have changed sign throughout the range of replacement of hexadecyltrimethylammonium bromide with decylammonium chloride. The value of + 1.0 KHz for the sodium quadrupole splitting in the decylammonium extreme of the mixed mesophase is characteristic for cationic mesophases and seems independent of the headgroup. Typically as seen here such values range between +0.7 and + 1.1 KHz, dependent on the proportions of components in the mesophase itself. This shows us that sodium ions in all cases are removed from the immediate contact bilayer interface and relatively unaffected by replacement of one type of cationic amphiphile by another.

As can be seen from Table IV replacement of potassium dodecanoate by sodium decylsulfate serves to increase the magnitude of both the sodium and deuterium quadrupole splittings. It follows that there can be no sign change of the deuterium splitting from that of water absorbed on the anionic micelles of the pure dodecanoate mesophase. The +3.2 KHz splitting re-

TABLE IV

Sodium and deuterium quadrupole splittings for the K Dodec/Na De S mixed mesophases indicated. K Dodec, potassium dodecanoate; Na De S, sodium decylsulfate.

Na De S (mgm)	K Dodec (mgm)	Na_2SO_4 (mgm)	Decanol (mgm)	H_2O (10%D_2O) (mgm)	$\Delta\gamma Na^+$ (KHz)	$\Delta\gamma D_2O^+$ (Hz)
556	—	82	100	851	5.540	439
445	102	82	75	861	4.082	289
335	201	83	62	857	3.420	271
224	302	82	57	858	3.218	288
112	402	82	56	867	+2.606	+240
—	502	90	58	886	+3.225	+254

The positive signs were determined from the temperature dependence of the splittints.

ported for the sodium splitting in the dodecanoate phase is much smaller than the +5 to +6 KHz usually observed in this system. This is the result of the quite different concentration range of total detergent for stability of the type II mesophase that aligns in the mixed dodecanoate/decylsulphate micelle system. The results do indicate that the structure of the water surrounding the carboxylate group is probably not much different from that around the sulfate headgroup. The decylsulfate sodium splitting of 5 KHz is typical of such mesophases and similar to those normally observed for dodecanoate systems, a good indication that the strong hydrated bindings of sodium in sodium decylsulfate mesophases is very similar to that in potassium dodecanoate systems.

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