

## USE OF INORGANO-ORGANO-CLAYS IN THE REMOVAL OF PRIORITY POLLUTANTS FROM INDUSTRIAL WASTEWATERS: STRUCTURAL ASPECTS

KEERAN R. SRINIVASAN AND H. SCOTT FOGLER

Department of Chemical Engineering, University of Michigan  
Ann Arbor, Michigan 48109

**Abstract**—Novel modified clay adsorbents were prepared by blocking cation-exchange sites of an expandable clay, such as montmorillonite, with polymeric or polyvalent inorganic ions and by using cationic surfactants as sources of surface organic carbon. Electrokinetic measurements demonstrated that the adsorbed polycations were essentially nonexchangeable. Adsorption and desorption experiments revealed that about 90% of the cationic surfactant was apparently irreversibly bound to the surface. Flocculation and peptization studies were performed to establish that the adsorbed surfactant moiety was oriented with its hydrocarbon tail towards the surface. Such a configuration of simultaneously adsorbed polycations and cationic surfactants was designated as an inorgano-organo-clay (IOC). As shown in an accompanying paper, these IOCs bind priority pollutants as strongly as granulated activated carbon.

**Key Words**—Adsorption, Chlorophenols, Flocculation, Hydroxy-Al, Inorgano-organo clays, Montmorillonite, Pollutants.

### INTRODUCTION

Research in this laboratory has focused on developing multi-purpose clay-based sorption technology for the treatment of industrial wastewaters and for the remediation of contaminated ground waters. A modified clay that is a powerful enough adsorbent to handle the entire gamut of toxic organics and that is considerably less expensive than granulated activated carbon (GAC) has been the chief goal. Establishing the link between the structure and the function of the modified clays to provide a basis for the development of more efficient adsorbents has been an equally important aim of these efforts.

Srinivasan *et al.* (1985) and Fogler and Srinivasan (1988) reported that hydroxy-Al montmorillonite was a powerful adsorbent for polychlorinated dibenzo dioxins (PCDDs) and polychlorinated biphenyls (PCBs) from industrial wastewaters. Srinivasan and Fogler (1986a, 1986b) showed that hydroxy-Al montmorillonite was as effective as GAC in binding dioxins and higher chlorinated biphenyls. Experiments using packed beds of hydroxy-Al montmorillonite revealed that octachlorodibenzodioxin (OCDD) was strongly bound to the modified clay columns, and that no breakthrough of OCDD in the effluent was observed (Srinivasan and Fogler, 1989). A detailed analysis of the binding of dioxins to hydroxy-Al montmorillonite suggested that hydroxy-Al itself may be the active component involved in the sorption of dioxins (Nolan *et al.*, 1989); however, hydroxy-Al montmorillonite was found to exhibit much weaker adsorption for less hydrophobic, but equally toxic pollutants, such as pentachlorophenol (PCP) (Srinivasan and Fogler, 1987). A similar finding was reported by Zielka and Pinnavaia (1988).

Thus, the present investigation explored the possibility of using two types of organo-clays. First, a traditional, cation-exchanged organo-clay was prepared, in which the hydrocarbon portion of the adsorbed cationic surfactant acted as the source of organic carbon. This approach was taken recently by Boyd *et al.* (1988a, 1988b). The second organo-clay was a novel formulation, in which the exchange sites were blocked by polycations and a cationic surfactant acted as the source of surface organic carbon. Blocking of exchange sites by polycations may lead to charge reversal and render the modified clay surface positively charged (Pashley, 1985). The strong lateral interaction of long-chain hydrocarbon tails driven by the hydrophobic effect should more than compensate for the possible unfavorable coulombic part of the surfactant adsorption free energy. Increasingly, researchers are recognizing that the role of the coulombic term in surfactant adsorption is generally overestimated (Moudgil *et al.*, 1987). Binding of an anionic surfactant to a polycationic inorgano-clay, such as hydroxy-Al montmorillonite, should be equivalent to the formation of an organo-clay of the first kind, mentioned above.

The second type of organo-clay is herein designated as an inorgano-organo-clay (IOC). Cetyl pyridinium (CPC) montmorillonite and cetyl pyridinium hydroxy-Al montmorillonite should be, respectively, examples of these two classes of organo-clays. Results from a preliminary evaluation of these two adsorbents are shown in Table 1 (Fogler and Srinivasan, 1986; Srinivasan and Fogler, 1987). The reported partition coefficient values (more correctly, the phase distribution ratios) were obtained at an initial sorbate concentration equal to 50% of the respective aqueous solubilities of

the toxic organics at that temperature. The traditional organo-clay was found to be quite effective. These preliminary results for pentachlorophenol adsorption on the traditional organo-clay agreed with those obtained by Boyd *et al.* (1988a). One of the factors, however, used to judge the efficacy of a sorbent is its organic carbon content; by this criterion and by its sorption potential for all the toxic organics compared with GAC, CPC-hydroxy-Al montmorillonite proved to be superior to the traditional organo-clay, i.e., CPC-montmorillonite (see Fogler and Srinivasan, 1986; Srinivasan and Fogler, 1987). The present investigation was prompted by this initial finding.

In particular, the long-term stability of IOCs against the desorption of the adsorbed surfactant was of interest. The surface orientation of the adsorbed surfactant may also provide a clue to the high sorption potential of IOCs. Extension of the concept of simultaneous adsorption of inorganic, polymeric cations, and cationic surfactants to polyvalent cations, such as lanthanum ions, and other cationic surfactants, i.e., cetyl benzyl dimethyl ammonium (cetyl alkonium chloride; CBDAC), was expected to establish the general validity of the approach. The effect of the basicity of the cationic head group, i.e., pyridinium vs. ammonium, was also considered.

## METHODS

Na-montmorillonite (SWy-1) was obtained from the Source Clay Repository of The Clay Minerals Society. Fractions having a mean particle size of  $<1.0 \mu\text{m}$  were converted to the Na form prior to use. CPC and CBDAC were obtained, respectively, from Fluka Chemicals and PolySciences. Fresh hydroxy-Al solutions (Chlorhydrol 50% solution having an OH/Al ratio of 2.5 and an Al/Cl molar ratio of 2.0) were obtained from Reheis Inc.;  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  was purchased from Aldrich Chemicals. All other chemicals and reagents were of analytical grade. Deionized water available from Milli-Q water system (Millipore Corporation) was filtered through a Nalgene 0.22- $\mu\text{m}$  filtration unit prior to use.

Organic carbon analyses, both solid phase and dissolved organic carbon, were carried out on a Coulometrics Inc. carbon analyzer. The organic carbon in the sample (solid or liquid) was quantitatively converted at  $950^\circ\text{C}$  to  $\text{CO}_2$ , which then reacted stoichiometrically with a proprietary base developed by Coulometrics, Inc. The electrical current required to regenerate the base was related to the amount of organic carbon in the sample. For some of the surfactant adsorption measurements, a Varian DMS-200 spectrophotometer was used to monitor the concentration of CPC and CBDAC at 259 and 221 nm, respectively. Calibration equations of the type:

$$\begin{aligned} A_{259} &= 0.007 + 0.0118X & \text{and} \\ A_{221} &= 0.001 + 0.00284X \end{aligned}$$

were used, respectively, for CPC and CBDAC, where A is the absorbance at the given wavelength and X is the concentration of the surfactant in mg/liter. The above calibration curves were checked by direct organic carbon analyses and found to be valid over a wide range of surfactant concentrations up to the maximum used in this study. At the lower end of the surfactant concentration, however, solution-phase organic carbon analysis was used.

Table 1. Binding of toxic organics to modified clays and granulated activated carbon.

Sorbate	Partition coefficient $\times 10^{-3}$ ( $\text{dm}^3/\text{kg}$ )		
	CPC, <sup>1</sup> montmorillonite	CPC-hydroxy- Al montmorillonite	Activated carbon
OCDD	105.0	100.0	105.0
HCB	118.0	87.0	86.0
TeCB	124.0	125.0	168.0
TCB	33.0	35.0	65.0
PCP	16.0	155.0	210.0
B(a)P	35.0	95.8	38.6

OCDD = octachlorodioxin; HCB = hexachlorobiphenyl; TeCB = tetrachlorobiphenyl; TCB = trichlorobiphenyl; PCP = pentachlorophenol; B(a)P = benzo(a)pyrene. Each partition coefficient value represents the mean of measurements in quadruplicate with a relative error of 10%. The initial concentrations of the toxic organics were equal to 50% of their respective aqueous solubilities at room temperature. The organic carbon content of CPC-montmorillonite and CPC-hydroxy-Al montmorillonite was 19.2% and 12.0% by weight, respectively.

<sup>1</sup> CPC = cetyl pyridinium.

The Na-montmorillonite (SWy-1) was initially treated with 0.5 M NaCl to ensure complete transformation to the Na form. The treated clay was then washed with deionized water to remove excess NaCl. Each washing step involved stirring the slurry in deionized water, followed by centrifugation and the removal of the supernatant. Using this clay as the starting material at a slurry concentration of 50 mg/ml, hydroxy-Al montmorillonite and La-montmorillonite were prepared by cation exchange. The total equivalents of the polymeric or the polyvalent ion used were 30 times the cation-exchange capacity (CEC) of the clay. The modified montmorillonite samples were then extensively washed with deionized water, dried at  $90^\circ\text{C}$ , and ground prior to use. Further details are given elsewhere (Srinivasan and Fogler, 1986a).

The kinetics and the extent of surfactant adsorption were monitored in batch-type experiments in quadruplicate (50 mg of clay per batch). To measure initial rates of surfactant adsorption, 0.2- $\mu\text{m}$  inorganic membranes (ANOPORE, Alltech Associates, Inc.) were used in a filtration device to separate the two phases rapidly. Separate control tests established that the loss of surfactant by adsorption to the inorganic membrane material was  $<3\%$ ; however, for equilibrium adsorption and for long-term kinetic measurements, phase separation was achieved by centrifugation (bench top, temperature-controlled centrifuge; Beckman model TJ-6). Similar control experiments (i.e., in the absence of clay) were performed to rule out non-specific adsorption of the surfactants, because, generally, the amount of adsorbed surfactant was determined from the difference between the initial and the final concentrations of surfactants. Most of the surfactant adsorption measurements were carried out in deionized water at an ambient pH of 5.5. The effects of pH and the ionic strength of the medium on surfactant adsorption were also examined. HCl or NaOH + NaCl were used respectively to adjust the pH and the ionic strength of the medium to the specified values.

Two types of desorption experiments were attempted. An aliquot of the adsorbent slurry (following adsorption for 2 hr) was diluted 20-fold into deionized water, and desorption was allowed to proceed for 24 hr, following which the phases were separated by centrifugation and analyzed. Sequential desorption was carried out as well by separating the two phases, removing a portion of the supernatant, and replacing it with

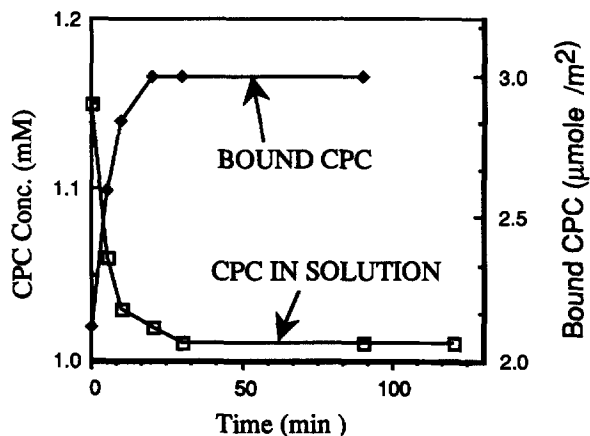


Figure 1. Kinetics of adsorption of cetyl pyridinium on hydroxy-Al montmorillonite. Depletion of the surfactant from solution and the adsorbed amount are shown separately in the figure. See text for details.

an equal volume of deionized water. Five such steps were carried out, each lasting 24 hr.

Electrophoretic measurements were made in aqueous suspensions of the sorbents (250 ppm) using a Lazer-Zee model 500 (Pen Kem Inc.). This instrument converts the observed electrophoretic mobility to zeta potential using Smoluchowski's equation (Hunter, 1987). The possible existence of extended double layers or the occurrence of large surface potentials were considered, but, corrections to the experimental zeta potentials were not made for the following reasons. Our interest was mainly to assess the dependence of double layer charge upon successive polycation and cationic surfactant adsorption. Hachisu (1984) and Horikawa *et al.* (1988) reported that the zeta potential, if measured under similar particle size and solution conditions, is a valid basis for such a comparison. In addition, Natarajan and Schechter (1987) recognized that in the limit of a thin double layer, significant deviations from Smoluchowski's theory occur only at fairly large zeta potentials. The greatest zeta potential recorded in the present study was only 45 mV. Changes in the double layer charge due to specific adsorption, however, will be reflected in the observed zeta potentials, although not necessarily in a quantitative manner.

Flocculation tests were carried out by established procedures (van Olphen, 1987). Briefly, suspensions of inorgano-montmorillonite (i.e., hydroxy-Al montmorillonite or Lamontmorillonite; 1 mg/ml) or Na-montmorillonite (also at 1 mg/ml) were equilibrated with known levels of surfactants and mixed. After 2 hr, the slurries were mixed by inversion 10 times, and the particles were allowed to settle quiescently by sedimentation and sedimentation flocculation. Exactly 30 min later, an aliquot of the slurry was carefully withdrawn and its turbidity at 600 nm measured. Each experiment was repeated twice, and the average turbidity values were normalized using similar values obtained for Na-montmorillonite or hydroxy-Al montmorillonite slurries, respectively, at the same volume fraction.

## RESULTS

### Kinetics of adsorption of surfactants

The adsorption of CPC on hydroxy-Al montmorillonite was monitored as a function of time to establish

the optimal time period for adsorption isotherm measurements; the results are shown in Figure 1. Control experiments under identical conditions ensured that the depletion of the surfactant from the solution was due only to surface adsorption. The BET  $N_2$  adsorption surface area of the hydroxy-Al montmorillonite used in the present study ranged from 160 to 220  $m^2/g$  (Nolan, 1988). Consequently, bound surfactant was plotted in the form of surface adsorption density to reflect the available surface area for binding. A stationary state of adsorption was clearly attained within 20 min, which indicates that adsorption of CPC on hydroxy-Al montmorillonite may be of the high-affinity type (see below). The initial surfactant concentration of 1.6 mM used to obtain these results is more than twice the critical micelle concentration (CMC, 0.7 mM in deionized water at room temp; Mysels and Mukerjee, 1971). Therefore, with a constant monomer concentration and no mass-transfer limitations, surfactant adsorption, as expected, was rapid. Even so, for adsorption isotherm experiments, an equilibration time of 2 hr was routinely used.

### Adsorption-desorption of surfactants

As shown by the results in Figure 2A, the adsorption of CPC on hydroxy-Al montmorillonite was not only rapid, but also appears to have been of the high-affinity type. A plateau adsorption density of 3.3  $\mu\text{mole}/m^2$  was attained at a final solution concentration of 0.4 mM, which was less than the CMC of the surfactant. Initial concentrations ranging from 0.07 to 3.5 mM were used. Because the monomeric units were depleted by adsorption, the solution concentration continuously decreased to a final value less than the CMC. Initial concentrations of 7.0 and 10.5 mM were also used (data not shown in Figure 2A) to verify that no further adsorption occurred beyond monolayer coverage. From the monolayer capacity, a cross-sectional area of 50  $\text{\AA}^2/\text{adsorbed ion}$  was calculated at the endpoint of adsorption. This value is greater than the 30  $\text{\AA}^2$  derived from solution-phase measurements on CPC micelles (Nagarajan and Ruckenstein, 1984). On the other hand, it agrees well with the 54  $\text{\AA}^2$  value reported by Greenland and Quirk (1964) for the projected area of an end-on adsorbed alkyl pyridinium ion. Note that cetyl pyridinium ion adsorption was used by Greenland and Quirk to measure surface areas of clay particles. Finally, according to Claesson *et al.* (1986) who studied the adsorption of dioctadecyl dimethyl ammonium ions on mica surfaces by the Langmuir-Blodgett technique, which yielded a monolayer on the surface, a surface area of 50  $\text{\AA}^2/\text{ion}$  was indicated. Thus, the CPC ion on hydroxy-Al montmorillonite must have been adsorbed in a vertical orientation.

Remarkably, CPC adsorption on hydroxy-Al montmorillonite appears to have been far removed from a

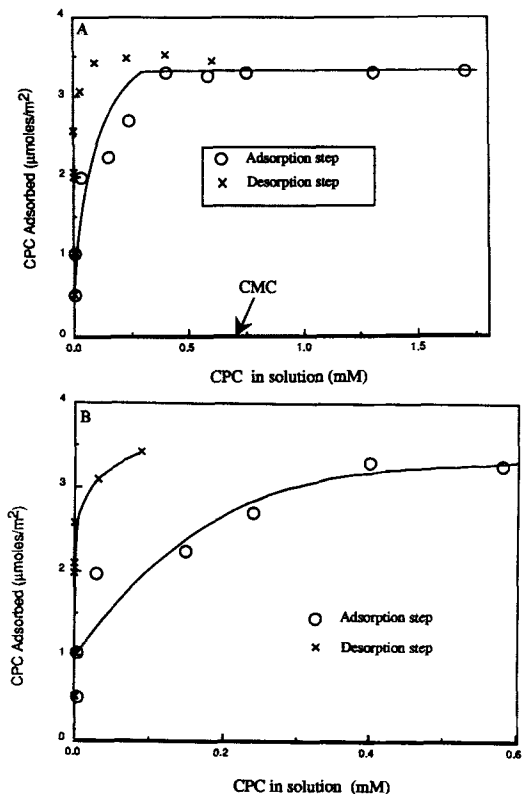


Figure 2. (A) Adsorption-desorption of cetyl pyridinium (CPC) on hydroxy-Al montmorillonite. The critical micelle concentration (CMC) of the surfactant is indicated by arrow. Desorption was carried out by the one step, 20-fold dilution method. Similar results were obtained with cetyl benzyl dimethyl ammonium on hydroxy-Al montmorillonite. Note that, within experimental error, amount of bound surfactant on the adsorption and desorption curves is the same. (B) Low-concentration portion of isotherm showing more clearly the extent of hysteresis between adsorption and desorption.

true thermodynamic equilibrium. As pointed out above, each CPC-hydroxy-Al montmorillonite slurry obtained from the adsorption step was diluted 20-fold in deionized water to monitor the extent of desorption. The results are shown in Figure 2A. An apparent irreversibility of adsorption is clearly indicated by the occurrence of a y-intercept in the desorption curve. The low-concentration range of the isotherm is plotted on an expanded scale in Figure 2B; a hysteresis between the adsorption and desorption steps can be seen. Presumably, the highly cohesive and strongly cooperative interaction between the hydrocarbon tails of the adsorbed surfactants greatly enhanced the strength of surfactant binding, resulting in the apparent irreversibility of adsorption.

Similar results (Figure 3) were obtained by binding CPC on La-montmorillonite. Here also, a significant amount of adsorption/desorption hysteresis was discernible (note the y-intercept on the desorption curve).

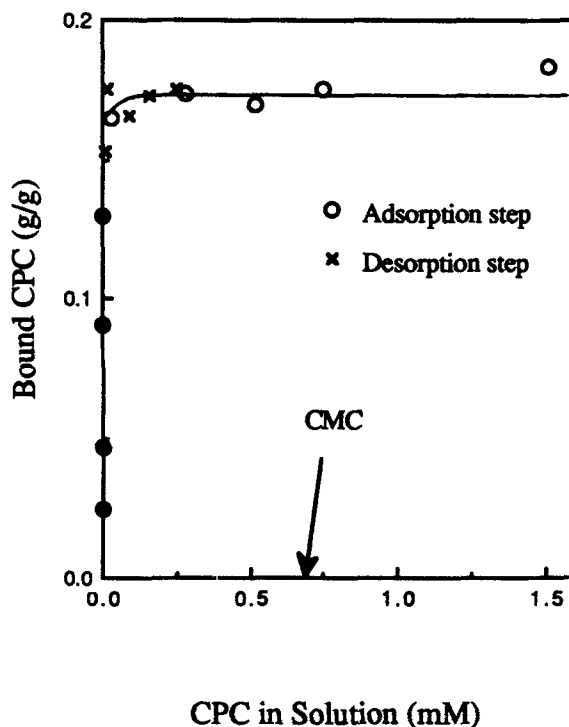


Figure 3. Adsorption-desorption of cetyl pyridinium (CPC) on La-montmorillonite. The y-intercept is easily discernible. Similar results were obtained with cetyl benzyl dimethyl ammonium on La-montmorillonite. CMC = critical micelle concentration.

The amount adsorbed is plotted in terms of g/g, because separate BET surface areas were not measured. A comparison of adsorption density expressed as mmole/g, however, showed identical results for CPC-hydroxy-Al montmorillonite and CPC-La-montmorillonite (top part of Table 2). Table 2 also reveals that pH and ionic strength, in the ranges used in this study, had no discernible effects on surfactant adsorption. The above adsorption densities were also compared with the adsorption density value obtained for the traditional, cation-exchanged smectite, such as CPC-montmorillonite, prepared under identical experimental conditions. The CPC adsorption density of 0.93 mmole/g on CPC-montmorillonite was 120% of the CEC (77 meq/100 g) of the montmorillonite sample (Table 2). A similar result, (Table 2) was obtained for the adsorption of cetyltrimethylammonium ion on Ca-smectite (Boyd *et al.*, 1988b). On the other hand, CPC-hydroxy-Al montmorillonite and CPC-La-montmorillonite adsorbed less of surfactant, which reflects the respective available surface areas for adsorption and not the CECs of the starting smectite samples. This finding distinguishes IOCs from the traditional organoclays.

The results summarized in Table 2 also show that the adsorption capacity of hydroxy-Al montmorillonite

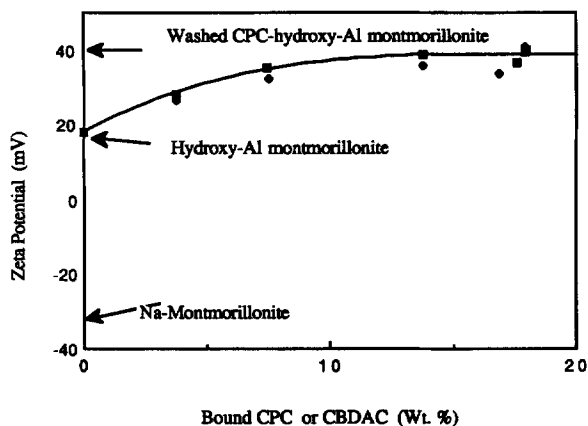


Figure 4. Zeta potentials of Na-montmorillonite, hydroxy-Al montmorillonite, and inorgano-organo-clay containing bound cetyl pyridinium (CPC) or cetyl benzyl dimethyl ammonium (CBDAC) as a function of adsorbed surfactant. Also shown is observed zeta potential for an extensively washed sample of CPC-hydroxy-Al montmorillonite.

ite or La-montmorillonite for CBDAC ions was identical to that for CPC. Further, CBDAC adsorption and desorption isotherms (not shown here) were found to be quite similar to those shown in Figures 2A and 3. Thus, the basicity of the head group did not appear to play a key role in the surfactant adsorption process leading to the formation of IOCs.

#### Nonexchangeability of polycations

One of the key structural characteristics of IOCs derives from the fact that the polycations at the cation-exchange sites of the clay were not exchangeable, which arises from the specific adsorption of these ions in the

innermost part of the electrical double layer. Electrokinetic measurements (specifically, zeta potentials) have been traditionally used to verify such adsorption between the surface and the hydrodynamic shear plane (Lyklema, 1982). For a charged particle having adsorbed ionic moieties in the Stern layer, overall electroneutrality requires that:

$$\sigma_0 + \sigma_s = \sigma_d,$$

where the subscripts 0, s, and d refer to charge densities at the surface, the Stern layer, and the diffuse layer, respectively. At a fixed ionic strength and pH (conditions under which the surface charge will be invariant) increasing values of zeta potential imply increasing amounts of double layer charge, which means a greater adsorption density of surfactant molecules in the Stern layer. On the other hand, if the cationic surfactant displaces polycations from the surface, the observed zeta potential should either decrease or remain the same. The observed zeta potential of hydroxy-Al montmorillonite increased with the binding of CPC or CBDAC ions to form the respective IOCs (Figure 4).

The observed zeta potential of  $-27.0$  mV for Na-montmorillonite in deionized water agrees with previously reported values in the range of  $-28$  to  $-47$  mV (Low, 1958, 1981; Delgado *et al.*, 1986; Horikawa *et al.*, 1988). Such variations in zeta potentials have been attributed to sample preparation techniques and possibly to adsorbed impurities (Horikawa *et al.*, 1988).

The binding of hydroxy-Al to Na-montmorillonite produced a charge reversal, indicating super equivalent adsorption of hydroxy-Al to form hydroxy-Al montmorillonite. Surfactant adsorption (either CPC or CBDAC) added even more positive charge to the surface, leading to even larger values of electrokinetic mo-

Table 2. Binding of cationic surfactants to inorgano-clays.

Cationic surfactant and conditions	Adsorbed amount (mmole/g)	
	Hydroxy-Al montmorillonite	La-montmorillonite
Cetyl pyridinium		
Deionized water; pH = 5.6	0.57	0.57
Ionic strength = 2 mM; pH = 3.0	0.58	n.d.
Ionic strength = 2 mM; pH = 5.6	0.57	0.58
Cetyl benzyl dimethyl ammonium		
deionized water; pH = 5.6	0.53	0.55
	Na-montmorillonite <sup>1</sup>	Ca-smectite <sup>2</sup>
Cetyl trimethyl ammonium		
Deionized water	n.d.	1.1
Cetyl pyridinium		
Deionized water; pH = 5.6	0.93 (this work)	—

Adsorbed amounts are the mean values obtained from two sets of duplicate measurements; the relative error was estimated to be 10%. n.d. = not determined.

<sup>1</sup> Cation-exchange capacity of Na-montmorillonite = 77 meq/100 g.

<sup>2</sup> Boyd *et al.*, 1988b.

bilities. Thus, the observed zeta potentials imply that the successive adsorption of hydroxy-Al and the surfactant ions on montmorillonite was additive. In other words, the adsorbed surfactant ions did not displace hydroxy-Al from the surface. As a further confirmation of the apparent irreversibility of hydroxy-Al and surfactant adsorption, a sample of CPC-hydroxy-Al montmorillonite, containing a saturation level of adsorbed surfactant, was extensively washed in deionized water and re-suspended in the same medium. The zeta potential measured under these conditions was +44 mV (as shown by the arrow in Figure 4).

The nonexchangeability of hydroxy-Al inferred in this study agrees with Foolad's (1984) observations that the CEC of Na-montmorillonite reduces to nearly zero upon binding hydroxy-Al, provided a large excess of hydroxy-Al is used. Because a 30-fold excess of hydroxy-Al was used in the present investigation, the exchange sites were irreversibly blocked by hydroxy-Al polyions, as expected. Similar studies with CPC-La-montmorillonite are summarized in Table 3. The low negative zeta potential of La-montmorillonite suggests only partial charge neutralization by the adsorbed La ion; however, adsorption of cationic surfactant led to charge reversal and electrophoretic mobilities comparable to those obtained with CPC-hydroxy-Al montmorillonite. Inasmuch as only a small amount of specific adsorption was needed to bring about charge reversal, most of the adsorbed surfactant must have had a similar surface structure in both IOCs.

#### Flocculation-peptization of IOCs

The successive adsorption of hydroxy-Al and the cationic surfactant was expected to have an effect on the colloidal stability of the modified montmorillonite particles in an aqueous medium. Because the stability of a dispersion of particles having a layer of adsorbed surfactant can be correlated with the surface orientation of the adsorbed surfactant, flocculation tests were undertaken to establish the surface orientation of CPC or CBDAC ions on the respective IOCs. For a given level of surfactant adsorption, increased stability against sedimentation flocculation of IOCs is possible only if the charged head groups of the surfactants point towards the dispersion medium. Repulsion due to the overlapping double layers of the IOC particles that approach one another is the main stabilizing force. On the other hand, for the traditional organo-clays, such as CPC-montmorillonite, extensive flocculation results not only from charge neutralization, but from the hydrophobic attraction between the hydrocarbon tails pointing away from the surface towards the dispersion medium (Claesson, 1986). In the former situation, the measured turbidity should increase due to increased stabilization, whereas in the latter situation, the turbidity should sharply decrease at the onset of floccu-

Table 3. Zeta potentials of La-cetyl pyridinium montmorillonite.

Surfactant adsorption density (wt. %)	Zeta potential (mV)
0	-13.0
4.5	+34.6
9.8	+38.8
13.6	+43.1
17.5	+41.5
17.6	+44.0

Observed zeta potential is the mean of eight different measurements on the sample; the variation was  $\pm 3.0$  mV. In the absence of any adsorbed surfactant, 10–15 data points were averaged, and the sign of the observed zeta potential was verified on two different samples.

<sup>1</sup> CPC = cetyl pyridinium.

lation followed by settling of the flocs. These concepts are schematically illustrated in Figure 5.

The results of such sedimentation tests are shown in Figures 6A and 6B. From the initial turbidity vs. time measurements (not shown here), a 30-min settling time was found to be optimal. In Figure 6A, flocculation of Na-montmorillonite by the two surfactants, CPC and CBDAC is shown, along with flocculation and re-stabilization of the same starting clay by hydroxy-Al. Flocculation of the edge-to-face type may occur in Na-montmorillonite and observed turbidity may be due to the fine particle size of the flocs that do not settle out (van Olphen, 1987). Thus, for an initial surfactant amount of 55% of the CEC (arrow in Figure 6A), extensive flocculation and settling were observed. Partial charge neutralization and the significant hydrophobic attraction between the hydrocarbon tails extended away from the surface were probably responsible, in agreement with the concepts depicted in Figure 5. Even for adsorption beyond the CEC, only partial re-stabilization took place. These results establish that strong flocculation can be directly correlated with an outward orientation of the surfactant tail. The results presented here are in agreement with earlier findings on ferric hydroxide sols (Glazman *et al.*, 1986), montmorillonite (Kay, 1972), and mica (Claesson *et al.*, 1984).

Polycationic hydroxy-Al is a strongly adsorbed counter ion for Na-montmorillonite and was able to flocculate it even at an initial hydroxy-Al concentration of 33% of the CEC (arrow in Figure 6A). This equivalence is based on a OH/Al ratio of 2.5 for the Reheis hydroxy-Al solution used in the present experiments. Changes in the OH/Al ratio due to storage were not considered; hence, the concentration of 33% at the turbidity minimum may not have been the exact flocculation concentration of hydroxy-Al. More importantly, for hydroxy-Al, re-stabilization of the dispersion did take place near the CEC, probably due to specific adsorption of the inorgano polymer (Figure 6A). The re-stabilization arose from the double layer repulsion between hydroxy-Al coated particles. Super equivalent

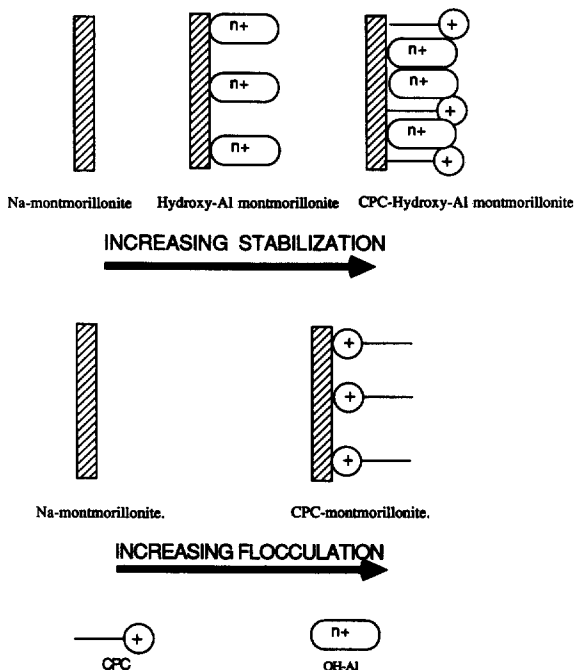


Figure 5. Conceptual diagram of possible flocculation-peatization behavior of modified montmorillonites. See text for details. CPC = cetyl pyridinium.

adsorption of hydroxy-Al beyond the CEC, the concomitant charge reversal, and the restabilization of hydroxy-Al montmorillonite can be deduced from the fact that  $\text{Cl}^-$  ions (originating from the hydroxy-Al solutions used) became the counter ions. Lyklema (1983) reported that chloride ions, at low concentrations, do not affect the electrostatic stability of suspensions. Thus, the observed peptization is not surprising.

Also of interest is the increase in colloidal stability when hydroxy-Al montmorillonite bound CPC or CBDAC ions. The turbidity ratios shown in Figure 6B are based on the turbidity of hydroxy-Al montmorillonite suspensions of the same volume fraction. Therefore, a continued increase in the turbidity of CPC or CBDAC-hydroxy-Al montmorillonite is indicative of greater double layer repulsion if IOCs were formed. Significantly, the overall interaction potential between CPC-hydroxy-Al montmorillonite particles was even more repulsive than that between hydroxy-Al montmorillonite particles, probably because of the surfactant orientation of the IOCs suggested in Figure 5.

#### Sequential desorption

The results of the five-step sequential desorption of adsorbed surfactants from IOCs are shown in Figure 7. At a surfactant solution concentration indistinguishable from zero, about 15.2% by weight of the surfactant (corresponding to about 90% of the initially adsorbed

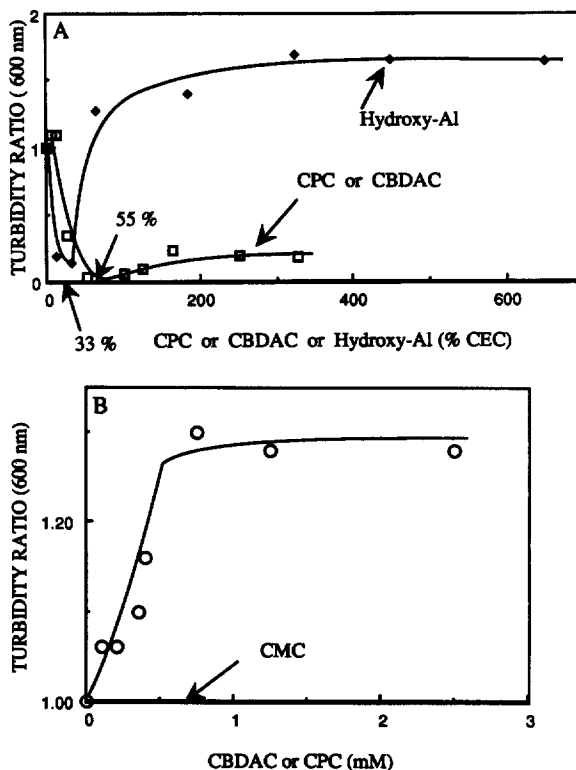


Figure 6. (a) Turbidity of Na-montmorillonite samples as a function of added surfactant or hydroxy-Al. The values along the x-axis are given in terms of the cation-exchange capacity (CEC) of clay sample. The two arrows represent the lowest turbidity ratio or the greatest amount of flocculation in the system. (b) Turbidity of inorgano-organo-clays as a function of surfactant concentration in solution. Turbidity can be seen to be leveling off near the critical micelle concentration of the surfactant suggesting saturation adsorption. Note that the critical micelle concentrations of cetyl pyridinium (CPC) (0.7 mM) and cetyl benzyl dimethyl ammonium (CBDAC) (0.5 mM) are nearly identical.

amount) was still bound to the surface. This amount corresponds to about 12% by weight surface organic carbon. Boyd *et al.* (1988b) reported that the adsorption of cetyl trimethyl ammonium ions (CTA+) on Ca-smectite yielded an initial adsorption plateau of 1.1 mmole/g or about 30% by weight of the surfactant. The final organic carbon content, however, was only 17.3%, which corresponds to 21% by weight of the surfactant in the clay-organic complex. Thus, the stability against desorption of the surfactant molecules adsorbed on IOCs appears to have been comparable to that obtained with the traditional organo-clays.

In fact, the results shown in Table 1 for CPC-hydroxy-Al montmorillonite were obtained in the following manner: CPC-hydroxy-Al montmorillonite containing saturation levels of CPC was extensively washed with deionized water, dried at 90°C, and resuspended in aqueous solutions of toxic organics without addi-

tional surfactant. Further, in seven-day, packed-bed adsorption experiments using a similar preparation of CPC-hydroxy-Al montmorillonite, no discernible change in the adsorption of benzo(a)pyrene onto such a column was noted. Thus, the IOCs prepared by the above procedure were apparently stable with respect to surfactant desorption. The question of extended stability for a year or more can not be answered without further experimentation.

### DISCUSSION

The energetics of the adsorption of ionic surfactants at the solid/liquid interface is well understood (Hough and Rendall, 1983; Moudgil *et al.*, 1987). The main components of the adsorption free energy are coulombic and hydrophobic. The coulombic part can be subdivided into interaction between head group and the surface, as well as between head groups themselves near the saturation point of adsorption.

For the inorgano-organo-clays of the type described here, the coulombic part is mainly repulsive. Assuming that the zeta potential of hydroxy-Al montmorillonite (+20 mV) represents the potential of mean force at the adsorption layer, the coulombic contribution to the standard free energy of adsorption is about +3 kJ/mole for a cationic head group of unit charge. On the other hand, the cohesive energy per CH<sub>2</sub> group has been estimated to be about 2.5 kJ/mole (Moudgil *et al.*, 1987); therefore, lateral interaction between C<sub>16</sub> chains can result in adsorption free energy of more than -35 kJ/mole. In other words, the hydrophobic component can be an order of magnitude larger than the coulombic component. Thus, the resultant adsorption free energy change is negative, and high-affinity adsorption of the surfactant moiety is facilitated. The use of localized charge density in above calculations (in place of the Bragg-William approximation of smeared out charge density) would, of course, lead to a larger value of electrostatic interaction (Levine *et al.*, 1967). By the same token, counter-ion binding to surfactant head groups can significantly lower the repulsion between the head group and the surface and between head groups in the adsorbed layer (Hough and Rendall, 1983). Finally, because identical results were obtained with alkyl pyridinium and alkyl aryl ammonium surfactants containing head groups having different basicities but having the same hydrocarbon chain, suggests that, under our conditions, head-group interaction was of minor consequence in the stability and the surface structure of the IOCs.

A model for IOC formation is shown in Figure 8. At extremely low surfactant concentrations, the adsorption profile is concave due to weak surface-head group interaction (point A in Figure 8). This weak interaction is indicated by the head group pointing away from the surface. Furthermore, the hydrocarbon tails may be attached to the hydrophilic surface by weak

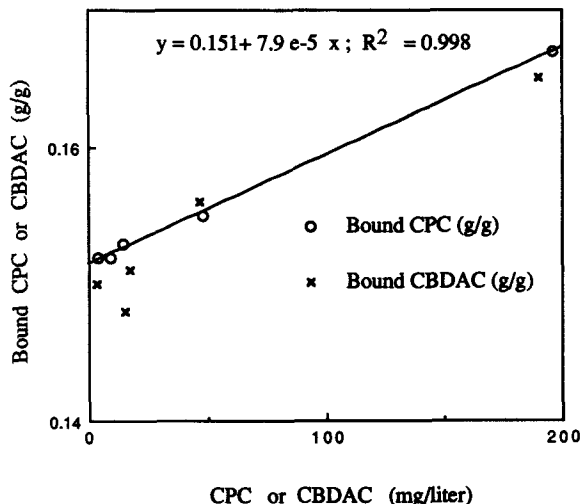


Figure 7. Residual amount of surfactant on inorgano-organo-clays during sequential desorption. Following five such steps, about 15% by weight of surfactant was still surface-bound. Final solution concentration of the surfactants was <2 mg/liter. CPC = cetyl pyridinium; CBDAC = cetyl benzyl dimethyl ammonium.

van der Waals type forces. This situation at the surface is depicted in the middle part of Figure 8 (diagram 1).

At higher surfactant concentrations, however, the lateral interaction between the hydrocarbon tails, as illustrated by diagram 2 in Figure 8, produces a singular transition (point B in Figure 8) resulting in monolayer coverage and "irreversible" adsorption below CMC (point C in Figure 8). Further increase of surfactant concentration above CMC produces no measurable change in adsorption. The key to the formulation of IOCs is to work in the regions between points B and C in Figure 8, i.e., in a narrow range of surfactant concentration in the vicinity of CMC. Sharp transitions (of the high-affinity type) in adsorption density as illustrated by Figure 8 are most likely to occur for surfactant molecules containing long hydrocarbon chains.

In agreement with our model is the finding of Nakamura and Thomas (1986) that adsorbed cetyl pyridinium ions are oriented vertically on montmorillonites at an initial concentration of 100  $\mu$ M. Cases *et al.* (1986) and Clunie and Ingram (1983) reported similar results for weakly interacting non-ionic surfactants on mineral oxides. An equilibrium adsorption model has also been proposed recently to describe the adsorption of weak organic electrolytes at a charged solid-aqueous solution interface (Koopal and Keltjens, 1986). The strong irreversibility of adsorption seen in the present work suggests that such models need to be re-examined.

In summary, novel modified clay adsorbents containing polyvalent or polymeric cations at the exchange sites and cationic surfactants as the source of organic carbon have been prepared. Strong hydrophobic in-



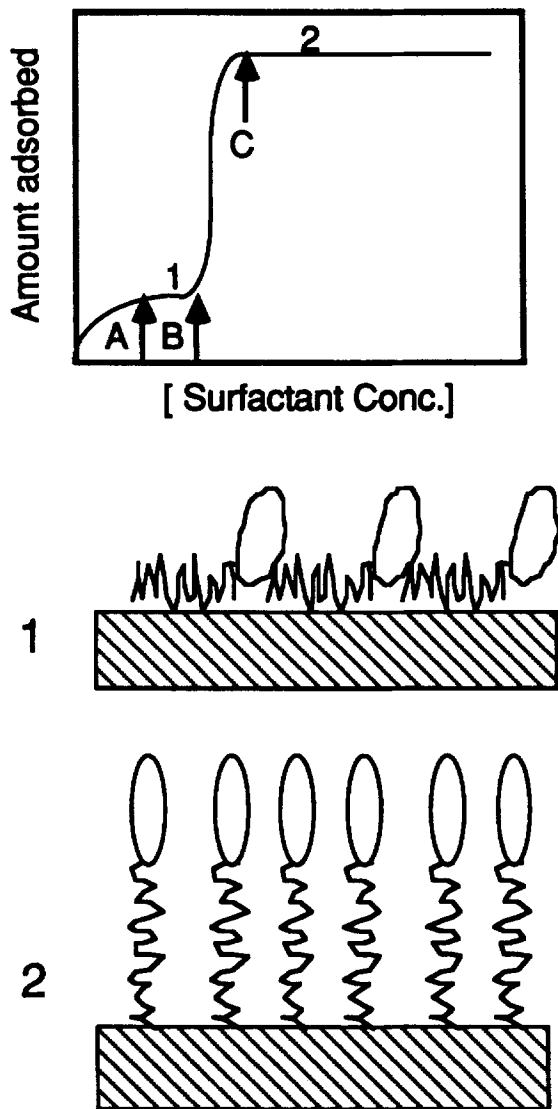


Figure 8. Proposed model for the formation of inorgano-organo-clays. Numbers 1 and 2 refer to surface adsorption density values; possible surface orientations of adsorbed surfactant at these adsorption densities are shown in middle and bottom diagrams. See text for details.

teraction between the surfactant tails promoted irreversibility of adsorbed surfactants. Electrokinetic measurements showed specific adsorption of polycations and cationic surfactants at the Stern layer. Finally, flocculation tests suggest that the hydrocarbon tails were oriented towards the surface.

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