Sorption and Desorption of Quaternary Amine Cations on Clays

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We have studied the sorption and desorption of three quaternary amines, namely, nonyltrimethylammonium, dodecyltrimethylammonium, and hexadecyltrimethylammonium, on homoionic Na- and K-montmorillonite using a titration procedure. More than 99% of all three of the quaternary amine cations studied were sorbed on the montmorillonite when the added amines were less than 70% of the cation-exchange capacity of the montmorillonite. Sorption of quaternary amine cations involves at least two types of reactions, namely, an exchange reaction and the adsorption of amines at nonexchangeable sites. The exchange reaction proceeded almost to completion when Na^+ was the exchangeable cation. Exchangeable K^+ was much more difficult to replace. The adsorbed quaternary amine cations were not easily desorbed in the presence of 0.1 M NaCl and KCl solutions. In addition, desorption of quaternary amines did not increase with prolonged equilibrium time, up to 180 days. Therefore, it appears that there is good promise in using quaternary amine-modified clays as effective sorbents for removing organic pollutants or mitigating their mobilities in the environment.

Introduction

The sorption of organic cations on soils and clays was perhaps first observed by Lloyd in 1916 when he found that fuller's earth adsorbed nicotine from aqueous solution, especially when the alkaloid was in the salt form (1). But it was not until the 1930s that systematic investigations appeared on reactions of clays with organic cations and bases (2). Smith (3) found that montmorillonite was capable of taking up hydrazine, n-amylamine, di-n-amylamine, piperidine, nicotine, and strychnine cations from aqueous solutions. He concluded that the nature of the sorption process was cation exchange, since washing the clay samples with water alone only displaced trace amounts of the sorbed organic cations, whereas washing with a 1% aqueous solution of NaCl released appreciable quantities of adsorbed species. Gieseking (4) reported that several organic cations were strongly adsorbed in the interlayers of smectitic clay minerals by cation exchange, resulting in larger basal (001) spacings. Gieseking (4) also found that these organic cations could be exchanged by other organic cations of approximately the same size, but they were not easily exchanged by hydrogen ions. Hendricks (5) studied the sorption of aliphatic and aromatic amines, alkaloids, purines, and nucleosides on H-montmorillonite. He found that the sorption of organic cations on clays was influenced by both electrostatic and van der Waals forces. Grim et al. (6) investigated the sorption of n-butylamine, n-dodecylamine, and ethyldimethyloctadecenylamine on clays. They reported that for the

relatively small n-butylamine adsorption did not occur beyond the cation-exchange capacity (CEC) of the clays, even when there was an excess amount of amine cations in the solution. Under similar conditions, however, the two larger amines were adsorbed in excess of the CEC. The excess amount of amines adsorbed beyond the CEC of the clays was ascribed to van der Waals interactions.

Gieseking (4) noticed that organic cations were very effective in flocculating dispersed clays and that once the clay was flocculated, it failed to show a significant increase in the basal spacing when exposed to water vapor or liquid water. The transformation of a natural hydrophilic clay to a clay–organic complex or an organo-clay that exhibits hydrophobic properties when alkylamine cations are adsorbed has led to the wide use of organo-clays as thickeners or gelling agents of organic systems (2).

More recently, increasing concern about pollution of groundwater and surface water by organic chemicals has led to research on the use of various adsorbents for removal of organic pollutants from water. Clay minerals, especially the 2:1 smectitic minerals, are of particular interest because of their large specific surface areas. Natural clays with exchangeable metal cations, however, usually are not very effective in adsorbing neutral organic molecules from aqueous solutions, because of the hydrophilic nature of the clay surfaces induced by the metal cations. When the metal ions are replaced by large surfactant cations, such as long-chain alkylamine cations, the nature of the clay surfaces is drastically altered. While natural clays are hydrophilic, the surfactant-modified clays (organo-clays) are hydrophobic or organophilic in nature. This property makes the organo-clays attractive to poorly water-soluble organic molecules (7). Consequently, it has been suggested that organo-clays can be used for wastewater treatment, spill control, and oil or gasoline tank and landfill liners (8-10). Several investigators studied sorption of neutral organic chemicals from aqueous solutions on clays and soils exchanged with quaternary amine cations (11-15).

Although considerable attention has been given to the sorption of organic contaminants by surfactant-modified clays and soils, the sorption of quaternary amine cations themselves on clays and soils, however, has not been fully investigated. Furthermore, desorption of quaternary amine cations from clays has not been well-characterized, and the extent of the reversibility of the exchange reaction with these large organic cations still remains unknown. Therefore, to determine the optimal use of organo-clays for environmental applications, with minimal adverse effects, the following fundamental problems should be first addressed: (1) What are the factors which control the extent of sorption of organic cations on clays? What quantity of the organic cations is being adsorbed, and how much is remaining in solution? (2) Are the organo-clays stable? What is the extent of the reversibility of the exchange reaction? Can the adsorbed organic cations be desorbed from clay surfaces in the presence of excess electrolyte? (3) Are these organic cations environmentally

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safe themselves? (4) What are the controlling factor(s) for the preferential or selective adsorption of a given group of organic pollutants on organo-clays? (5) What are the sorption and desorption kinetics and mechanisms of organic pollutants on the organo-clays?

The present study was conducted to address the first two problems stated above. We investigated the sorption as well as the short-term (less than 7 days) and long-term (10, 30, 90, and 180 days) desorption of three quaternary amine cations on Na- and K-montmorillonite. Sorption of amines was conducted at an ionic strength of 0.008 or 0.01 M, and the desorption of amines was studied by adding excess electrolyte to increase the concentration of Na$^+$ and K$^+$ ions to 0.1 M.

Experimental Section

Homoionic Na-, K-, and Ca-montmorillonite samples were prepared from Wyoming montmorillonite (SWy-1, obtained from the Source Clays Repository of the Clay Minerals Society located at the University of Missouri), NaCl, KCl, and CaCl$_2$ using the procedures outlined by Zhang et al. (16). The cation-exchange capacity of the clay samples was 0.90 mequiv g^{-1}. Three quaternary amines were investigated in this study, nonyltrimethyl-ammonium (NTMA), dodecyltrimethylammonium (DTMA), and hexadecyltrimethylammonium (HDTMA). All chemicals used in the study were analytical reagents, and they were used without further purification.

Determination of Quaternary Amines. A titration procedure developed by Furlong and Elliker (17) was used in this study. A total of 2–5 mL of quaternary amine solution was placed into a capped test tube containing 2 mL of tetrachloroethane, 0.5 mL of pH 4.5 buffer, and 0.1 mL of eosin Y indicator. The pH buffer was prepared by dissolving 25 g of citric acid (monohydrate) in 100 mL of deionized water and adjusting the pH to 4.5 with 10 M NaOH. The eosin Y indicator was prepared by dissolving 50 mg of eosin yellowish dye in 100 mL of deionized water. Before titrating the sample, the test tube was vigorously shaken for 30 s on a vortex mixer to facilitate the extraction of the quaternary amine from the aqueous phase to the tetrachloroethane phase. A pink to red color in the tetrachloroethane phase indicates the presence of a quaternary amine. The solution was then titrated with a standard anionic surfactant solution to a colorless end point. The test tube was vigorously shaken on a vortex mixer during the titration. The detection limit of quaternary amines by this method is below 1.0×10^{-5} M. Three anionic surfactant standard solutions ranging from 1.0×10^{-4} to 2.00×10^{-3} M were prepared from 75% Aerosol OT (dioctyl sodium sulfosuccinate).

Sorption and Desorption of Amines. Solutions of NaCl, NTMA, and DTMA were prepared at 0.02 M. A total volume of 10 mL of NaCl and NTMA (or DTMA) solutions at different volume combinations (from 5:5 to 0:10) was added (NaCl solution was added first) to each of the Na-montmorillonite samples (0.2222 g of dry weight) prewetted with 10 mL of deionized water to yield different amounts of added amines. Duplicate or triplicate clay samples with added amounts of amines from 50% to 100% of the CEC were prepared this way. The initial concentration of added amines ranged from 0.005 to 0.01 M. Clay samples with the added amines above 100% of the CEC were achieved by proportionally decreasing the mass of

the clay samples. The NaCl solution was not added to the clay samples when the added amine was equal or above 100% of the CEC. The resulting initial ionic strength for these solutions was slightly above 0.01 M (due to the free NaCl on the clay sample).

Since an attempt to prepare a 0.02 M HDTMA solution failed, 0.01 M solutions of NaCl and HDTMA were prepared instead. Similar to the procedure above for NTMA and DTMA, a total volume of 10 mL of the NaCl and HDTMA solutions at different volume combinations (4:6 to 0:10) were added to each of the Na-montmorillonite samples (0.1111 g) prewetted with 2.5 mL of deionized water. The initial concentration of HTDMA ranged from 0.0048 to 0.008 M, and the initial ionic strength was 0.008 M.

The clay suspensions were agitated on a reciprocal shaker for at least 48 h at 25 °C. Then they were centrifuged, and one-half of the total solution from each clay sample was removed to determine the equilibrium concentrations of Na$^+$ ions and the quaternary amine cations by ion chromatography and titration, respectively. Thereafter, each clay suspension sample was brought back to its initial volume by adding 0.2 M NaCl solution to yield a Na$^+$ concentration slightly above 0.1 M (considering the exchangeable Na$^+$ ions desorbed from the clay sample). The short-term desorption was conducted by shaking the clay suspensions on a reciprocal shaker for 4–7 days at 25 °C. Sorption and desorption of amines on K-montmorillonite were studied using the same procedures, except KCl was used rather than NaCl.

The long-term desorption experiments were conducted in duplicate in the presence of three electrolytes, namely, 0.1 M NaCl and KCl as well as 0.05 M CaCl$_2$. First, homoionic Na-, K-, and Ca-montmorillonite samples (0.4444 g) were added to separate glass bottles, and they were prewetted with 10 mL of deionized water. Then 8 mL of 0.01 M NaCl and KCl and 0.005 M CaCl$_2$ solutions and 32 mL of each of the three quaternary amine solutions (0.01 M) were added to the respective clay samples. The added amines constituted 80% of the CEC of the clay samples, and the initial concentration of amines was 0.0064 M. The clay samples were shaken on an orbital shaker at a speed of 200 rpm for 7 days. After removing 5 mL of the supernatant solution for the adsorption study, 5 mL of NaCl and KCl solutions (1.0 M) and CaCl$_2$ solution (0.5 M) were added to the respective clay samples to yield a 10-fold increase in the electrolyte concentration. Thereafter, the desorption of the quaternary amines was determined at 10, 30, 90, and 180 days. During the long-term desorption, the clay samples were shaken on an orbital shaker periodically.

Results and Discussion

The percentage of quaternary amines sorbed on Na- and K-montmorillonite is presented in Table I. The data presented in Table I and in subsequent tables are the average values of duplicate or triplicate clay samples. It is evident that more than 99% of all three quaternary amines were sorbed on Na-montmorillonite when the added amount was less than 70% of the CEC. The percentage of amine sorption decreased gradually with an increase in the amount of added amines up to 100% of the CEC, and thereafter the percentage decreased rapidly for both NTMA and DTMA. The percentage of HDTMA

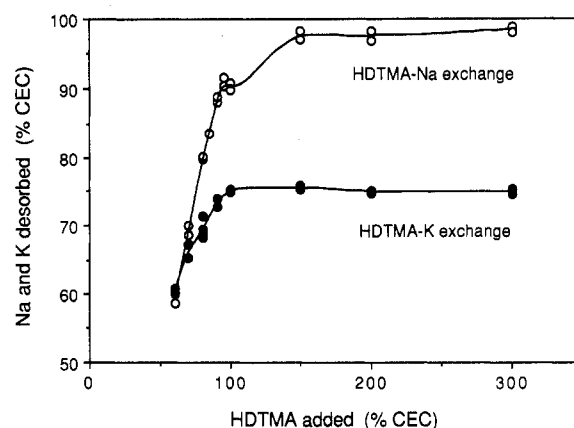Table I. Percentage Sorption of Quaternary Amines on Na- and K-Montmorillonite at Different Amounts of Added Amines

added amine (% CEC)	amine sorbed (% added amine)					
	Na-montmorillonite			K-montmorillonite		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
50				99.5	99.6	
60	99.8	99.8	99.7	98.1	98.5	99.6
70	99.4	99.8	99.4	93.5	94.2	99.7
80	98.4	99.6	99.2	86.3	88.2	99.7
85	96.2	99.3	99.3	81.8	86.7	
90	94.2	98.4	99.2	79.8	85.3	99.5
95	91.7	96.2	98.9	76.5	82.4	
100	87.6	94.3	98.9	73.1	79.1	99.2
150	62.5	70.6	97.7	52.8	57.3	97.1
200	46.4	56.5	96.2	41.1	47.3	88.8
250				34.7	39.5	
300	31.5	40.5	74.6	29.7	34.1	60.8

Figure 1. Desorption of Na^+ and K^+ ions from Na- and K-montmorillonite as affected by HDTMA.

Table II. Values of Ratio of Quaternary Amine Sorbed to Na^+ and K^+ Desorbed for Sorption of Quaternary Amines on Na- and K-Montmorillonite at Different Amounts of Added Amines

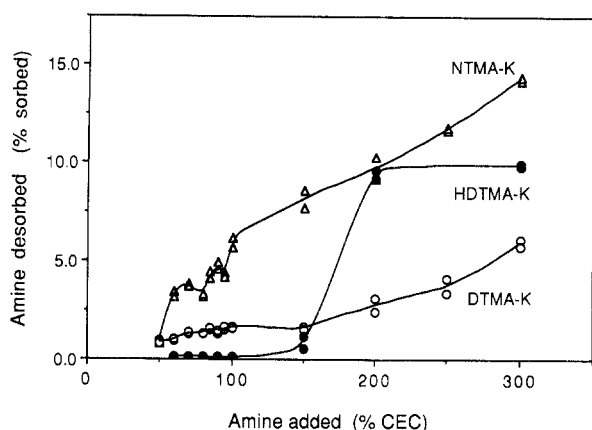| added amine (% CEC)	Na-montmorillonite			K-montmorillonite		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
50				1.08	1.07	
60	1.02	1.01	1.01	1.07	1.06	0.989
70	1.03	1.01	0.994	1.04	1.05	1.05
80	1.03	1.04	0.983	1.04	1.10	1.15
85	1.02	1.05	1.00	1.06	1.14	
90	1.04	1.05	1.00	1.10	1.14	1.22
95	1.04	1.05	1.02	1.06	1.16	
100	1.08	1.07	1.08	1.07	1.17	1.32
150	1.09	1.13	1.50	1.13	1.28	1.93
200	1.06	1.18	2.07	1.13	1.33	2.37
250				1.18	1.41	
300	1.04	1.24	2.23	1.24	1.40	2.44

Table III. Percentage Desorption of Exchangeable Na^+ and K^+ Ions from Na- and K-Montmorillonite at Different Amounts of Added Amines

added amine (% CEC)	Na^+ desorbed (% CEC)			K^+ desorbed (% CEC)		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
50				46.2	46.5	
60	59.7	59.6	59.3	55.0	55.8	60.5
70	68.7	68.8	69.3	62.8	62.7	66.3
80	77.7	77.6	80.1	66.2	64.5	70.4
85	81.7	83.8	83.5	65.4	64.5	
90	81.4	87.4	88.4	65.5	67.2	73.4
95	87.4	87.3	91.0	68.4	67.3	
100	84.4	88.5	90.3	68.5	67.7	75.1
150	89.8	93.8	97.6	69.9	67.4	75.6
200	92.8	96.8	97.6	72.8	71.3	74.9
250				73.4	70.2	
300	97.6	98.3	98.5	72.0	72.9	74.8

sorption, however, did not decrease dramatically until the amount of added HDTMA was above 200% of the CEC. The data clearly demonstrate that HDTMA was sorbed beyond the CEC. The percentage sorption of NTMA and DTMA on K-montmorillonite was significantly lower than that on Na-montmorillonite except when the amount of added amine was less than 60% of the CEC. The percentage sorption of HDTMA on K-montmorillonite, however, did not differ from that on Na-montmorillonite until the amount of added amine was above 200% of the CEC. These data show that except for HDTMA, the sorption of quaternary amines on K-montmorillonite was generally less than that on Na-montmorillonite, probably due to the inability of amines with shorter alkyl chains to replace the tightly-held K^+ ions on clays.

It is evident that the ratio of quaternary amine sorbed to Na^+ and K^+ ions desorbed would provide information as to the nature and mechanisms of the sorption reaction. This ratio would be unity if the sorption of quaternary amines is solely due to cation exchange. The measured values of this ratio are reported in Table II. One sees that with a few exceptions due to experimental errors, most of the ratios were slightly above unity when the amounts of added quaternary amines were less than the CEC. With increasing amounts of added amines, the ratio increased gradually. Therefore, it is conceivable that sorption of quaternary amines on montmorillonite involves at least two types of reactions, i.e., a cation-exchange reaction and the adsorption of amines at nonexchangeable sites. The exchange reaction dominated for the sorption of both

NTMA and DTMA, whereas adsorption of HDTMA at nonexchangeable sites could exceed that on cation-exchange sites, provided additional HDTMA was available.

Based on these data, the following mechanisms appeared to be plausible. During the initial sorption process, the cation-exchange reaction predominated, and then, as more quaternary amine cations were sorbed on the surface, the degree of adsorption at nonexchangeable sites also increased. The degree to which quaternary amine cations were adsorbed at nonexchangeable sites was also directly related to the lengths of the alkyl chains of the amines. We have observed that NTMA was essentially not adsorbed beyond the CEC, DTMA was only slightly adsorbed beyond the CEC, while HDTMA was significantly adsorbed beyond the CEC. Therefore, it appeared that the interactions involving alkyl chains were not strong enough to contribute to the adsorption at nonexchangeable sites until a critical length of 12 carbons was reached.

These results appear to suggest that the adsorption of quaternary amine cations at nonexchangeable sites involves interactions between alkyl chains of these cations and between the alkyl chains and the clay surfaces. It was reported earlier that the adsorbed amine cations on clays in excess of the CEC were not easily removed with water. Therefore, it would seem that the binding of the excess quaternary cations involved ion–dipole and ion–ion interactions in addition to the van der Waals forces (18). It appears that the quaternary amine cations adsorbed in excess of the CEC retained their cationic form, i.e., they were not as an amine salt. This was supported by the data from electrophoresis studies. A charge reversal was

Figure 2. Short-term desorption of NTMA, DTMA, and HDTMA from montmorillonite in the presence of 0.1 M KCl.

Table IV. Short-Term Desorption of Quaternary Amines in Presence of 0.1 M NaCl and KCl

added amine (% CEC)	amine desorbed (% adsorbed amine)					
	0.1 M NaCl			0.1 M KCl		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
50				0.880	0.889	
60			0.552	3.30	0.986	0.119
70	2.88	0.532	0.244	3.77	1.33	0.117
80	2.91	1.00	0.150	3.21	1.31	0.131
85	2.86	1.01	0.239	4.28	1.55	
90	3.45	1.04	0.292	4.78	1.36	0.080
95	3.54	1.22	0.732	4.29	1.56	
100			0.657	5.93	1.60	0.084
150			1.58	8.14	1.59	0.849
200			2.54	9.74	2.74	9.40
250				11.7	3.74	
300			10.2	14.3	5.95	9.88

observed from ζ potential measurements when HDTMA was sorbed in excess to the CEC of the clays (19, 20). Similar charge reversal was also found for adsorption of quaternary amine cations on kaolinite and for adsorption of cobalt(III) chelate complexes on montmorillonite (18).

Figure 1 shows the amounts of Na^+ and K^+ ions desorbed during the exchange reaction with HDTMA. Similar data were also obtained for the exchange reactions with NTMA and DTMA and are reported in Table III. More than 95% of the exchangeable Na^+ ions could be easily exchanged by the quaternary amines, provided there were enough quaternary amine cations present. In contrast, only 70–75% of exchangeable K^+ ions could be easily exchanged by the quaternary amine cations under our experimental conditions. This would indicate that about 25% of the exchangeable K^+ was held rather tightly on the clay surfaces, hence it was not easily exchanged by the quaternary amine cations. Earlier cation-exchange studies also showed that K^+ ions were preferentially adsorbed on smectitic clays over other alkali metal ions such as Li^+ and Na^+ and alkaline metal ions such as Ca^{2+} and Mg^{2+} (21, 22).

The short-term desorption data for quaternary amines in the presence of 0.1 M KCl are presented in Figure 2. Similar data were also obtained with 0.1 M NaCl and are reported in Table IV. Two factors contributed to amine desorption, i.e., an increase in the metal cation concentration and a decrease in the amine concentration, both resulting from the addition of an electrolyte solution. The data in Table IV clearly demonstrate that desorption of quaternary amines decreased with increasing amine alkyl

length, but increased with increasing amount of adsorbed amines. The desorption of NTMA and DTMA in the presence of 0.1 M KCl solution was higher than in the 0.1 M NaCl solution, whereas the desorption of HDTMA appeared to be indifferent with respect to K^+ or Na^+ ions. This would indicate that K^+ ions are more effective than Na^+ ions in exchanging the adsorbed NTMA and DTMA cations, which are not as tightly held to the clay surfaces as the HDTMA cations. The desorption of HDTMA in the presence of 0.1 M NaCl and KCl appeared to be less than 1.0% of the total adsorption when the added amount of HDTMA was up to 100% of the CEC of the clays. However, as the added HDTMA increased beyond 150% of the CEC, desorption in the presence of both NaCl and KCl increased significantly. This increase was likely due to desorption of HDTMA adsorbed at nonexchangeable sites.

The long-term desorption data for the three quaternary amines are presented in Figures 3–5. They are in good agreement with the short-term desorption data presented in Figure 2 and Table IV. It is evident that desorption did not increase with prolonged equilibrium time. In fact, we can see that desorption of NTMA and DTMA, which were sorbed on K-montmorillonite and HDTMA that was sorbed on all three homoionic montmorillonites, gradually decreased with reaction time. Note in Figure 5 that the desorption of HDTMA decreased to negative values, indicating that additional HDTMA was being adsorbed on the clay samples rather than being desorbed. The decreased desorption was inferred from a slight decline in the quaternary amine concentrations over time in the supernatant solutions of the clay samples. The decline in the quaternary amine concentrations was not caused by a hydrolysis reaction, since parallel experiments showed that all three quaternary amines were stable in electrolyte solutions containing no clay samples. It appears that sorption of NTMA and DTMA on K-montmorillonite and sorption of HDTMA on all three homoionic montmorillonites did not reach equilibrium in a relatively long period of time. Although these reactions may be very fast initially, they are not completed even after a few months. Consequently, the adsorption reactions continued in the presence of electrolytes, resulting in a net decrease in desorption over time. Presumably, the driving force for the continuous adsorption reaction is due to a redistribution of the sorbed quaternary amine cations within clay layers through interparticle diffusion.

Earlier investigators (23–25) attempted to evaluate the selectivity and affinity coefficients for exchange reactions on clays involving various amine cations. The exchange reaction can be written as

$$clay\text{-}M + amine^+ \rightleftharpoons clay\text{-}amine + M^+ \qquad (1)$$

and the selectivity coefficient, K_m, is given by

$$K_m = \frac{[C_{M^+}][N_{amine^+}]}{[C_{amine^+}][N_{M^+}]} \qquad (2)$$

where M^+ denotes monovalent metal ions, such as Na^+ and K^+, C represents the concentrations of the appropriate ions in solution, and N is the mole fractions of the specified ions exchanged in the solid phase. Cowan and White (22) studied the sorption of several primary amines on Na-montmorillonite and reported that the values of K_m were constant over the concentration range they studied. They used the values of K_m to calculate the free energy change,
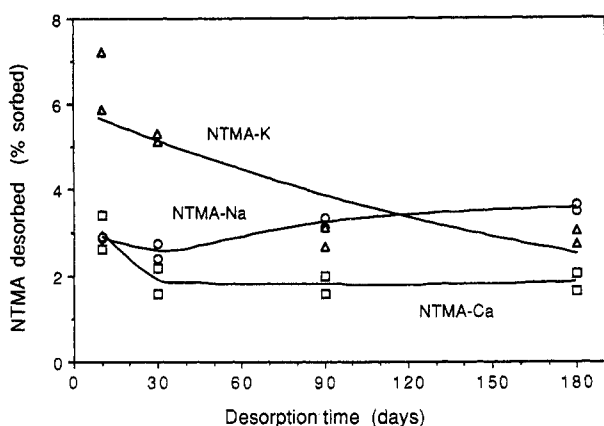
Figure 3. Long-term desorption of NTMA from montmorillonite in the presence of 0.1 M NaCl and KCl and 0.05 M CaCl$_2$ (added amine constituted 80% of the CEC).
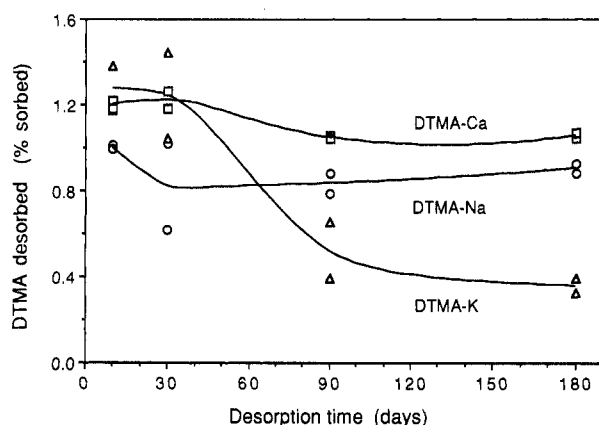
Figure 4. Long-term desorption of DTMA from montmorillonite in the presence of 0.1 M NaCl and KCl and 0.05 M CaCl$_2$ (added amine constituted 80% of the CEC).
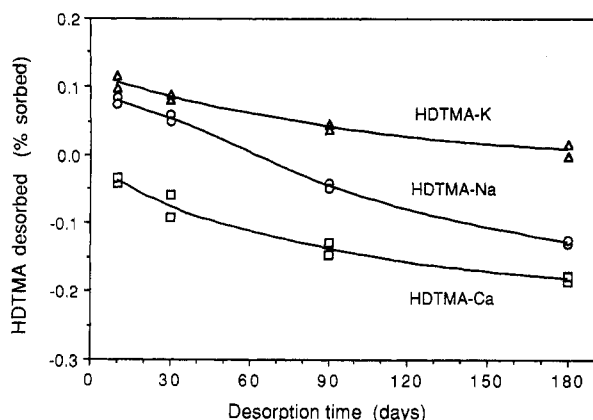
Figure 5. Long-term desorption of HDTMA from montmorillonite in the presence of 0.1 M NaCl and KCl and 0.05 M CaCl$_2$ (added amine constituted 80% of the CEC).

ΔG^m, for the cation-exchange reaction. A linear relationship between ΔG^m and the number of carbon atoms in the alkyl chain of the amines was found from amylamine to decylamine, and the increment of ΔG^m per CH$_2$ group was 1.67 kJ mol^{-1}.

Theng (2) noted that the relationship between free energy change and molecular weight or chain length is of general applicability to the adsorption of organic compounds on montmorillonite, due to the increased contribution of van der Waals forces to the adsorption energy. Theng et al. (24) extended Cowan and White's (23) study

to the secondary, tertiary, and quaternary amine cations (with an alkyl chain length from one to four carbons) in an attempt to clarify the effect of cation size and shape on relative adsorption affinity. They used the method of Gaines and Thomas (26) to determine the integrated selectivity coefficients for the exchange reactions involving amine cations. Theng et al. (24) recognized that the extent of reversibility was unknown, and in addition, hysteresis was likely to occur. They also noted that the Gaines and Thomas method (26) implicitly assumed a reversible exchange reaction. Consequently, they referred to the integrated selectivity coefficient as an affinity coefficient, K_a, rather than an equilibrium constant. Theng et al. (24) showed that the natural logarithm of K_a was linearly related to the molecular weight of the amines, with the exception of the small methylamine and the large quaternary amine cations. Vansant and Uytterhoeven (25) also studied the sorption of several relatively small primary amines (with one to four carbons) on Na-montmorillonite and reported that the affinity of the organic cations for clays increased with chain length. Contrary to the other investigators, however, they concluded that the variations in hydration properties and the Coulombic interactions between the cations and the clay surfaces were more important than the van der Waals forces.

It is important both theoretically and practically to establish if the exchange reaction between metal ions and large quaternary amine cations with long alkyl chains is reversible. If the exchange reaction is completely reversible, a rigorous thermodynamic analysis can be carried out. However, a completely reversible exchange reaction could preclude the use of organo-clays in a number of important environmental applications. The degree of reversibility of the exchange reaction is best characterized by the values of K_m for the forward (adsorption of quaternary amine cations) and backward (desorption of quaternary amine cations) reactions. For this reason, the values of K_m were determined using eq 2 for both the forward and backward reactions. The data are reported in Tables V and VI for the exchange reactions between quaternary amine cations and Na$^+$ ions and K$^+$ ions, respectively. Strictly speaking, the [N_{amine^+}] term in eq 2 represents the sorbed quaternary amine cations solely due to a cation-exchange reaction. Experimentally, however, the measured sorption of quaternary amine cations was the combined effects of cation exchange as well as adsorption at the nonexchangeable sites. Therefore, the reported values of K_m would be larger than the true values for the exchange reaction unless the cation exchange is the dominate reaction mechanism.

It can be seen from Tables V and VI that values of K_m for the desorption of quaternary amine cations were generally 1 order of magnitude higher than the corresponding values for the adsorption reaction. This clearly indicated that the exchange reactions involving large quaternary amine cations, namely, NTMA, DTMA, and HDTMA, were essentially irreversible in the presence of 0.1 M NaCl and KCl. The values of K_m also increased with the length of the alkyl chain of the amines, demonstrating the increasing contributions of the chain–chain interaction and chain–surface interaction and van der Waals forces to the free energy changes for the sorption of quaternary amine cations. Furthermore, one sees that for the sorption reactions involving NTMA and DTMA, K_m decreased with increasing amounts of amines, and the values of K_m for

Table V. Values of K_m for Adsorption and Deposition of Quaternary Amine Cations on Na-Montmorillonite

added amine (% CEC)	adsorption			desorption		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
60	1.06×10^3	1.42×10^3	738			4.24×10^3
70	538	1.39×10^3	543	3.35×10^3	4.89×10^3	5.98×10^3
80	271	818	1.13×10^3	1.81×10^3	3.36×10^3	10.8×10^3
85	139	896	813	2.04×10^3	3.70×10^3	11.9×10^3
90	82.3	456	1.02×10^3	1.28×10^3	3.42×10^3	14.3×10^3
95	82.9	191	1.02×10^3	1.26×10^3	1.70×10^3	9.93×10^3
100	39.8	132	844			9.63×10^3
150	15.5	40.0	1.09×10^3			10.6×10^3
200	11.5	36.1	1.08×10^3			7.25×10^3
300	19.6	37.0	207			518

Table VI. Values of K_m for Adsorption and Deposition of Quaternary Amine Cations on K-Montmorillonite

added amine (% CEC)	adsorption			desorption		
	NTMA	DTMA	HDTMA	NTMA	DTMA	HDTMA
50	361	423		1.61×10^3	1.69×10^3	
60	111	137	726	481	1.25×10^3	10.5×10^3
70	37.0	40.0	889	335	587	12.9×10^3
80	16.1	16.9	1.11×10^3	235	340	15.3×10^3
85	10.9	13.3		166	292	
90	9.00	12.4	667	144	292	14.3×10^3
95	7.65	9.25		140	237	
100	6.19	7.10	362	108	198	9.46×10^3
150	2.72	2.28	108	71.5	112	3.06×10^3
200	1.95	1.75	24.6	63.1	106	340
250	1.53	1.15		56.7	89.7	
300	1.14	1.04	4.76	47.6	82.8	180

the reactions involving Na^+ ions were larger than the corresponding values of K_m involving K^+ ions. This observation clearly showed the heterogeneity of the clay surfaces, i.e., not all of the cation-exchange sites have the same affinity for the quaternary amine cations, and the latter tend to occupy the most energetic sites first. For the sorption reactions involving HDTMA cations however, the heterogeneity of the clay surface sites was overcome by the increasing contributions of the chain–chain interaction and chain-surface interaction and van der Waals forces. Consequently, the values of K_m did not decrease with increasing amounts of HDTMA.

Summary

In summary, we have shown that all three of the quaternary amines studied were almost completely sorbed on Wyoming montmorillonite when the added amines were less than 70% of the CEC. Sorption of quaternary amines involves at least two types of reactions. When the amounts of amine cations present were less than 100% of the CEC of the clays, the exchange reaction predominated. The exchange reaction proceeded almost to completion when Na^+ was the exchangeable cation. Exchangeable K^+ was much more difficult to replace. The degree of sorption at nonexchangeable sites increased with sorption on the exchangeable sites and with the alkyl chain length of the amines. The adsorbed quaternary amines were not easily desorbed when excess amounts of NaCl and KCl were present. The degree of desorption, however, increased with amine sorption but decreased with the alkyl chain length of the amines.

The selectivity coefficients for the desorption reaction were about 1 order of magnitude higher than those for the adsorption reaction, indicating that the exchange reactions were essentially irreversible. In addition, the desorption

of quaternary amines did not increase with prolonged equilibrium time.

Therefore, it appears that there is good promise in using organo-clays as effective sorbents for removing organic pollutants from water or mitigating their mobilities in the environment. However, the amount of quaternary amine used to modify the clay should not exceed 70–80% of the CEC so as to maintain a low amine concentration in the solution. In addition, studies on the environmental safety of the organic cations themselves and the long-term stability of organo-clays under field conditions should be thoroughly investigated before they can be used in large-scale field applications.

Literature Cited

(1) Lloyd, J. U. *J. Am. Pharm. Assoc.* **1916**, *5*, 381–390, 490–495.
(2) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*; Adam Hilger: London, 1967.
(3) Smith, C. R. *J. Am. Chem. Soc.* **1934**, *56*, 1561–1563.
(4) Gieseking, J. E. *Soil Sci.* **1939**, *47*, 1–13.
(5) Hendricks, S. B. *J. Phys. Chem.* **1941**, *45*, 65–81.
(6) Grim, R. E.; Allaway, W. H.; Cuthbert, F. L. *J. Am. Chem. Soc.* **1947**, *30*, 137–142.
(7) Mortland, M. M. *CMS News* **1990**, *June*, 22–23.
(8) Alther, G. R.; Evans, J. C.; Pancoski, S. E. *Proceedings of the 9th National Conference Superfund; Hazardous Ma-*

terials Control Research Institute: Silver Springs, MD, 1988; pp 440–450.

(9) Cadena, F.; Garcia, R. *Environ. Prog.* **1990**, *9*, 245–253.

(10) Boyd, S. A.; Lee, J. F.; Mortland, M. M. *Nature* **1988**, *333*, 345–347.

(11) Lee, J. F.; Mortland, M. M.; Chiou, C. T.; Boyd, S. A. *Environ. Sci. Technol.* **1989**, *23*, 1365–1372.

(12) Lee, J. F.; Mortland, M. M.; Kile, D. E.; Chiou, C. T.; Boyd, S. A. *Clays Clay Miner.* **1990**, *38*, 113–120.

(13) Smith, J. A.; Jaffe, P. R.; Chiou, C. T. *Environ. Sci. Technol.* **1990**, *24*, 1167–1172.

(14) Smith, J. A.; Jaffe, P. R. *Environ. Sci. Technol.* **1991**, *25*, 2054–2058.

(15) Jaynes, W. F.; Boyd, S. A. *Soil Sci. Soc. Am. J.* **1991**, *55*, 43–48.

(16) Zhang, Z. Z.; Sparks, D. L.; Pease, R. A. *Soil Sci. Soc. Am. J.* **1990**, *54*, 351–356.

(17) Furlong, T. E.; Elliker, P. R. *J. Dairy Sci.* **1953**, *36*, 225–234.

(18) Swartzen-Allen, S. L.; Maijevic, E. *Chem. Rev.* **1974**, *74*, 385–400.

(19) Xu, S.; Boyd, S. A. *Agron. Abstr.* **1992**, 247.

(20) Dentel, S. K., University of Delaware, personal communication, 1992.

(21) Goulding, K. W. T. *Adv. Agron.* **1983**, *36*, 215–263.

(22) Sparks, D. L. *Adv. Soil Sci.* **1987**, *6*, 1–63.

(23) Cowan, C. T.; White, D. *Trans. Faraday Soc.* **1958**, *54*, 691–697.

(24) Theng, B. K. G.; Greenland, D. J.; Quirk, J. P. *Clay Miner.* **1967**, *7*, 1–17.

(25) Vansant, E. F.; Uytterhoeven, J. B. *Clays Clay Miner.* **1972**, *20*, 47–54.

(26) Gaines, G. L.; Thomas, H. C. *J. Chem. Phys.* **1953**, *21*, 714–718.