

Figure 2. Arrhenius plot of corrected ϕ_{RuI} (see text) vs 1/T.

activation energy of 6.87 ± 0.11 kcal/mol.

The quantum yield of [Ru(bpy)₂(bpy⁻)]⁺(ads) formation reflects photoionization of $Ru(bpy)_3^{2+}(ads)$, electron transport on the glass surface, and reduction of a second $Ru(bpy)_3^{2+}(ads)$ (eq 4) that lies within the electron migration distance.¹⁰ As described above, $\phi_{\rm isc}$ and $\phi_{\rm ion}$ are taken to be independent of temperature in the 5-95 °C range. Meisel, Matheson, and Rabani report that the rate constant for reduction of $Ru(bpy)_3^{2+}$ by the hydrated electron in aqueous solution is 6.0×10^{10} M⁻¹ s⁻¹,³⁵ which is in close agreement with the value $8.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, reported by Baxendale and Fiti.³⁶ Both values suggest a reaction unfettered by an activation barrier. Furthermore, assuming that the reduction potential of the electron on the glass is equivalent to that in aqueous solution, 2.7 eV,^{37,38} since its optical spectrum is essentially

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equivalent to that in aqueous solution, 10,39 reaction 4 has a net driving force of ca. 1.5 eV, while that for reaction 5 is ca. 4 eV. In view of these exothermicities, we assume that reactions 4 and 5 possess little or no activation barriers, and their respective rate constants, k_7 and k_8 , are essentially independent of temperature. Consequently, the measured activation energy, 6.87 ± 0.11 kcal/mol, is attributed principally to barriers encountered during electron transport on the glass surface. Within the proposed surface conduction model,¹⁰ this suggests that the average depth of the surface acceptor site(s) is $\leq 6.87 \pm 0.11$ kcal/mol.

Conclusion

Emission polarization and the lack of macroscopic redistribution of $Ru(bpy)_3^{2+}$ on PVG establishes that the electrostatic interaction binding $Ru(bpy)_3^{2+}$ to PVG is of sufficient strength to prevent adsorbate mobility in the 5-90 °C range. The quantum yields of [Ru(bpy)₂(bpy⁻)]⁺(ads) formation, corrected for the temperature dependence of the MLCT state lifetime, increase with increasing temperature and, within the proposed surface conduction model, suggest that the average depth of the surface acceptor site(s) is $\leq 6.87 \pm 0.11$ kcal/mol.

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Anion Exchange in Lithium Aluminate Hydroxides

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The vibrational spectra of the positively charged framework of the lithium aluminate clay [Al₂Li(OH)₆]⁺ along with its deuteriated analogue have been examined. The site symmetry of the AlO_6 unit is determined to be D_3 , on the basis of the vibrational spectra. Characteristic bands due to the AlO₆ and OH groups in the clay were found. From the ion-exchange studies of the clay with nitrate, sulfate, and phosphate ions, the siting of the anions as well as ion-exchange selectivities was determined. It was found in the phosphate series that the ion-exchange selectivities followed the order $PO_4^{3-} > HPO_4^{2-} > H_2PO_4^{-}$. Organic anions such as benzoate can also be ion exchanged, and the vibrational spectroscopy indicates that they occupy sites both parallel and perpendicular to the lithium aluminate layer. Finally, ion exchange with organometallic anions $Fe(CN)_6^4$ and nickel(II) phthalocyaninetetrasulfonate has been examined.

Introduction

Layered claylike materials that exhibit anion-exchange properties are far less common that the ubiquitous cationic clays.¹ The natural minerals belonging to this class comprise of the pyroaurite sjogrenite group.² Hydrotalcite, a member of this group, is represented by [Mg₃Al(OH)₈]⁺Cl⁻ and has been one of the most extensively studied.³⁻⁵ These materials can be thought of as comprised of brucite-like $(Mg(OH)_2)$ layers, in which each Mg^{2+} is surrounded by six hydroxyl groups in an octahedral arrangement. These octahedra share edges to form long sheets. The Mg²⁺ can be replaced by an Al³⁺, with the result that the layer gains a positive charge and needs to be neutralized by intercalated anions, which can be readily ion exchanged.⁶⁻⁸

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TABLE I: Interlayer Spacing in Ion-Exchanged [Al₂Li(OH)₆]⁺Xⁿ⁻

	X*-							
	Cl-	NO3-	SO4 ²⁻	PO4 ³⁻	C ₆ H₅COO ⁻	Fe(CN) ₆ ⁴⁻	phthalocyanine	
c, ^a Å interlayer spacing ^b	15.14 2.77	18.06 4.23	21.54 5.97	21.16 5.82	40.01, 19.58 15.2, 4.99	21.96 6.18	21.22 5.81	

^a Hexagonal cell, a = 3.07 Å. ^b Basal spacing, 4.8 Å.

Recently, Serna et al. reported on the synthesis of a [Al₂Li- $(OH)_6$ ⁺ type compound, which can be thought of as gibbsite-like (Al(OH)₃), in which the Al³⁺ atom in the octahedral layer is replaced by Li⁺, resulting in a positively charged layer.⁹ The spectroscopic and ion-exchange properties of these materials are still relatively unexplored $^{10-12}$ and form the focus of this study. The vibrational spectra of the $[Al_2Li(OH)_6]^+$ layer and ion exchange with oxyanions and organic and organometallic anions have been explored. Structural assignments, siting of the anions, and selectivity for ion exchange are studied with the help of X-ray diffraction and vibrational spectroscopy.

Experimental Section

Our synthesis procedure is a variation of the method described by Serna et al.⁹ Aluminum (0.05 mol) was dissolved in 100 mL of 2 M sodium hydroxide. LiCl (0.25 mol) was dissolved in this solution, and the mixture heated for 48 h at 90 °C. The products were washed with water followed by 0.1 M NaCl. Care was taken to exclude CO_2 during the synthesis. Similar synthesis procedure was followed with $NaOD/D_2O$ to obtain the deuteriated product. All materials used were analytical grade reagents. Ion exchange of the clay was carried out with 0.1 M solutions of anions for a period of 24 h. The samples were washed with deionized water and air-dried prior to the spectroscopic experiments.

Excitation for the Raman spectrum was done with 10-50 mW of 457.9-nm radiation from a Spectra Physics argon ion laser except when mentioned differently in the text. The scattered light was collected and dispersed through a Spex 1403 double monochromator and detected with a GaAs PMT with photon counting. Infrared spectra were collected on a Mattson Cygnus FTIR spectrometer. Powder X-ray diffraction was obtained with a Rigaku Geigerflex D/Max 2B diffractometer using Cu K α radiation.

Results and Discussion

The powder X-ray diffraction pattern of the chloride containing clay is shown in Figure 1a. Reflections at d values of 7.668, 3.801, 2.596, and 1.929 Å are observed. Sharpness of the reflections (widths ~ $0.2(2\theta)$) indicate the formation of good quality crystals. Similar reflections have been reported for [Al₂Li(OH)₆]₂CO₃ synthesized by different procedures and indexed on the basis of a hexagonal unit cell.⁹ The presence of a reflection at d = 4.4Å (101) has been correlated with an ordered arrangement of Li and Al atoms.⁹ Hydrotalcites also exhibit a similar reflection due to cation ordering, and in such cases indexing requires the presence of a supercell.¹³ An alternate indexing has been proposed for the Li-Al compound utilizing a monoclinic unit cell, with the d= 4.4 Å reflection indexed as (110).¹⁰ This change in assignment was prompted by the lack of shift of this reflection upon change in spacing between the basal planes (in the c direction).

We do not observe a reflection at d = 4.4 Å in our samples. However, upon washing with dilute HCl (0.005 M), a weak reflection at d = 4.4 Å is observed along with other weak re-



Figure 1. (a) XRD pattern of [Al₂Li(OH)₆]Cl; (b) sample in (a) washed with 0.005 M HCl; (c, c') Raman spectrum of [Al₂Li(OH)₆]·Cl.

TABLE II: Framework Vibrations of AlO₆ in [Al₂Li(OH)₆]⁺ (in cm⁻¹)

$Al(OH_2)_6^{2+a}$	O _h	D_3	Al ₂ Li(OH) ₆ ⁺	Al ₂ Li(OD) ₆ ⁺	assgnmt
542	A _{1g}	A ₁	602	593	$v_1(vA1-O)$
473	E	Е	460	NO ^b	$v_2(vOAlO)$
347	F _{2g}	A_1	362	353	$\nu_5(\delta OAlO)$
	-0	E	402	NO	
590	F _{1u}	A2 E	752 (br)	740	<i>v</i> ₃ (<i>v</i> Al−O)
350	\mathbf{F}_{1n}	Ā,	535	526	ν₄(δOAlO)
		Ē	555	NO	. ,
NO	F _{2u}	\mathbf{A}_1	NO	NO	$\nu_6(\delta AlO)$
		E	380	NO	

^aReferences 18 and 19. ^bNO: not observed.

flections at 4.792, 2.22, 1.724, and 1.633 Å. The original peaks due to the clay are largely unperturbed (Figure 1b). Peaks at these reflections were also reported by Sissoko et al. for [Al₂- $Li(OH)_{6}_{2}SO_{4}$ and assigned to the monoclinic unit cell.¹⁰ These reflections are all characteristic of bayerite, a form of Al(OH)₃.¹⁴ We assign these reflections due to impurities of bayerite and do not consider them to be arising from the Li-Al clay. The appearance of these peaks upon acid washing of the samples indicates that $Al(OH)_3$ is present as impurities in the synthesized LiAl hydroxide.

The extensive diffraction studies of hydrotalcites, including a single-crystal study of coalingite¹⁵ indicates that a rhombohedral or hexagonal structure is appropriate for these compounds. All of the materials in this study were indexed by using a hexagonal unit cell with a = 3.07 Å. The calculated c parameters are listed in Table I along with the interlayer spacing. The basal spacing is half of the "c" parameter. The interlayer spacing is calculated by subtracting 4.8 Å from the basal spacing.^{6,7} The lack of the reflection corresponding to the supercell would indicate a disordered arrangement of Li and Al atoms in our samples. The structure of this material can be pictured as layers of edge sharing M(OH)₆ octahedra, with -OH groups positioned above and below the anions that occupy interlayer space.

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The Raman spectrum of the synthesized clay is shown by Figure 1c, c'. Bands are observed at 362, 402, 460, 555, 602, 880, 1030, 3250, 3484, and 3590 cm⁻¹. In the infrared spectrum, bands are observed at 380, 405, 460, 535, 752, and 1018 cm^{-1.9} The assignment of these vibrations are listed in Table II. The framework vibrations arise from LiO₆ and AlO₆ units. The modes involving Li-O motion are expected at low frequencies. In systems such as LiNO₃¹⁶ or Li-exchanged zeolites,¹⁷ these bands are found to occur at less than 300 cm⁻¹. Efforts at obtaining Raman spectra in this low-frequency region are frustrated by the strong scattering from these microparticles. The vibrational bands observed in the 300-800-cm⁻¹ region are arising from motions of the AlO₆ unit. A strict inversion symmetry in the factor group would mutually exclude infrared and Raman bands. Coincidences of these bands e.g., at 402 and 460 cm⁻¹, would indicate the lack of an inversion symmetry and would suggest that the site symmetry of the AlO_6 unit is of D_3 or lower symmetry. The correlation between the O_h and D_3 symmetry is shown in Table II and indicates that coincidences between the infrared and Raman bands due to E vibrations is expected.

A good model for the AlO₆ unit in the clay is the hexaaquoaluminum cation (Al(OH₂) $_{6}^{3+}$). Both infrared and Raman spectra of many alums $(M(OH_2)_6^+Al(OH_2)_6^{3+}2SO_4^{2-}, M = alkali-metal$ cation) have been reported.^{18,19} Single-crystal Raman spectra of cesium alums exhibit bands at 542 (ν_1 , A_{1g}), 473 (ν_2 , Eg), and 347 cm⁻¹ (v_5 , F_{2g}) due to the AlO₆ unit. The corresponding bands in the solution are at 525, 447, and 340 cm^{-1} .²⁰ The infrared spectra of Cs and K alums show bands at 590 (v_3, F_{1u}) and 350 (ν_4, F_{1u}) cm⁻¹ from the AlO₆ unit. On the basis of these data, we assign the bands in the clay as 362, 402 (ν_5 , δ OAlO), 380 (ν_6 , δOAlO), 460 (v₂, vOAlO), 532, 555 (v₄, δOAlO), 602 (v₁, vOAL), and 752 cm⁻¹ (ν_3 , ν OAL). These assignments are also supported by vibrational data of clays synthesized in D_2O (Al₂Li(OD)₆⁺). For v_1 and v_5 , the calculated value for v_D/v_H is 0.972, whereas the observed values are 0.985 and 0.975, respectively. For the infrared-active v_3 and v_4 modes, the ratio $(v_3v_4)_D/(v_3v_4)_H$ is calculated to be 0.964, whereas the observed value is 0.972.

Weak bands are also observed in the Raman spectrum at 880 and 1030 cm⁻¹ due to the O-H bending mode. There is also a sharp band at 1074 cm⁻¹, due to the carbonate ion, which is incorporated during the synthesis, even though precautions were taken to exclude CO₂. This band disappears upon washing with dilute HCl (0.005 M), without any effect on the other Raman bands. The corresponding O-D bending modes in the deuteriated sample were not observed.

In the O-H stretching region (Figure 1c'), broad bands at 3250 and 3484 cm⁻¹ along with a sharper band at 3590 cm⁻¹ are observed. The corresponding bands in the deuteriated sample occur at 2398, 2440, and 2651 cm⁻¹. On the basis of the reported data for water,²¹ the bands at 3250 and 3484 cm⁻¹ can be assigned to intercalated water in the clay layers. The sharper band at 3590 cm⁻¹ is assigned to O-H groups of the clay H bonded to the chloride anion. The siting of the chloride ion in the interlayer is of interest in relation to this band. Adjacent layers of $M(OH)_6$ octahedra are stacked upon another with the OH groups extending into the interlayer space. Taylor has pointed out that in mineral hydroxides there are groups of sites clustered around each -OH group in the interlayer.² The number of sites and their orientation may vary. Three or six sites have been proposed for sjogrenite and pyroaurite.² Only one of these sites would be occupied by atoms of the interlayer species, such as water and anions. The



Figure 2. (a,a') Raman spectrum of [Al₂Li(OH)₆]·NO₃.



Figure 3. (a) Raman spectrum of $[Al_2Li(OH)_6]_2SO_4$; (b) Raman spectrum of 0.1 M sulfate solution used for ion exchange to obtain (a).

interlayer spacing in the chloride clay is ~2.8 Å as compared to the diameter of the anion of 3.6 Å (Table I). The chloride ion must position itself at the center of the three OH groups along the C_3 axis. The band at 3590 cm⁻¹ is assigned to the O-H stretch of the hydroxyl groups bonded to the chloride. Water molecules are also present in the interlayer, along the OH sites, as described by Taylor.² The OH stretching frequency of these hydroxyl groups of the clay are buried beneath the water vibrations (3484 cm⁻¹).

Exchange with Oxyanions

Nitrate Ion. The chloride ion in the clay can readily by replaced by ion exchanging with sodium nitrate. The powder pattern indicates that the spacing in the nitrate-exchanged clay increases to \sim 4.2 Å, the diameter of the nitrate anion being \sim 3.8 Å. The Raman spectrum of this material is shown in Figure 2. Three Raman bands are typically observed for the nitrate anion, e.g., in crystalline LiNO₃¹⁶ the bands are at 735 (E'), 1071 (A_1 '), and 1384 cm⁻¹ (E'). Four bands are observed in the clay at 720, 1060, 1356, and 1409 cm⁻¹. The splitting of the E' mode at 1384 cm⁻¹ is characteristic of a reduction in symmetry of the nitrate anion (typically D_{3h}) in the clay. The spectrum in Figure 2a resembles that observed for vitrified aqueous LiNO₃ solutions.²² The magnitude of splitting in the clay is 53 cm⁻¹ as compared to 66 cm⁻¹ in the vitrified solutions. The high-frequency component of this band is (1409 cm⁻¹) similar to that in the vitrified solutions, whereas the lower frequency component is at 1356 as compared to 1342 cm⁻¹. The position of the low-frequency band has been shown to be dependent on polarizing power of the cation, and moves to higher frequency with increasing mass (from Li⁺ through Rb⁺).²² This would indicate that in the clay the polarizing power of the Li⁺ is diminished as compared to the vitrified solution. This is not surprising considering that the interaction of the cation with the anion is now mediated through a hydroxyl group (Li-OH-NO₃) as compared to a direct Li-NO₃ interaction in the solution. The siting of the nitrate ion in the interlayer spacing is similar to that of carbonate in pyroaurite,² with each oxygen atom at a site around the OH groups with N at the center (along the C_3 axis). The O-H stretching frequency of the hydroxyl groups H bonded to the nitrate oxygen atoms appear at 3623 cm⁻¹ (Figure

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TABLE III: Concentration of Phosphate Species upon Ion Exchange As Determined by Raman Spectroscopy

pH of	concn ratios					
soln	soln	clay				
2.3	$[H_2PO_4^-]/[HPO_4^{2-}] = 10^6$	$[H_2PO_4^-]/[HPO_4^{2-}] = 2.5$				
5.3	$[H_2PO_4^-]/[HPO_4^{2-}] = 78$	$[H_2PO_4^-]/[HPO_4^{2-}] = 0.4$				
10	$[HPO_4^{2-}]/[PO_4^{3-}] = 238$	$[HPO_4^{2-}]/[PO_4^{3-}] = 0.3$				
12.5	$[HPO_4^{2-}]/[PO_4^{3-}] = 1$	only PO ₄ ³⁻				

2a'), indicating a weaker H bond than with the previously described chloride ion. This is not surprising, considering the increased interlayer spacing in the nitrate-exchanged clay, which would lead to a longer OH...ONO₂ band.

Sulfate Ion. Complete exchange of chloride with sulfate ion can be observed in the pH range 1-10. The interlayer spacing increases to 5.97 Å, whereas the diameter of the sulfate ion is 4.6 Å. The Raman spectrum of the sulfate-exchanged clay is shown in Figure 3a. Bands at 457, 467 (weak), 620 (weak), 986, and 1116 (broad) cm^{-1} are due to sulfate ion. The free tetrahedral anion has bands at 450 (E), 611 (F₂), 983 (A₁), and 1105 (F₂) cm⁻¹.²³ The splitting of the E band in the clay and the considerable broadening of the asymmetric stretch F_2 band (~45 cm⁻¹) indicates a symmetry lowering in the clay. The site symmetry of the sulfate ion has to be D_2 or lower for the band of symmetry E to split into two components. Bish,²⁴ on the basis of infrared studies of sulfate-exchanged takovite, proposed a C_3 site symmetry for the anion. This would not be compatible with the Raman data. We propose that two of the four oxygen atoms are on opposite interlayer sites with the S atom positioned in the middle of the layer. There will have to be an additional layer of water molecules in the interlayer to account for the spacing.

A most interesting aspect of the sulfate ion exchange is seen on comparing parts a and b of Figure 3. Figure 3b is the Raman spectrum of the solution used for ion exchange. This solution primarily contains HSO₄⁻ (906, 1055 cm⁻¹, pH 1.3) ions, in a molar ratio of HSO_4^{-}/SO_4^{2-} of 4.5. However, upon ion exchange, only SO_4^{2-} ion is incorporated into the clay, and within the limits of detection for Raman spectroscopy (~ 0.01 M), no spectroscopic evidence for HSO_4^- is found. Clearly, the ion exchange is favored for the divalent anion. To investigate this discrimination of ion exchange between almost identical species varying only in charge, we studied the phosphate ion system.

Phosphate Ion. Four 0.1 M sodium phosphate solutions at pH 2.3, 5.3, 10, and 12.5 were used for ion-exchange studies. From the acid dissociation constants of phosphoric acid, the ratios of the concentration of the two major species in the ion-exchanging solution were determined and are listed in Table III. The ratio of the phosphate species in the ion-exchange clay was obtained from the Raman spectrum shown in Figure 4 and is also listed in the table. The various phosphate ions are readily distinguished by their characteristic P-O and P-OH stretches in the Raman spectrum.²⁵ These bands occur at 883 $(P(OH)_2)$ and 1083 (PO) cm^{-1} for H₂PO₄⁻, 867 (weak, POH) and 993 (PO) cm^{-1} for HPO_4^{2-} , and 941 (PO) cm⁻¹ for PO_4^{3-} anions. At pH 12.5, the ion-exchanging solution contains equimolar quantities of HPO₄²⁻ and PO_4^{3-} , whereas Raman bands due to only PO_4^{3-} are observed in the clay (940 cm⁻¹, Figure 4a). At pH \sim 10, the primary ions in solution are HPO_4^{2-} , with a molar ratio of HPO_4^{2-} to PO_4^{3-} of 238. In the Raman spectrum (Figure 4b), there is a strong band at 940 cm⁻¹ due to PO₄³⁻ and a weaker band at 988 cm⁻¹ due to HPO_4^{2-} . The intensities of these two bands was used to estimate the ratio of the concentration in clay. To do this, we obtained Raman spectra of a series of phosphate solutions at various pH's and measured the ratio of the PO_4^{3-} (941) to HPO_4^{2-} (994 cm⁻¹) bands. From the pH of the solution, the molar ratio was estimated. A correlation between the ratios of the Raman intensities and the molar concentration was established. This correlation was applied to the Raman data from the clay (Figure



Figure 4. Raman spectrum of phosphate-[Al₂Li(OH)₆]⁺ obtained by ion exchange at different pH's: (a) 12.5; (b) 10; (c) 5.3; (d) 2.3.

4) and used to determine the ratio of the phosphate species. Table III lists these values at different pH. The assumption in this correlation is that the Raman extinction coefficients of the phosphate species on the solid and in solution are similar. Such an assumption is probably semiquantitative, at best. However, it does provide a measure of the selectivity of ion exchange. At pH = 10, even though the solution contains considerably higher concentration of HPO_4^{2-} (a factor of 238), the primary species in the clay is PO_4^{3-} (940 cm⁻¹, figure 4b), indicating a high selectivity of ion exchange. At pH = 5.3, the prominent species in the clay is HPO_4^{2-} (975 cm⁻¹), even though the solution mostly contains $H_2PO_4^-$ (a factor of 78). No evidence for any PO_4^{3-} peaks were observed. The most drastic effect is noticed with the solution at pH ~ 2.3, which contains only $H_2PO_4^-$. However, in the clay bands at 975 cm⁻¹ due to HPO_4^{2-} and 890 and 1080 cm⁻¹ due to $H_2PO_4^-$ are observed. The X-ray powder diffraction pattern of the clay under all exchange conditions indicates an interlayer spacing of ~6 Å. The diameter of PO_4^{3-} is ~4.76 Å, indicating that as in the sulfate-exchanged clay, there is water present in the interlayer space.

The ion-exchange process contains of many competing factors. These include the energy required to disrupt the hydrated structure of the ion in solution, the electrostatic interaction between the cation (both in solution and in clay) and the anion and the energy gained by coordination of the anion in the clay. Using the formalism described by Liberti and Passino,²⁶ the free energy change for these three processes can be described as

$$\Delta G_{\text{dehydr}} = -\left(1 + \frac{1}{D_{w}}\right) \frac{N(eZ_{-})^{2}}{4r_{-}} f$$

$$\Delta G_{\text{electr}} = \frac{-N(eZ_{+}Z_{-})^{2}}{r_{+} + r_{-}} f$$
(1)
$$\Delta G_{\text{hydr}} = -\left(1 + \frac{1}{D_{w'}}\right) \frac{N(eZ_{-})^{2}}{4r_{-}} f$$

where D_{w} and $D_{w'}$ are the dielectric constant of water and the clay, Z is the charge, N is Avogadro's number, r is the radius of ion, f is a conversion factor, and e is the charge of the electron. The

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Figure 5. (a) X-ray diffraction pattern of $[Al_2Li(OH)_6] \cdot C_6H_5COO;$ (b) sample in (a) partially exchanged with Cl⁻; (c) Raman spectrum of sample (a).

standard free energy change for change of Y⁻ for Z⁻ (ΔG° exchange) can readily be calculated from eq 1.

The terms neglected here are due to ion-induced dipole interactions and multipole interactions, which usually make much smaller contributions due to the $1/r^n$ dependence. It is useful to consider the predictions made by the above equation for monovalent ions. In the case of conventional anion-exchange resins such as Dowex, the ion selectivities of monovalent anions follow the order $I^- > Br^- > Cl^- > F^-$ and monovalent ions are preferred over divalent ions (ReO₄⁻ > WO₄²⁻; MnO₄⁻ > CrO₄²⁻).²⁷ The exact opposite trend has been reported for anionic magnesium aluminum hydratalcites in which F > Cl > Br > I and divalent ions have higher selectivities than monovalent anions. The fundamental difference between these two anion-exchange materials arises from hydration effects. In typical anion-exchange materials, such as Dowex 1, the energy gained by rehydration of the anion inside the exchange materials is small since the resin pores do not allow sufficient room for complete solvation.²⁷ So, the energy lost by breaking the structure of hydration of the anion is not compensated. In the extreme case, considering the $\Delta G_{hydr}^{resin} = 0$, eq 1 predicts that the ion selectivities should follow $I^- > Cl^- > Br^-$ > F^{-} for an ion-exchange resin containing $N(CH_3)_4^+$ as the cation and considering r_{-} to be the anionic radii of the halides. On the other hand, as discussed before, in the anionic clay the anion is surrounded by hydroxyl groups which provide solvation similar to that in solution. The dielectric constant inside the clay layers is unknown. However, since the "free" water in the clay is considerably reduced, the value of the dielectric constant can be considered to have values similar to that of concentrated salt solutions ($\sim 40-50$).

On the basis of such a simple hydration model of the anions in the clay, eq 1 predicts that the ion-exchange selectivities should follow $F^- > Cl^- > Br^- > I^-$, considering Li⁺ as the cation in the clay. Therefore, it appears that the distinguishing feature in these two ion-exchange systems is the difference in solvation of the anion in the ion-exchange medium. On the basis of eq 1, the anionexchange selectivities in the clay should follow $PO_4^{3-} > HPO_4^{2-}$ > Cl^- > $H_2PO_4^-$, considering Li^+ as the cation. The spectroscopic studies described above confirm this trend.

Organic Anions. The exchange of benzoate ion into the clay was examined. Figure 5a shows the X-ray diffraction pattern upon complete exchange of the chloride with benzoate anion. Two sets of reflections are noted at 10.96, 4.80, and 3.25 Å and 20.34, 10.01, and 6.65 Å, besides the 4.8-Å reflection due to bayerite. The reason for considering these two sets of reflections separately is that the latter set of reflections disappear as the benzoate clay



Figure 6. Raman spectrum of $[Al_2Li(OH)_6] \cdot 1/4Fe(CN)_6$ in the CN stretching region.

sample is reexchanged with chloride along with the reappearance of the characteristic reflection of the chloride ion. The interlayer spacing corresponding to these two arrangements of the benzoate ion are 15.2 and 5 Å, indicating that the anion is held in the clay in two distinct orientations, parallel and perpendicular to the lithium aluminate layer. The Raman spectrum of the sample, shown in Figure 5b, also supports this conclusion. There is good agreement between this spectrum and that published for lithium benzoate²⁸ except in two regions: C-O stretching bands at $800-900 \text{ cm}^{-1}$ and CO₂ stretching bands at 1400-1550 cm⁻¹. The published Raman spectrum of lithium benzoate exhibits bands at 843, 1392, and 1544 cm⁻¹ due to C-O, symmetric CO₂ stretch, and asymmetric CO₂ stretch, respectively. The corresponding bands in the infrared are at 828 and 846 cm^{-1} for C–O, 1406 and 1427 cm⁻¹ for symmetric CO₂, and 1561 cm⁻¹ for asymmetric CO₂ stretches. In the benzoate clay sample, Raman bands are observed at 830, 843, 859, 1405, 1429, 1464, 1502, 1536, and 1545 cm⁻¹. The last two bands are weak in intensity. We assign the bands at 830, 843, 1405, and 1429 cm⁻¹ to benzoate positioned perpendicular to the aluminate layers (spacing ~ 15.2 Å) and the bands at 859, 1464, and 1502 cm⁻¹ to those lying in the layer. The difference in frequencies arise from H-bonding interactions with the hydroxyl groups of the clay. The large lattice expansion observed upon exchanging the chloride with benzoate also results in doubling of the surface area as measured by the BET method (21 to 37 m^2/g samples activated at 65 °C).

Organometallic Anions

Ferrocyanide Ion. The Raman spectrum of the ferrocyanide ion exchanged clay is shown in Figure 6 in the C-N stretching region. In solution, the octahedral $Fe(CN)_6^4$ exhibits bands at 2098 (A_{1g}, Raman), 2062 (E_g, Raman), and 2044 cm⁻¹ (F_{1u}, infrared).²⁹ In the clay, Raman bands are observed at 2094, 2074, 2063, 2042, and 2027 cm⁻¹, clearly indicating that a reduction in O_h symmetry is occurring in the clay. This spectrum bears a resemblance to the Raman spectrum of cyrstalline K₄Fe(CN)₆,²⁹ where the site symmetry of ferrocyanide is C_2 or C_1 . The interlayer spacing in the clay is 6.18 Å, indicating that the ferrocyanide anion is not positioned along the C_4 axis (~11 Å).³⁰ The most appropriate siting will be along the C_3 axis, so that the layers of three CN groups are parallel to the lithium aluminate layer. A site symmetry of C_3 would predict four bands in the Raman spectrum (2A + 2E) and is not in agreement with the observed data. A lower site symmetry or intermolecular coupling effects may be responsible for the observed spectrum.

Nickel Phthalocyaninetetrasulfonate Ion. There is considerable interest in stacked metal over metal structures of phthalocyanines as novel conducting materials.³¹ The channels in the clay provides opportunities for such a stacking arrangement. We studied the ion exchange of nickel(II) phthalocyaninetetrasulfonate ion, which is readily and completely ion exchanged into the clay as evidenced from the X-ray diffraction pattern of Figure 7. The interlayer spacing increases to 5.81 Å and is comparable to the SO_4^{2-} -exchanged clay discussed earlier. This would indicate that the

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Figure 7. (a) Raman spectrum and (b) X-ray diffraction pattern of nickel(II) phthalocyaninetetrasulfonate exchanged $[Al_2Li(OH)_6]^+$.

phthalocyanines are parallel to the aluminate layer and not arranged in a stacked fashion (spacing ~ 17 Å). The arrangement of such a large molecule in the interlayer spacing is of interest and indicates the potential for novel ion exchange into these materials.

The resonance Raman spectrum is shown in Figure 7a. This resembles the published spectrum of phthalocyanine,³² except for shift of bands at 512, 608, and 664 cm⁻¹ to 520, 598, and 653 cm⁻¹

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in the clay. These bands are assigned to twisting motion of the five-membered rings and could arise from interactions with the OH groups extending into the clay interlayer.

Conclusions

The vibrational spectra of the $Al_2Li(OH)_6^+$ framework exhibit bands characteristic of the AlO_6 and OH groups. A D_3 site symmetry for the AlO_6 group has been proposed. The Raman spectra of the anions intercalated into the clay layers also provides information about the siting and interaction with the clay. Incredible selectivities toward ion exchange were discovered for the higher charged species in a series of oxyanions, e.g., $PO_4^{3-} >$ $HPO_4^{2-} > H_2PO_4^{-}$. Organic anions can also be ion exchanged into the clay, and it was found that benzoate ions can stack up in an arrangement perpendicular to the aluminate layer. This study illustrates that the anionic clays provide opportunities for diverse chemistry complementary to that of the extensively studied cation-exchange materials.

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Registry No. $[Al_2Li(OH)_6]^+$, 117872-71-6; NO₃⁻, 14797-55-8; SO₄²⁻, 14808-79-8; PO₄³⁻, 14265-44-2; HPO₄²⁻, 14066-19-4; H₂PO₄⁻, 14066-20-7; C₆H₅COO⁻, 766-76-7; Fe(CN)₆⁴⁻, 13408-63-4; [Al₂Li(OD)₆]⁺, 117872-69-2; nickel(II) phthalocyaninetetrasulfonate, 102497-93-8; [Al₂Li(OH)₆]Cl, 68949-09-7; [Al₂Li(OH)₆]NO₃, 117872-70-5; [Al₂Li(OH)₆]2SO₄, 117872-72-7; [Al₂Li(OH)₆]-C₆H₅COO, 117895-85-9; [Al₂Li(OH)₆]-¹/₄Fe(CN)₆, 117895-84-8.

Structure of Aqueous Decyltrimethylammonium Bromide Solutions at the Air/Water Interface Studied by the Specular Reflection of Neutrons

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The technique of specular reflection of neutrons has been used to investigate the adsorption of decyltrimethylammonium bromide (DTAB) at the aqueous solution/air interface over the concentration range 0.002-0.1 M. Hydrogen-deuterium substitution in both surfactant and solvent has been used to highlight different features of the adsorbed layer and to distinguish between solvent and solute in this layer. At the lowest concentration the thickness of the adsorbed layer is 16 ± 3 Å, indicating that the molecules are aligned with the long axis perpendicular to the interface. At a concentration of 0.05 M, where the monolayer is essentially complete, the thickness is found to be 21 ± 1 Å. This suggests that in the more closely packed monolayer the head groups, which carry a positive charge, may be "staggered" in order to minimize their mutual repulsion. A detailed analysis of the structure at 0.05 M indicates that the layer may be divided into two regions: a head group region, 6 Å thick, containing the trimethylammonium head group, counterion, water, and about 10% of the alkyl chain tails; and a tail group region, 15 Å thick, containing only tail groups. The area per molecule of surfactant at the saturated monolayer is found to be $58 \pm 5 \text{ Å}^2$. Above the critical micelle concentration (0.065 M) the structure of the interface is more complex. The monolayer itself is some 15% more dense than the saturated monolayer formed below the cmc. The shape of the reflectivity profile is shown to be consistent with some ordering of the micelles beneath the surface, separated from the monolayer by a thin layer of water, which contains no surfactant and which has a density more akin to that of water in hydrates. Mixtures of DTAB and sodium decanoate have also been investigated. Equimixtures of the two oppositely charged surfactants are much more strongly adsorbed than either of the two individual components. Even at the low total concentration of 0.01 M the area per surfactant molecule of the mixed monolayer is 36 Å² compared with 73 Å² for 0.01 M DTAB alone.

Introduction

It has been shown in two earlier papers how the specular reflection of neutrons may be used to determine the structural properties of adsorbed layers at the air/water interface.^{1,2} In this paper we apply the technique to the determination of the structure of a decyltrimethylammonium bromide (DTAB) layer adsorbed at the air/water interface. DTAB was chosen for two

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