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However, the spectra presented in this study clearly indicate that $C_{10}Cd$ in phase C is more disordered than $C_{10}Cl$ in phase II, i.e., the two phases which have been described as resembling smectic liquid crystals. Again, we ascribe this difference in gauche concentration to the looser hydrogen bond arrangement of $C_{10}Cd$ compared to that in $C_{10}Cl$.

While the nonreversibility of the conformational melting transition (phase I → phase II) of $C_{10}Cl$ is not limited to the alkyl chains, the rearrangement of the head group seems to lag behind that of the alkyl chains.

Registry No. $C_{10}Cl$, 143-09-9; $C_{10}Cd$, 53188-91-3; $CdCl_2$, 10108-64-2.

Clay-Modified Electrodes. 5. Preparation and Electrochemical Characterization of Pillared Clay-Modified Electrodes and Membranes

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Methods of preparing pillared clay layers on electrode surfaces by treatment of montmorillonite with $[Fe_3(OCOCH_3)_7O\text{-}H\cdot 2H_2O]NO_3$, zirconyl chloride, or hydroxy–aluminum solutions followed by heating are described. X-ray diffraction of the pillared clay layers shows larger basal plane splittings (ca. 17 Å) than unpillared clays. The cyclic voltammetric behavior of ions incorporated in these pillared clay layers, e.g., $Fe(bpy)_3^{2+}$, in both aqueous and nonaqueous solutions is described and contrasted to that of unpillared clay layers. Pillaring is also shown to attenuate the penetration of anionic species through the films. Free standing pillared clay films (5–10-μm thick) were shown to behave as cation-exchange membranes by measurements of the membrane potential developed across them when separating aqueous NaCl and KCl solutions (0.01 to 1 M).

Introduction

There has been considerable interest recently in modified electrodes using clay,[1-5] zeolite,[6] metal oxide,[7] and other inorganic layers.[8,9] Modification of electrode surfaces by coverage with a thin layer of clay has been reported in previous studies from this laboratory.[1,2] Spectroscopy and photochemistry of $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) in colloidal smectites have also been studied recently.[10] Clays were used extensively as commercial catalysts before they were replaced by more thermally stable and selective zeolite catalysts. However, there have been several recent efforts to study the formation of stable, high surface area modified clays by developing oxide pillars between the layers of expanded layer silicates.[11] Pillared clays are formed when a "pillar" (e.g., a metal oxide) is introduced between the silicate layers that maintains the interlayer spacing. Since pillared clays can have fixed pore sizes larger than those of zeolites, they can offer a promising new means of facilitating reactions of various molecules.[11] Moreover, pillaring fixes the interlamellar spacing in the clay particles and makes them less susceptible to large changes via solvation. The above considerations encouraged us to explore the effect of pillaring on the behavior of clay-modified electrode surfaces.

We also found in this study that free-standing pillared clay membranes with reasonable mechanical strengths could be prepared easily. Preheated (but unpillared) montmorillonite membranes were described over 40 years ago by Marshall et al.[12,13] and were suggested for the potentiometric determination of potassium and ammonium ions. However, the properties of these membranes were reported to be very dependent upon the preheating temperatures. Membranes heated below 250 °C reached equilibrium quickly but were extremely fragile and dispersed or cracked readily.[12] Marshall et al. mainly used the membranes preheated at 490 °C for montmorillonite. However, it is known that sodium montmorillonite heated at 500 °C for 1 h regains interlayer water upon immersion and expands over long intervals of rehydration.[14,15] Such membranes did not appear to be useful in electrochemical studies of long duration, and investigations of them were discontinued.

In this paper, we describe methods of preparation of pillared clay-modified electrodes and pillared-clay membranes and characterize these by electrochemical measurements.

Experimental Section

Materials. Calcium montmorillonite (STx-1) was purchased from the Source Clay Minerals Repository (University of Missouri, Columbia, MO). The clay, purified by the method described in previous papers,[1,2] was used for this study. A colloidal suspension in aqueous solution was prepared by weighing the desired amount of freeze-dried clay and dispersing it in triply distilled water in an ultrasonic bath. $Os(bpy)_3(ClO_4)_2$ and $Fe(bpy)_3(ClO_6)_2$ were synthesized and purified according to published procedures.[16,17]

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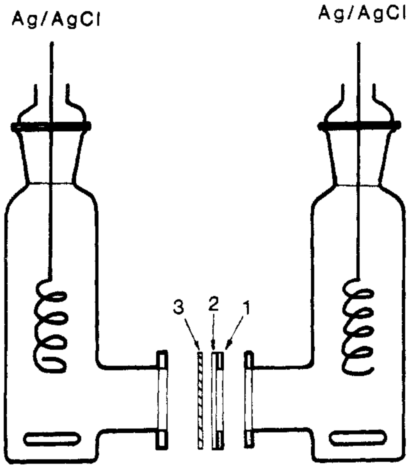

Figure 1. Apparatus for membrane potential measurement: 1, Teflon gasket; 2, pillared clay membrane; 3, nylon mesh.

Trinuclear acetatohydroxoiron(III) nitrate, $[Fe_3(OCOCH_3)_7O\text{-}H\cdot 2H_2O]NO_3$, zirconyl chloride, and hydroxy–aluminum ions were used for the preparation of the pillared clays. $[Fe_3(OCOCH_3)_7OH\cdot 2H_2O]NO_3$ was prepared according to the method reported by Starke[18] and purified carefully by washing with acetic acid and petroleum ether. The hydroxy–aluminum solution was prepared by slowly adding with vigorous stirring appropriate amounts of a 0.05 M NaOH to 0.1 M $AlCl_3$ to give an OH–Al(III) ratio of 2.0.[19] Commercially available $ZrOCl_2\cdot 8H_2O$ was used without further purification. Distilled acetonitrile, *N,N*-dimethylformamide, methanol, and ethanol were used as solvents.

Procedure. A clay suspension (2 g/L) was prepared as described previously.[2] Briefly, the calcium-montmorillonite (cation-exchange capacity, 84 mequiv/100 g) was converted to the Na^+ form with 1.0 M NaCl, repeatedly washed with water, and centrifuged until washings were free of chloride. Films for electrochemical studies were prepared by placing a drop on the transparent SnO_2 electrode and spreading with a glass rod until a film that appeared blue was produced. This was usually air-dried for about 1 h. The electrode area was about 0.4 cm^2. A typical thickness of the films was ca. 1000 Å, as estimated by the observed interference color of the clay film (blue). $Os(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ were incorporated into the film by soaking the electrodes in 5–10 mM aqueous solutions of these ions for about 10 min. After the incorporation reaction, the electrodes were washed with distilled water and then used in the electrochemical experiments.

The pillared clay-modified electrodes were prepared by soaking the electrodes, cast on SnO_2 as described above, in aqueous solutions of 0.1 M trinuclear acetatohydroxoiron(II) ions,[20] 0.1 M $ZrOCl_2$,[21] or hydroxy–aluminum[19] for 3 h. After this ion exchange, the electrodes were thoroughly washed with distilled water for 1 h and then heated in air at 400 °C for 3 h. Free-standing films of the pillared clays were prepared on Pyrex glass plates by a similar procedure. Films of sodium montmorillonite with a thickness of about 5–10 μm were cast on a Pyrex plate, air-dried, and soaked in the solutions of the pillaring reagents for 10 h. The films on the substrate were washed with distilled water for at least 1 h and then heated at 400 °C for 3 h. A peripheral Teflon gasket (outer diameter, 25 mm; inner diameter, 15 mm; thickness, 0.5 mm) was placed on the film surface with silicone grease as an adhesive material. The glass plate with a pillared clay layer was then immersed in distilled water for 1 h. The film with the peripheral Teflon gasket attached gradually peeled off of the Pyrex substrate during this immersion. The membrane with the Teflon gasket was held in a cell as shown in Figure 1. A nylon mesh was used as backing to avoid stresses on the clay membrane during measurement of membrane potentials. The membrane potential was measured with Ag/AgCl electrodes in both compartments by using solutions of potassium chloride and sodium chloride. The solutions in both compartments were vigorously stirred with a magnetic stirrer and Teflon stirring bars to maintain the concentration at the membrane surface equal to that in the bulk. A measured steady-state membrane potential was obtained typically within 10 min. Each measurement was carried out by changing the concentrations (1.0, 0.5, 0.2, 0.1, 0.5, 0.02, and 0.01 M) in one compartment, with the other kept at a 1.0 M concentration.

TABLE I: X-ray Diffraction Data

pillared clays	basal spacing,[a] Å	interlayer separation,[b] Å
Fe pillared	16.8	7.0
Zr pillared	17.2	7.4
Al pillared	17.0	7.2

[a] The distance between repeating 2:1 units. [b] The thickness of the silicate layer of montmorillonite is 9.8 Å.

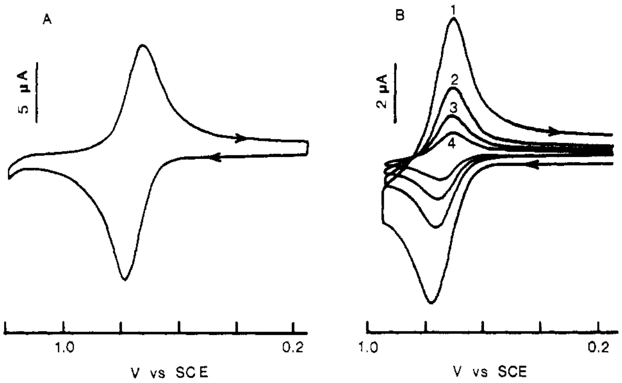

Figure 2. Cyclic voltammograms of $Fe(bpy)_3^{2+}$ incorporated sodium montmorillonite modified electrode (A) and $Fe(bpy)_3^{2+}$ incorporated Fe-pillared clay-modified electrode (B) in 0.1 N Na_2SO_4. Scan rates: (A) 50 mV s^{-1}; (B) 50 (1), 20 (2), 10 (3), and 5 (4) mV s^{-1}.

Apparatus. A Princeton Applied Research (PAR) Model 173 potentiostat, a Model 175 universal programmer, and a Houston Instruments Model 2000 X–Y recorder comprised the instrumentation for electrochemistry. X-ray diffraction data were obtained with a General Electric (Model xrd-5) X-ray powder diffractometer with an Ortec (Model 401S) ratemeter. The Cu anode was operated at 35 kV and 15 mA.

Results and Discussion

X-ray Diffraction of Pillared Clay Layers. X-ray diffraction patterns for pillared clay films always exhibited a first-order peak in the region of $2\theta < 10°$ with higher-order reflections. This (001) reflection corresponds to the basal spacing of the pillared clays. The values of basal spacing and interlayer separation are tabulated in Table I. The full-widths at half-maximum peak height were always within 1°. The values obtained here agree well with previously reported values.[19,20] Note that the basal spacings in the pillared clays were essentially the same for all three pillaring agents. When a freshly prepared pillared clay layer was soaked in distilled water overnight, exactly the same basal spacing was observed. This contrasts with an unpillared sodium montmorillonite film, where the basal spacings are very dependent upon the water-vapor pressure in the atmosphere.[14,15] The pillared clay films have basal spacings of ca. 17 Å for all cases; these are much larger than the spacing of 9.8 Å for the completely collapsed silicate layers.

Electrochemistry in Aqueous Solutions. We showed in previous papers[1,2] that many positively charged electroactive species are held fairly strongly by smectite clays as exchangeable cations. A typical example of the cyclic voltammogram of $Fe(bpy)_3^{2+}$ incorporated in the sodium montmorillonite film immersed in a 0.1 N Na_2SO_4 solution is shown in Figure 2A. The change in the cyclic voltammetric behavior as a function of sweep rate is similar to that reported in a previous paper.[2a] The peak current was

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approximately proportional to the scan rate (v) up to 20 mV s^{-1} and then proportional to $v^{1/2}$ at sweep rates greater than 50 mV s^{-1}. Similar behavior was observed for $Os(bpy)_3^{2+}$, although the peak current for this species was about twice as large as that obtained for $Fe(bpy)_3^{2+}$. The electrochemical response of these films depended upon the nature of the supporting electrolyte. The electrochemical studies of $Fe(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ in the clay film were carried in 0.1 N solutions of H_2SO_4, $LiClO_4$, Na_2SO_4, NaCl, KCl, CsCl, and NH_4Cl. However, the waves were almost totally suppressed in 0.1 N solutions of $LiClO_4$, KCl, and TEACl after a 5-min equilibration. This result suggests that the cations of the supporting electrolyte play an important part in the electron transfer through the film. The zeolitic nature of the Prussian blue film has been recently demonstrated by Itaya et al.,[9] where cations with Stoke's radii less than 3.2 Å (the channel diameter in Prussian blue) can transport through the crystal of Prussian blue. Although the basal spacing of the $Ru(bpy)_3^{2+}$-incorporated clays is not constant but depends upon the hydration state, a value measured under wet conditions was recently reported as 14.7 Å for the $Fe(phen)_3^{2+}$ (phen is 1,10-phenanthroline) incorporated into sodium montmorillonite.[22] While it is difficult to find a single explanation of these results, the basal spacing seems to be of primary importance in the ionic transport through the films. The rate of exchange of the electroactive cation by supporting electrolyte cations is also important.[23]

Figure 2B shows the cyclic voltammogram of $Fe(bpy)_3^{2+}$ incorporated in the iron oxide pillared clay (Fe-pillared clay) obtained in a 0.1 N Na_2SO_4 solution. The same magnitude of current was observed with soaking times in the $Fe(bpy)_3^{2+}$ solution of 10 min to 3 h. This indicates that the voltammogram in Figure 2B is probably that for full incorporation of the electroactive species in the Fe-pillared clay-modified electrode. The number of moles of incorporated electroactive species depends upon the extent of pillaring and can be obtained by integrating the area under the oxidation peak obtained at 5 mV s^{-1}. For $Fe(bpy)_3^{2+}$ this yielded 2.3×10^{-10} mol, which corresponded to 2–6% loading based on the cation-exchange capacity of a sodium montmorillonite layer with a thickness of 1000 Å. The current observed at the Fe-pillared clay-modified electrode was obviously smaller than that for the unpillared sodium-montmorillonite electrode, probably because a large fraction of the ion-exchangeable sites were occupied by the pillaring reagents. The voltammetric behavior with the pillared clay as a function of scan rate was similar to that shown in the Figure 2A, suggesting that a diffusion coefficient for the electron-transfer reaction due to $Fe(bpy)_3^{2+}$ in the Fe-pillared clay was of the order of 10^{-12} cm^2 s^{-1}. A similar value has been reported for $Os(bpy)_3^{2+}$ incorporated in a sodium montmorillonite.[2a] The same experiments were carried out with zirconium pillared (Zr-pillared) and aluminum-pillared (Al-pillared) clay-modified electrodes. In both cases, the cyclic voltammetric behavior was similar to that for Fe-pillared layers, but the numbers of moles of incorporated electroactive species was reduced to about one-half of that obtained for the Fe-pillared clay. The amount of the incorporated complexes appears to depend upon the nature of the pillaring agent, but not on that of the incorporated complexes. The same amount of $Os(bpy)_3^{2+}$ was incorporated into the pillared clays.

Electrochemistry in Nonaqueous Solutions. The basal spacing of sodium montmorillonite is also strongly affected by the nature of the solvent.[14,15] In this study, MeCN, *N,N*-dimethylformamide (DMF), MeOH, and EtOH were used with $NaClO_4$ (0.1 N) as supporting electrolyte. The cyclic voltammograms of $Fe(bpy)_3^{2+}$ at an unpillared electrode in EtOH (dashed line) and in 0.1 N Na_2SO_4 aqueous solution (solid line) are given in Figure 3A. The rate of the electron transfer through the layer of sodium montmorillonite is much attenuated in EtOH solution. Note that the same electrode after the experiment in EtOH, when transferred to a 0.1 N Na_2SO_4 aqueous solution, yielded almost an identical wave as that shown in Figure 3A. This indicates that the incorporated $Fe(bpy)_3^{2+}$ was not leached out from the clay layer in EtOH. A similar reversible behavior upon changing solvents was observed for MeOH. However, $Fe(bpy)_3^{2+}$ was quickly leached out in MeCN and DMF, because almost no wave reappeared on transfer to 0.1 N Na_2SO_4 aqueous solution. EtOH and MeOH are probably relatively strongly adsorbed on the basal plane surfaces of sodium montmorillonite,[15] displacing water but not $Fe(bpy)_3^{2+}$ from these surfaces. Under these circumstances, the diffusion rates of Na^+ or $Fe(bpy)_3^{2+}$ might be lower than those in aqueous systems. With MeCN and DMF, the solvent molecules are strongly adsorbed on the basal plane surfaces, displacing both water and $Fe(bpy)_3^{2+}$.

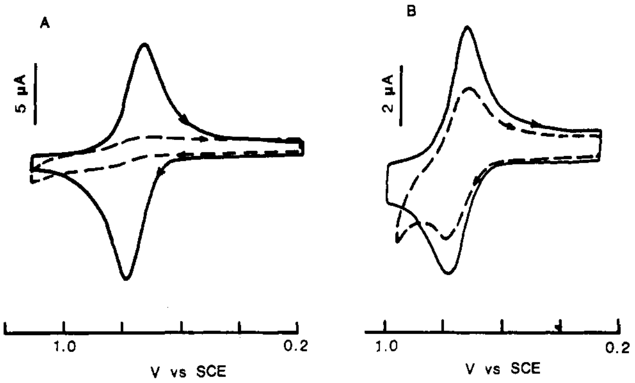

Figure 3. Cyclic voltammograms of $Fe(bpy)_3^{2+}$ incorporated sodium-montmorillonite modified electrode (A) and $Fe(bpy)_3^{2+}$ incorporated Fe-pillared clay-modified electrode (B). Solid and dashed lines were obtained in a 0.1 N Na_2SO_4 aqueous solution and in a 0.1 N $NaClO_4$ ethanol solution, respectively. Scan rate: 50 mV s^{-1}.

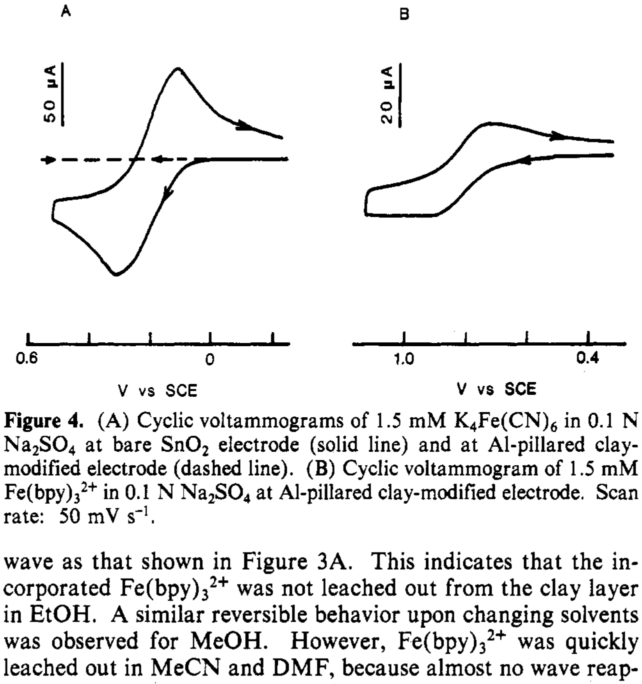

Figure 4. (A) Cyclic voltammograms of 1.5 mM $K_4Fe(CN)_6$ in 0.1 N Na_2SO_4 at bare SnO_2 electrode (solid line) and at Al-pillared clay-modified electrode (dashed line). (B) Cyclic voltammogram of 1.5 mM $Fe(bpy)_3^{2+}$ in 0.1 N Na_2SO_4 at Al-pillared clay-modified electrode. Scan rate: 50 mV s^{-1}.

On the other hand, very different behavior was observed for the pillared clay-modified electrodes. Figure 3B shows the cyclic voltammograms obtained in 0.1 N $NaClO_4$/EtOH (dashed line) and in 0.1 N Na_2SO_4/aqueous (solid line) solutions. Even in an EtOH solution, a well-characterized electron-transfer reaction can be seen. The peak current was slightly smaller in EtOH compared with that in water. This seems to be simply explained by decreased diffusion coefficients of Na^+ and $Fe(bpy)_3^{2+}$ in the pillared clay layers. For the pillared clay, the basal spacing cannot be changed by changing the solvent as discussed above, so that electron-transfer reactions in the pillared clay are possible. The behavior shown in Figure 3B might be important for further study of the electrochemistry of organic substances at clay-modified electrodes.

Penetration of Clay Layers. As discussed in a previous paper,[2a] negatively charged redox species such as $C_2O_4^{2-}$, $Mo(CN)_8^{4-}$, and I^-, which would be expected to be totally repelled by the clay, penetrate freely sodium montmorillonite clay films. The solid line in Figure 4A shows a cyclic voltammogram of 1.5 mM $K_4Fe(CN)_6$ in 0.1 N $NaSO_4$ at a bare SnO_2 electrode. Exactly the same

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[22] Yamagishi, A. *J. Phys. Chem.* **1982**, *86*, 2472.

[23] Rudzinski, W.; Bard, A. J. *J. Electroanal. Chem.*, submitted for publication.

experiment carried out at air-dried sodium montmorillonite modified SnO_2 (film thickness 1000–3000 Å) yield essentially the same voltammogram at 50 mV s^{-1}. However, no wave or a greatly attenuated wave, due to the oxidation of $Fe(CN)_6^{4-}$, was observed at an Al-pillared clay-modified electrode as shown in Figure 4A (dashed line). This demonstrates clearly that it is possible to prepare an Al-pillared clay which dramatically attenuates the penetration of $Fe(CN)_6^{4-}$ ions. The interlayer separations of the pillared clays prepared here are a about 7 Å as shown in Table I. There is abundant evidence for some sort of definite configuration of water molecules initially adsorbed on the surfaces of the clay minerals.[14] These water molecules should be strongly bound to the surfaces, yielding much narrower channels for the transport of $Fe(CN)_6^{4-}$ ions through the pillared clay layers. In addition to this structural restriction, the remaining fixed negative charge in the pillared clays seems also to be important for the rejection of negatively charged species. The pillaring agent may also help to interconnect clay particles and remove channels through which neutral and anionic species can move.

In contrast to $Fe(CN)_6^{4-}$ ions, a clear mediated electron-transfer reaction can be seen for a positively charged electroactive species such as $Os(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ with a pillared clay layer. A typical example of the cyclic voltammogram of 1.5 mM $Fe(bpy)_3^{2+}$ in 0.1 N Na_2SO_4 at the Al-pillared clay-modified electrode is shown in Figure 4B. The wave due to the oxidation of $Fe(bpy)_3^{2+}$ incorporated in the Al-pillared clay was also observed at 0.8 V vs. SCE in 0.1 N Na_2SO_4 alone as discussed above. The current observed in Figure 4B with the electrode immersed in 1.5 mM $Fe(bpy)_3^{2+}$ was much lower than that observed at a bare SnO_2 electrode under the same conditions. This reveals that the oxidation of $Fe(bpy)_3^{2+}$ in the solution is not diffusion controlled but rather is controlled by the rate of electron propagation through the $Fe(bpy)_3^{2+}$ incorporated in the clay layer or by the rate of electron transfer at the clay/solution interface. Detailed kinetic investigations for mediated electron-transfer reactions through clay layers are underway.

Membrane Potentials. A number of authoritative books and review articles describe the properties of ion-exchange membranes of various organic and inorganic materials.[24] Preheated montmorillonite membranes were studied by Marshal et al. in 1941 for the potentiometric determination[25] of potassium and ammonium ions.[12,13] However, these membranes could not be extended to real applications because the films were too unstable to use for a long time period. On the other hand, the pillared clay membranes prepared here are mechanically very stable as described in the Experimental Section. Fairly thin free-standing films of the pillared clays have been prepared easily for the measurement of membrane potentials. The total potential difference ($\Delta E = E_2 - E_1$) between two Ag/AgCl electrodes in Figure 1 can be expressed by the following equation:[24]

$$\Delta E = E_2 - E_1 = (RT/F) \ln (a_1/a_2) + E_M \qquad (1)$$

where a_1 and a_2 are the Cl^- activities of the solutions (e.g., KCl and NaCl) in each compartment, and E_M is the membrane potential. The activities of all solutions were calculated by using the activity coefficients taken from the data compiled by Latimer.[25]

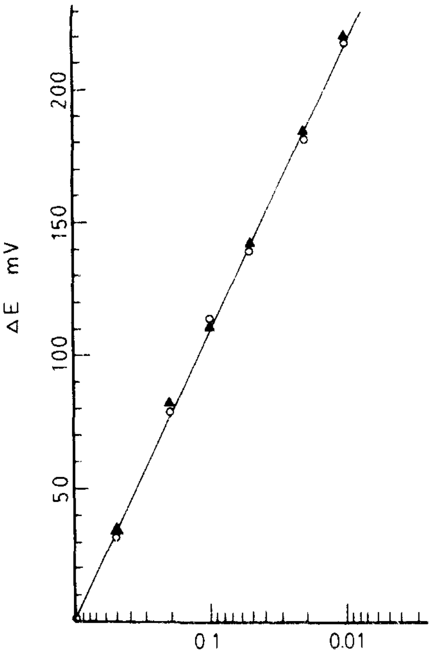

Figure 5. Dependence of potential difference between Ag/AgCl electrodes on concentration (a) of NaCl (O) and KCl (▲) in compartment 1; compartment 2, 1 M. Solid line is theoretical curve for ideal cation-exchange membrane.

ΔE values obtained with the Al-pillared clay membranes in NaCl and KCl solutions are given in Figure 5. Two sets of data, one for KCl (1 M/C_2) and NaCl (1 M/C_2) are given in this figure. The solid line is the predicted one based on the assumption of an "ideal cation-exchange membrane," whose membrane potential is given by [24]

$$E_M = (RT/F) \ln (a_1/a_2) \qquad (2)$$

The observed values agree with the theoretical line, within experimental error. This implies that the membranes show preferential cation transport even at high ionic concentrations. Marshall et al.[12,13] found that preheated montmorillonite membranes had a high cationic transport (sieving action) at lower concentrations (a_1 and $a_2 < 0.1$). There are two important factors involved in obtaining conditions favorable for relatively high cation transport and anion rejection in these membranes: high negative fixed charge in the membrane and a pore- or channel-free structure. The pillared clays described here appear to lose a large fraction of the available negative charges on the silicate layers because of the ion exchange of the pillaring reagents. If this is the case, the very high selectivity observed cannot be explained by the TMS (Teorell, Meyer, and Sievers) theory[24b] and structural aspects of the pillared clays may play an important role in repelling chloride ions.

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