of 1100 nm, the limit of our studies.

Summary

In this paper we have used the IEH model to determine low-energy excited states of other than (π,π^*) origin in Co, Ni, Rh, and Pd porphyrins. [The congeners Ir and Pt should be similar to Rh and Pd, respectively.] The model does not accurately predict the transition energies from orbital energy differences, but it does provide a useful guide for explaining emission properties and also provides a basis for a serious search of the absorption spectra to the red of the lowest Q band for other than (π,π^*) transitions. We here summarize our conclusions and predictions by using P to stand for our calculations on porphine although the experiments could be on any porphyrin.

$Co^I(P)$. Emission is quenched due to (d,π^*) transitions, which are identified in absorption. The doubly excited states $[d,\pi \rightarrow (\pi^*)^2]$ strongly affect visible spectra.[31]

$Rh^I(P)$. There is very little study.[20] We predict no emission due to the (d,π^*) transitions. These should be at higher energy than in $Co^I(P)$, so doubly excited states should not affect the visible absorption spectra as strongly.

$Co^{II}(P)$. Emission is quenched due to (π,d) transitions, which are identified in the near-IR spectra with $\epsilon \sim 100\ M^{-1}\ cm^{-1}$.

$Rh^{II}(P)$. Recent work[37,38] has shown that the earlier reported species $Rh^{II}(TPP)$[20] was actually $Rh(TPP)O_2$ and that the species $Rh^{II}(TPP)$ dimerizes. For the true monomer, which perhaps can be obtained under the right conditions, our calculations predict that there will be no emission due to a low-energy (π,d) excited state. It is even possible that, under the right conditions, this CT state might become the ground state; i.e., the molecule could exist as the electronic isomer $Rh^I(P\cdot)$ rather than $Rh^{II}(P)$.

$Co^{III}(P)$. Emission is quenched by a low-energy $^3(d,d)$ state. We predict that this state may become manifest in picosecond flash spectroscopy. If sought, excited states $^1(d,d)$ and/or $^1(\pi,d)$ may be found in the near-IR absorption spectrum.

$Ni^{II}(P)$. Emission is quenched by a low-energy $^3(d,d)$ state, which has become manifest in picosecond flash spectroscopy.[32,33] States $^1(d,d)$ and $^1(d,\pi^*)$ have not been observed in the near-IR absorption region, although we find a much stronger tail absorption than in $Pd^{II}(P)$. Perhaps this tail may reveal $^1(d,d)$ and/or $^1(d,\pi^*)$ bands if observed in higher resolution conditions.

$Ni^{IV}(P)Cl_2$ and $Pd^{IV}(P)Cl_2$. Emission is quenched by low-energy (π,d) CT states. Transitions to such states should be sought in the absorption spectrum with $\lambda > 1100$ nm.

$Rh^{III}(P)X(py)$ and $Pd^{II}(P)$. [Here X is an anionic ligand.] No low-energy CT or (d,d) states are calculated, consistent with strong phosphorescence.[6-9] There are $Rh^{III}(P)$ complexes that will probably not emit, e.g., $Rh(P)NO$ and $Rh(P)O_2$.[37,38] These would be quenched by low-energy CT transitions of (π,l_π^*) origin where l_π^* refers to the lowest empty orbital of the axial ligand. Such states are presumed responsible for the lack of emission from Ru(OEP)NO(OMe).[4] Indeed a band at 595 nm is reported in the absorption spectrum of $Rh(OEP)O_2$[37,38] that may be of (π,l_π^*) origin.

Acknowledgment. The experimental studies on the radiationless transitions of Co and Ni complexes were carried out by Dr. Daniel Howell. The Co^{III}, Ni^{IV}, and "$Pd^{IV}(OEP)(Br_x)_2$" were supplied by Professor David Dolphin of the University of British Columbia. The $Pd^{IV}(TTP)Cl_2$ was supplied by Professor Johann W. Buchler now at the Technische Hochschule in Darmstadt. This research was supported in part by Public Health Services Research Grant AM 16508 and NSF Grant DMR-7823958.

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Interactions of the Aluminum(III) Ion in a Model Membrane System

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Abstract: The interactions of the aluminum(III) cation ($AlCl_3{\cdot}6H_2O$) with the carbonylated headgroups of potassium dodecanoate contained in a bilayer membrane have been studied. It was found that under dilute conditions aluminum binds very strongly to the carboxylate groups as the $Al(OH)_4^-$ ion but that this binding can be disrupted by the partial replacement of potassium dodecanoate with alkyltrimethylammonium. Disruption occurs only after about 25% of the dodecanoate is replaced by alkyltrimethylammonium indicating that aluminum causes the formation of an inhomogeneous bilayer, that is to say, regions from where cationic surfactant is excluded. No information concerning the size of the aggregates involved in such regions was obtained and they may simply be monomeric chelated aluminum complexes. When the bilayer is prepared from only dodecyltrimethylammonium bromide, the $AlCl_3{\cdot}6H_2O$ can be added to very high concentrations with no significant effect on the bilayer stability indicating that this aluminum compound has no intrinsic disruptive effect other than that of chemical binding. Adding NaOH to this last mesophase eliminates the $Al(H_2O)_6^{3+}$ resonance and provides a signal at 80 ppm corresponding to $Al(OH)_4^-$.

The interactions of monatomic ions with the polar regions of amphiphilic compounds are of considerable interest in various areas of chemistry, biochemistry, and medicine. Nuclear magnetic resonance (NMR) studies of such interactions have tended to be restricted to the ions lithium, sodium, and potassium, although to a lesser extent the rubidium, cesium, and halide ions have been studied.[1-8]

One ion which has received little attention is the aluminum trivalent cation, Al^{3+}. Although aluminum occurs abundantly in nature, it normally is present as chemical entities which are quite inert to further reactions. Aluminum has, however, been

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Table I. Deuterium and Aluminum Quadrupole Splittings Obtained from the Bilayer Materials Prepared according to the Composition Given in This Table[a]

					$\Delta\nu_D$, Hz			$\Delta\nu_{Al}$, Hz	
x[b]	KDodec[c]	DDTMABr[d]	DTMABr[e]	decanol	A	B	δ_{Al}, ppm	A	B
1.0	238			35.7	207	242	80.74	449	510
0.9	216	30		19.8	206	163	80.74	441	349
0.8	191	62		4.1	233	194	80.72	532	415
0.8	191		56	4.2	194	242	80.69	376	500
0.7	168		84		187	208	80.69	429	475
0.6	144		112		113	148	80.64	309	435
0.5	120		140	10.4	71	94	80.64	298	335
0.4	96		168	23.0	25	46	80.55	225	235
0.4	96	185		3.5	19	35	80.64	230	275
0.3	72	216		15.0	−5	0			
0.2	48	247		30.0	−30	−21			
0.1	24	277		43.3	−20	−23			
0.0	0	308		55.8	−13	−3	0	25[f]	58
0.0	0	308		55.8			80.50		−98[g]

[a] $AlCl_3 \cdot 6H_2O$, KBr, and D_2O were added in the proportions 0.6 mg:60 mg:600 mg, respectively. [b] Mole fraction of potassium dodecanoate in total detergent. [c] Potassium dodecanoate. [d] Dodecyltrimethylammonium bromide. [e] Decyltrimethylammonium bromide. [f] Value obtained when $AlCl_3$ replaced all KBr. [g] Negative sign expected from extrapolation of solid line of Figure 2. Signs of splittings are relative values.

implicated in the dialysis encephalopathy syndrome[9] where aluminum gels provide a source of the aluminum cation. Aluminum has also been shown to cause neuron degeneration and has been found in high concentrations in the brains of patients suffering from Alzheimer's disease, a form of senile dementia.[10]

It has been shown that aluminum inhibits yeast or brain hexokinases and that activation can be restored by various ligands such as phosphate or carboxylate.[11] A recent study of phosphate complexes of aluminum (Al^{3+}) in aqueous solution has been reported.[12] Aluminum chelates of carboxylic acids in aqueous solution have also been studied.[13]

Because of the preponderance of aluminum cookware, aluminum (as the cation Al^{3+}) is ingested by a large proportion of the population. Those working in the aluminum industry may ingest it in other forms. The subsequent interactions of the aluminum are of concern.

This is a study to investigate the interactions of the aluminum cation with carboxylate groups held in a liquid-crystalline bilayer matrix. Of particular interest here is how the cation binds to the carboxylate and whether the aluminum has a disruptive effect on the organization of the bilayer membrane.

Previous work has shown that for studies of this type the mixed amphiphilic system of potassium dodecanoate with alkyltrimethylammonium bromide provides readily interpretable results.[7,8] The advantage of this system is that one amphiphile may be replaced by another in any proportion with minimal effects on the bilayer.

The study of aluminum chelates with carboxylic acids in aqueous solution indicated that at lower pH (≈2–3) an exchange process was occurring. At higher pH (pH 11) resonances shifted from the aqueous $Al(H_2O)^{63+}$ cation by approximately 80–90 ppm were observed. These resonances were attributed to aluminum carboxylates.[13] A study of aluminum–phosphate complexes acidified to pH 2 showed that both free and complexed cations existed simultaneously and that exchange between the two species was slow on the NMR time scale (less than 10^3 s^{-1}).[12]

In the present study of the aluminum ion no acidification of the medium was carried out so that "neutral" solutions were employed. This removes the effects on the bilayer resulting from changes in pH. The results should also be more applicable to biological systems. The procedure utilized in this study has been discussed previously for the case of alkali and halide ions[7,8] and need not be repeated in detail here. In brief it has been found that the nematic bilayer mesophase prepared from potassium dodecanoate (potassium laurate) is stable to replacement of potassium dodecanoate by alkyltrimethylammonium ions on a 1:1 basis, where alkyl varies from C_{10} to C_{16} hydrocarbon. This stepwise replacement of one amphiphile by another of opposite charge provides an excellent means for probing the binding interactions between amphiphile and counterion. The binding interactions of Al^{3+} with the carboxylate headgroup of dodecanoate concerns us here.

The aluminum nucleus has a spin, I, of 5/2. Under the circumstances in which that nucleus is subjected to an anisotropic environment, the NMR spectrum shows five resonances arising from the interaction of the quadrupole moment of the nucleus and induced electric field gradients generated by the environment. The separation between transitions is the quadrupole splitting, $\Delta\nu_Q$, given by eq 1 where it is assumed that the distortion is symmetric.

$$\Delta\nu_Q = \frac{3}{2I(I-1)}QS \tag{1}$$

Q is the quadrupole coupling constant for the nucleus of interest and I is its spin. S is an order parameter which describes the alignment of the nucleus in the magnetic field of the NMR spectrometer. With other factors remaining constant this value is determined by the binding site and will be different for different sites.

The magnitude of the order parameter, S, is affected by the alignment of the amphiphilic micellar superstructure of the liquid-crystalline material. It is important that this alignment is constant throughout the range of liquid-crystalline materials employed in this study. A previous study of deuterium-labeled dodecanoate, decanol, and decytrimethylammonium in a system essentially the same as this has been reported.[14] Although rather large differences in deuterium quadrupole splittings for the individual components were observed, the average value was quite constant indicating that the overall alignment of the micellar components of the mesophase superstructure is also constant. With this being true the observed aluminum quadrupole splitting can be used to study the binding of the ion, and this splitting will, in the advent of fast exchange between the various binding sites, be an averaged value.

Experimental Section

The details concerning the materials used in this study have been previously discussed[7,8] while the proportions of the components utilized

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Table II. Deuterium and Aluminum Quadrupole Splittings Obtained at Two Temperatures from the Bilayer Materials Whose Composition Is Given in This Table[a]

x[b]	KDodec[c]	DDTMABr[d]	DTMABr[e]	decanol	$\Delta\nu_D$, Hz 25 °C	$\Delta\nu_D$, Hz 35 °C	$\Delta\kappa_{Al}$, Hz 25 °C	$\Delta\kappa_{Al}$, Hz 35 °C
1.0	239			36	218	191	446	374
0.9	215		28	20	252	240	504	468
0.8	190		57	6	232	213	485	440
0.7	167		85	4	207	205	495	461
0.6	143		113	4	130	130	373	340
0.5	119		142	13	71	76	303	270
0.4	95		170	24	31	37	230	
0.1	24	227		41	−17	−5		
0.0		308		56	−4	0	60	60

[a] $AlCl_3 \cdot 6H_2O$, KBr, and D_2O were added in the proportions 0.6 mg:60 mg:600 mg, respectively. [b] Mole fraction potassium dodecanoate in total detergent. [c] Potassium dodecanoate. [d] Dodecyltrimethylammonium bromide. [e] Decyltrimethylammonium bromide.

in each sample are given in the tables.

NMR spectra were obtained from a Bruker WM-400 NMR spectrometer operating in unlocked mode. Deuterium was observed by using the lock channel of a broad-band probe tuned to the aluminum frequency. This allowed switching between observation frequencies to occur simply by moving the transmitter input cable to the probe from the broad-band position to the lock position. A few seconds were thus required to change observation from one nucleus to the other.

Spectra were obtained at ambient temperature ~21 °C (Table I) and at 25 °C and 35 °C (Table II). Quadrupole splittings are accurate to about 2% or better, dependent on the line widths observed. No attempt to obtain more accurate measurements was made.

Results

Table I gives the results observed when the aluminum quadrupole splitting was measured as a function of the mole fraction of potassium dodecanoate in total detergent. Because of an unexpectedly large scatter in data obtained from the first set of experiments a second independent investigation was carried out, again providing a large scatter in the quadrupole splittings. The two sets of data are presented under columns A and B, respectively. This scatter is atypical for systems of this type where smooth curve are generally obtained.[7] However, even the quadrupole splittings from the deuterium of the D_2O used in these samples showed a scatter of splittings rather than a smooth curve. This indicates strongly that the source of the scatter lies with the samples themselves rather than with the aluminum. In this regard it should be noted that the salt $AlCl_3 \cdot 6H_2O$ was added as 1% of the total electrolyte utilized in bilayer formation, the second component being KBr. Higher concentrations of $AlCl_3$ than this resulted in the precipitation from solution of a product, presumably an aluminum carboxylate. A third set of experiments with slightly changed conditions provided more consistent results as can be seen in Table II.

There are several other aspects of this investigation which are important. One is that the spectra obtained from samples containing 70 mol % potassium laurate showed line broadening which progressively increased with decreasing mole fraction until no aluminum resonance could be observed (30, 20, 10 mol %). With no carboxylate component present in the bilayer a sharp resonance was observed even when all of the electrolyte was replaced by $AlCl_3 \cdot 6H_2O$. Under these conditions no Al^{3+} binding sites other than water are available to the aluminum cation. This result indicates that the $AlCl_3$ salt has no intrinsic disruptive effect on a bilayer. Therefore if aluminum does have a disruptive effect it will be caused by the binding of aluminum to the surfactant. In the present case the binding sites are carboxylate groups but clearly phosphate, sulfate, or even various zwitterionic species could serve as well.

The broadening of the aluminum resonance between mole fractions ≈0.7 and 0.0 has been attributed to chemical exchange between $Al(OH)_4^-$ ions bound to carboxylates through intermediate stages to the free ion in aqueous solution which also undergoes exchange. It was also observed that when the temperature was increased 10 °C from 25 to 35 °C that broadening became more pronounced as would be expected from chemical exchange considerations. Further evidence for this is provided by the chemical shifts observed for the cation. The shifts for $Al(H_2O)_6^{3+}$ in aqueous solution and the corresponding ion in the bilayer system containing only cationic amphiphile were the same. In the bilayer systems which contained carboxylate the aluminum shifts were +80.7 ppm.

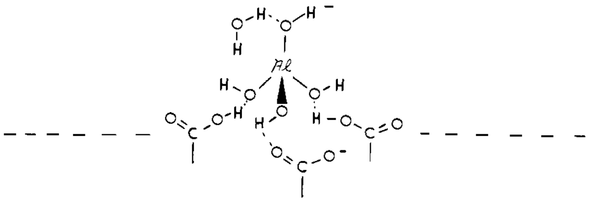
The equivalence of the shifts of aluminum in a cationic mesophase and in D_2O indicates that the aluminum ion ($Al(H_2O)_6^{3+}$) resides in the interstitial water and is removed from the bilayer surface. The interstitial water is expected to be nearly isotropic in character.

Chemical shifts of 80–90 ppm have previously been assigned to monomeric aluminum carboxylate species.[13] Shifts of 80 ppm were observed at high pH (≈11) with small shifts being observed at low pH (−2 to 5 ppm). The intermediate range gave only broad signals which are attributable to chemical exchange broadening. At the lower pH the carboxylates are present in the acid form which can chelate with aluminum while at high pH the carboxylates are present as the anions and more readily available for the formation of aluminum carboxylates. In the present work no dipole–dipole couplings between aluminum nuclei were observed as would be expected if polymeric aluminum species were formed, this in spite of the fact that the five-line quadrupole spectrum was well resolved. The results obtained in this study could possibly be attributed to the formation of aluminum carboxylates.

Chemical shifts of 80 ppm have also been attributed to the tetrahedral ion $Al(OH)_4^-$ when aluminum was observed under basic conditions.[15] A similar result was obtained here. When the cationic phase (no dodecanoate) was made slightly basic, pH ≈8, with NaOH the aluminum resonance broadened and no signal was observed. At higher pH a signal at 80.5 ppm was observed with a quadrupole splitting of 98 Hz and line widths of about 15 Hz. This resonance is ascribed to the ion $Al(OH)_4^-$.

The close agreement observed between the chemical shift of this ion and those of the aluminum in the carboxylate-containing mesophases strongly indicates that $Al(OH)_4^-$ is binding to the carboxylates. This is supported by the fact that the electric quadrupole moment for aluminum is moderately large and all quadrupole splittings observed here quite small. Consequently it is unlikely that other than a tetrahedral ion similar to the hydroxide is giving rise to the observed splitting.

Binding of this ion to the carboxylate groups might be envisioned as somewhat similar to that depicted here



Of course other possibilities are that only one or two carboxylates are involved in binding or that a complex water structure

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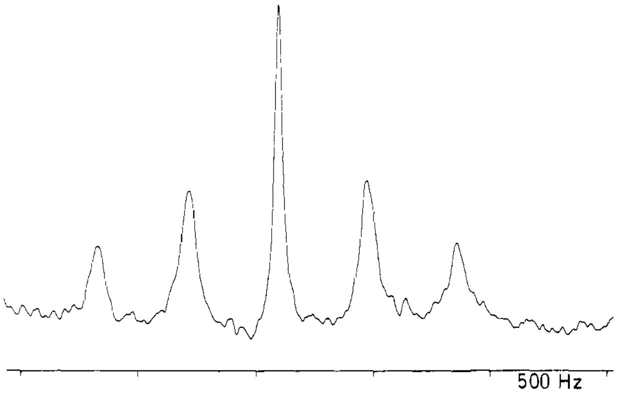


Figure 1. An aluminum spectrum (entry $x = 0.6$, Table I) showing the broadened outer transitions attributed to the effects of chemical exchange.

is built around the ion. Clearly the binding is sufficiently strong to destabilize the hydrate ion $Al(H_2O)_6^{3+}$ in favor of the hydroxide. The NMR spectrum gives no indication that significant proportions of other than one species are present in solution when no cationic amphiphile is present. This is not so for the mixed anionic/cationic mesophases.

As was seen, when about 30 mol % of potassium dodecanoate is replaced by decyltrimethylammonium the resonance lines broaden because of chemical exchange. The evidence suggests that exchange occurs in two steps. The first step is an exchange between bound and free aluminum hydroxide. The second involves an exchange between aluminum hydroxide and aluminum hydrate. Only the bound ion is detected since exchange broadening makes the others unobservable. The presence of the second exchange is inferred from the fact that there is a reduction in detected signal intensity. The exchange broadening observed for the detected signal is attributable to almost completely averaged quadrupole splittings. The exchange sites for the first equilibrium are taken to be either aluminum bound to carboxylate groups within the bilayers as depicted above, site I, or the corresponding aluminum hydroxide removed from the surface, site II. The second exchange involves an equilibrium between $Al(OH)_4^-$ and $Al(H_2O)_6^{3+}$.

Figure 1 shows a spectrum for which the line broadening of the outer transitions has been attributed to chemical exchange (Table I, mole fraction 0.6). It should be noted that deuterium line widths for the quadrupole split deuterium transitions are less than 2 Hz for splittings of 130 Hz establishing that inhomogeneity of the mesophase is not providing the broadened aluminum resonances.

The separation between the $Al(H_2O)_6^{3+}$ resonance and that of the hydroxide, $Al(OH)_4^-$, is about 80 ppm which chemical shift corresponds to about 8 kHz for the spectrometer utilized in this study. The rate of interconversion between these species must be in the order of 8 kHz since loss of signal intensity and observation of no second signal implies the occurrence of an averaging process of this time scale. There are presumably intermediate stages in this last exchange which are not observable with these experiments, for instance species such as $AlOH{\cdot}5H_2O^{2+}$ might be formed.

If chemical exchange is fast enough to average quadrupole splittings the observed splitting, $\Delta\nu$, is simply

$$\Delta\nu = \Delta\nu_I X_I + \Delta\nu_{II} X_{II} \tag{2}$$

where $\Delta\nu_i$ is the characteristic splittings for site i and the X_i are the corresponding mole fractions of nuclei in sites i. Since site II is undergoing further exchange, $\Delta\nu_{II}$ is not given by the NMR spectra; however, the $\Delta\nu$ for $Al(OH)_4^-$ is about 98 Hz in the cationic mesophase as compared to 60 Hz for the $Al(H_2O)_6^{3+}$ ion (Table I). The difference is small and $\Delta\nu_{II}$ must be close to these values; it is assumed to be 60 Hz.

No significant exchange broadening observed until about 30% of the dodecanoate is replaced by dodecyltrimethylammonium indicates that essentially all the aluminum is bound until 20 to 30% replacement is reached. From Table II and eq 2, $\Delta\nu_I$ is approximately 485 Hz and $\Delta\nu_{II}$ is –60 Hz. By a simple average eq 2 would predict that at 60% replacement of dodecanoate, X equals 0.5. A linear extrapolation of this would imply that all aluminum is bound at 20% replacement of dodecanoate. This value is in good agreement with that estimated from the observation of the onset of exchange broadening.

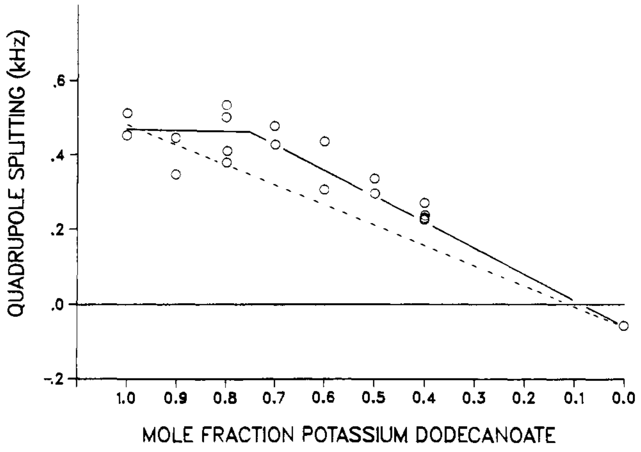


Figure 2. The aluminum quadrupole splittings of Table I are plotted as a function of the mole fraction of potassium dodecanoate in total detergent. The solid line represents quadrupole splittings calculated according to eq 3, and the dashed line according to eq 4. Even with the large scatter of points, eq 4 gives an unacceptable fit to the observations.

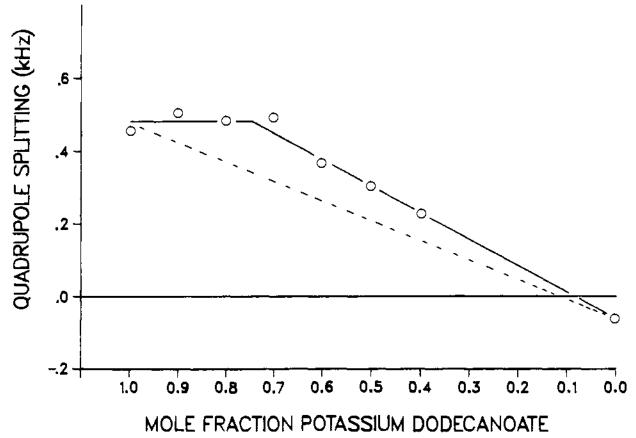


Figure 3. The aluminum quadrupole splittings of table II are plotted as a function of the mole fraction of potassium dodecanoate in total detergent. The solid line represents quadrupole splittings calculated according to eq 3, and the dashed line according to eq 4. Equation 3 fits the observations very well.

If 25% replacement of dodecanoate is accepted as a reasonable value for the onset of the occurrence of $Al(OH)_4^-$ in site II, then the quadrupole splitting can be written in terms of the mole fraction, x, of potassium dodecanoate in total detergent.

$x = 1.0 \rightarrow 0.75$

$$\Delta\nu = \Delta\nu_I \tag{3}$$

$x = 0.75 \rightarrow 0.0$

$$\Delta\nu = \left[\Delta\nu_I \frac{x}{0.75} + \Delta\nu_{II}\left(1 - \frac{x}{0.75}\right)\right]$$

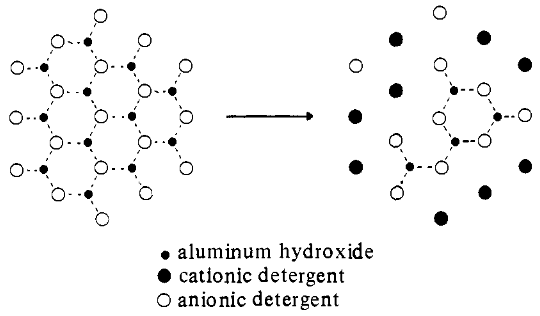
Figure 2 shows the calculated curve with the experimental points from Table II superimposed. For comparison purposes a second curve (dotted line) is also shown where it is assumed that $Al(OH)_4^-$ is displaced into the interstitial water linearly with cationic detergent concentration as expressed by eq 4. Even with the scatter of

$$\Delta\nu = \Delta\nu_I x + \Delta\nu_{II}(1 - x) \tag{4}$$

quadrupole splittings observed in Table I this last curve (Figure

3) is not in agreement with the results whereas the first agrees very well.

These results indicate that aluminum binds to the carboxylate amphiphile so strongly that this binding is disrupted only after a significant proportion of the anionic component has been replaced by the cationic amphiphile. This is a much different situation from the alkali metal binding where relocation from a site I to a site II occurs with even a small replacement of one amphiphile by the other.[8] The aluminum causes the formation of an inhomogeneous bilayer, inhomogeneous in the sense that $Al(OH)_4^-$/carboxylate aggregates are formed which are stable to the presence of 20–25 mol % replacement of carboxylate by alkyltrimethylammonium. (Note that concentrations of aluminum are such that this replacement can occur away from the aluminum-containing regions.) The result of this is that there are bilayer regions containing dodecanoate interspersed with dodecyltrimethylammonium and other regions containing aluminum carboxylate aggregates from which the dodecyltrimethylammonium is excluded. With continued replacement of carboxylate with trimethylammonium these complexes are destroyed. The size of these proposed aggregates is one of conjecture only. They may simply by molecular complexes or larger areas of inhomogeneity such as depicted below.



Conclusions

The results from this study of the aluminum cation in a bilayer liquid-crystalline system show that aluminum binds strongly to the carboxylate group of dodecanoate and indicate that binding occurs in only one way. When this binding site is destroyed by replacement of dodecanoate with dodecyltrimethylammonium the aluminum ion moves into the interstitial water. This behavior should be compared with that of the alkali metal cations where binding to the carboxylate group occurs in two different ways. Stepwise addition to trimethylammonium initially destroys the first binding site and the alkali ion moves into the second site. Finally with continued replacement of carboxylate with trimethylammonium the alkali cation is displayed into the interstitial water.[8]

The binding of aluminum to the carboxylates is sufficiently strong to cause the formation of an inhomogeneous bilayer. Only when about 25% of the bilayer consists of cationic surfactant are dispersive forces strong enough to break the aluminum–carboxylate complex and cause aluminum to move into the aqueous region of the bilayer system.

In the case where only cationic surfactant is used for sample preparation the aluminum resonance occurs at the chemical shift of $AlCl_3$ in D_2O; also in this case all the electrolyte (KBr) normally in sample preparation can be replaced by $AlCl_3{\cdot}6H_2O$ with minimal effect on the mesophase. This indicates that $Al(H_2O)_6^{3+}$ has no intrinsic disruptive effect on a bilayer. In the presence of carboxylate and when the concentration of aluminum cation is small the interaction of aluminum with the carboxylate causes the formation of an inhomogeneous bilayer and when more about 1% of the electrolyte is replaced by $AlCl_3{\cdot}6H_2O$ a precipitate is formed.

When the cationic mesophase is made slightly basic with NaOH the $Al(H_2O)_6^{3+}$ signal at 0 ppm disappears because of exchange broadening. With additional base a signal, attributed to $Al(OH)_4^-$, appears at 80.5 ppm. It is this ion rather than the positively charged $Al(H_2O)_6^{3+}$ ion which undergoes the binding interaction with carboxylate. The bound ion interconverts with $Al(OH)_4^-$ removed from the bilayer interface which in turn undergoes an equilibrium with $Al(H_2O)_6^{3+}$.

The behavior of this system is very complex and further studies are required.

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