NOTES

THE LAYERED SODIUM SILICATE MAGADIITE: AN ANALOG TO SMECTITE FOR BENZENE SORPTION FROM WATER

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INTRODUCTION

Smectites have long been recognized as useful adsorbents for environmental pollutants due to their ability to exchange interlayer cations for charged organic or metal cations in solution. In natural smectite, the negative charge within the interlayer is partially compensated by alkali and alkaline earth cations, particularly K, Ca and Na. In the presence of water, these cations become strongly hydrated and create a highly hydrophilic environment. Such an environment allows the adsorption of charged organic cations through ion exchange. Because non-ionic organic compounds (NOCs), such as benzene, cannot compete with the highly polar water molecules, they are not effectively adsorbed. A number of investigators have remedied this problem by intercalating large organic cations within the interlayer sites of smectite (reviewed by Sheng et al. 1996). These organic cations typically include a charged terminal group (such as $-NH_3$) attached to a long, nonpolar hydrocarbon chain. Through the substitution of large organic cations into the smectite interlayer, the formerly hydrophilic interlayer site is made increasingly hydrophobic as the hydrated metal cations are replaced with organic cations. As a result, the interlayer sites are more effective sorbents for NOCs.

Like smectite, the layered Na-silicate magadiite ($Na_2Si_{14}O_{29}\cdot 9H_2O$) is easily intercalated with large organic cations, such as hexadecyltrimethylammonium (HDTMA) or hexadecylpyridinium (HPD) (Lagaly et al. 1975a). Magadiite was first identified by Eugster (1967) in Lake Magadi, Kenya, but it has since been found in Alkali Lake, Oregon (Rooney et al. 1969), and Trinity County, California (McAtee et al. 1968). Although the structure of magadiite is not known, studies of the basal spacing of magadiite in air and vacuo (Brindley 1969) and after intercalation with various organic cations (Lagaly et al. 1975a, 1975b) strongly suggest that magadiite consists of layered silicate sheets that are loosely bonded by hydrated sodium cations.

The high propensity for cation exchange of magadiite suggests that it may serve as an analog to smectites for the sorption of NOCs. One possible advantage of magadiite-like sorbents is their ease of synthesis. Whereas the formation of smectite in the laboratory at low temperatures (≤ 150 °C) requires complex procedures and often results in poorly crystalline material (Guven 1988), magadiite readily precipitates from Na- and silica-rich solutions at temperatures from 100 to 175 °C (Beneke and Lagaly 1983; Fletcher and Bibby 1987; Muraishi 1989; Yates and Heaney 1995). In light of these observations, the present study was initiated to compare the sorption behavior of magadiite with that of bentonite in aqueous solutions containing a range of benzene concentrations.

EXPERIMENTAL

Sample Preparation

The natural magadiite used for this study was collected by R. Sheppard (USGS-Denver) from a locality near Trinity River, Trinity County, California, as 2–5 cm³ aggregates. Transmission electron microscopy (TEM) observations made with Philips CM20 transmission electron microscope reveal that the magadiite consists of nearly square, plate-like crystals with a range in particle size from 0.1 to 5.0 μm. The presence of minor amounts of rhodesite was identified by TEM; however, this impurity should have a negligible effect on the sorption experiments. Although no chemical pretreatment or size fractionation of the magadiite was warranted, the magadiite was ground dry with a mortar

881

Mineral	CEC (meq/100 g)	Source
Trinity Co. magadiite	159.1†	Present study
Trinity Co. magadiite	152.4‡	Present study
Wyoming bentonite	78.5	Smith et al. (1990)
Vermiculite	120–200	Drever (1982)
Smectite	80–150	Drever (1982)
Illite	10–40	Drever (1982)

† Measured with Na acetate.
‡ Measured with Sr acetate.

and pestle in order to break down aggregates of the raw material to a fine powder. Analyses of the magadiite by powder X-ray diffraction (XRD) yielded no evidence of structural damage as a result of sample preparation. Wyoming bentonite was obtained from the American Colloid Company as a powder that required no pretreatment. Identical material from the same batch was characterized by Smith et al. (1990), who found it to consist of 3.6% sand, 7.3% silt and 89.1% clay size fractions with a cation exchange capacity (CEC) of 78.5 meq/100 g.

CEC and Intercalation

We determined the CEC of magadiite using the ammonium acetate method of Mackenzie (1951) with both an initial Na and Sr saturation in order to identify unexchangeable Na in the magadiite interlayer. For the intercalation of the bentonite and magadiite samples, we used the procedure of Smith et al. (1990). The CEC value for each sample (see Table 1) was used to ensure 100% cation exchange of the HDTMA or HPD cations in the magadiite or bentonite interlayer sites. The effect of intercalation on the basal-layer spacing of magadiite and bentonite was measured by XRD on a Scintag PAD-V powder X-ray diffractometer using CuKα radiation. Oriented sample mounts for XRD analyses were made using the vacuum filter technique of Moore and Reynolds (1989). The analyses were conducted from 2 to 55 °2θ at a scan rate of 1 °2θ/min.

Isotherm Generation

Adsorption isotherms were developed for the organo-magadiite and organo-bentonite samples by the batch equilibration technique (Lee et al. 1990) for aqueous solutions ranging in benzene concentration from 0.5 to 1.5 mg/mL. For each benzene concentration, a set of replicate experiments were conducted by combining 0.5 g of organo-magadiite or organo-bentonite with 57 mL of benzene solution in 50-mL glass centrifuge tubes. A blank experiment with no added solids enabled us to assess the percentage of benzene loss due to evaporation and adsorption onto the tube wall. The tubes were shaken by a Burrell 75 Wrist-Action shaker for 24 h to achieve a steady-state equi-

librium prior to separating solution from solids by centrifugation. The concentration of benzene remaining in the supernatant after the experiment was determined by gas chromatography with a Perkin-Elmer Sigma 2000 Gas Chromatagraph. Adsorption isotherms were developed relating the equilibrium concentration of benzene remaining in solution to the amount of benzene sorbed in the samples.

RESULTS

CEC of Magadiite

Table 1 compares the CEC values measured for magadiite and bentonite with CEC values for other common clay minerals. The CEC of magadiite, ~156 meq/100 g, falls within the upper range of CEC values for clays and is more than twice that for the bentonite used in this study. The high CEC of magadiite is consistent with the findings of Eugster (1967), who reported that magadiite readily converts to a hydrous phase of silica, H-magadiite, upon treatment with dilute acid. When mixed with concentrated NaOH or Na_2CO_3, H-magadiite reversibly transforms to magadiite (Eugster 1967). The similarity in CEC values measured with Na versus Sr strongly supports the high exchangeability of the interlayer cations in magadiite. If some of the Na in magadiite were fixed (that is, not exchangeable) within the interlayer site, the CEC values determined with initial Sr saturation would have been lower than those determined with initial Na saturation. The similarity in CEC values measured with these 2 techniques demonstrates that all of the Na in the magadiite is exchangeable.

The cation exchange capacities of the dioctahedral sheet silicates, smectite and illite, are governed largely by layer charge. Smectite possesses a charge of ~0.2–0.6 eq/interlayer site (Bailey 1980), whereas illite has a higher layer charge of 0.89 eq/interlayer site (Środoń et al. 1992). Thus, the interlayer cations in illite are fixed due to the higher layer charge, resulting in a lower CEC (Table 1). In contrast to these minerals, magadiite possesses a high CEC despite its relatively high layer charge of −1 eq/interlayer site. These differences in CEC values likely result from the hydration state of the interlayer cations in these respective minerals. As smectite transforms to illite, water molecules that surround the interlayer cations are lost and K cations are fixed within their ditrigonal cavities. By contrast, if the interlayer of magadiite is similar to that of a related Na-silicate called makatite $(Na_2Si_4O_8(OH)_2 \cdot 4H_2O)$ (Annehed et al. 1982), then the Na cations within magadiite are always hydrated and easily exchanged. Therefore, magadiite displays an unusually high CEC because its high interlayer charge is satisfied by a high concentration of hydrated Na cations.

Table 2. Basal spacings of untreated and intercalated samples.

| Sample	Basal Spacing (Å)
Magadiite	15.71
HDTMA-magadiite	29.75
HPD-magadiite	37.02
Bentonite	14.23
HDTMA-bentonite	17.44
HPD-bentonite	16.61

Figure 1. Comparison of the relative adsorption of benzene in untreated magadiite, HDTMA-treated magadiite and HPD-treated magadiite in 1.0 mg/mL aqueous benzene solutions.

Intercalation

Intercalation of magadiite with HDTMA and HPD cations resulted in an increase in basal spacing from 15.71 Å in the untreated magadiite to 29.75 Å in HDTMA-magadiite and 37.02 Å in HPD-magadiite (Table 2). Lagaly et al. (1975a) reported basal spacings of 29.2 Å for HDTMA-magadiite and 36.2 Å for magadiite intercalated with tetradecylpyridinium (TDP) cations (which has 2 fewer CH_2 groups than HPD). Although the HPD and HDTMA cations have similar lengths, n-alkylpyridinium cations (such as HPD, TDP) produce larger basal spacings due to their arrangement in the interlayer. Lagaly et al. (1975a) found that n-alkylpyridinium cations occur as a bilayer in the magadiite interlayer with the chains oriented at a 35° angle to the silicate sheet, whereas alkylammonium cations (such as HDTMA) are arranged in a monolayer oriented perpendicular to the sheet. Although these cations produced distinctly different basal spacings in air-dried magadiite, Lagaly et al. (1975a) reported that TDP- and HDTMA-magadiite display basal spacings of 39.0 Å and 37.2 Å, respectively, while under the mother liquid. These results suggest that, in the present study, the basal spacings of the 2 organo-magadiites were similar under the aqueous conditions of the experiments.

Benzene Sorption

Benzene sorption experiments were conducted with untreated magadiite, as well as the prepared HDTMA- and HPD-magadiites. As with organo-smectites (Mortland et al. 1986), the intercalation of organic cations in magadiite induced a significant increase in the sorption of benzene from aqueous solution (Figure 1). The increased sorption in organo-magadiite is likely due to the more hydrophobic character of the interlayer in the treated magadiite. Moreover, HPD-magadiite more readily attracts benzene than does HDTMA-magadiite. The greater sorption in HPD-magadiite may reflect the degree to which organic cations replace hydrated Na cations in the magadiite interlayer. Lagaly et al. (1975a) found that TPD cations (similar to HPD) replace all of the Na cations in the magadiite interlayer, whereas HDTMA cations replace only 59% of the Na cations. The remaining Na in the magadiite interlayer
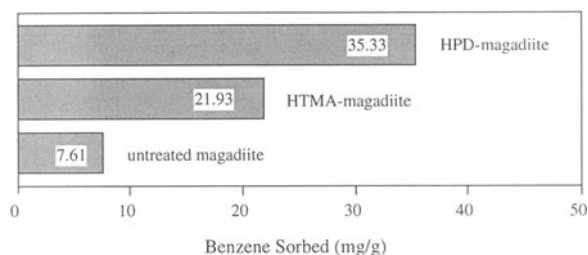
probably is strongly hydrated, inhibiting the sorption of nonpolar benzene molecules.

The dependence of the sorption of benzene in organo-magadiite and organo-bentonite on benzene concentration is shown in Figure 2. Each isotherm includes a theoretical "zero point", representing zero sorption of benzene in pure water. In decreasing order of sorptive capacity, the samples ranked as follows: HPD-bentonite, HDTMA-bentonite, HPD-magadiite and HDTMA-magadiite. This result reflects the increased sorption of benzene in HPD- versus HDTMA-treated samples demonstrated in Figure 1; however, it also is clear that the treated bentonite samples exhibited a higher sorptive capacity than did the treated magadiites.

DISCUSSION

Due to the higher CEC and layer charge of magadiite relative to bentonite, the intercalation treatment produced significantly larger basal spacings in magadiite than in bentonite (Table 2). Because increased expansion of the basal layers results in an increase in the surface area available for sorption, it was expected that organo-magadiite would exhibit greater sorption of benzene than organo-bentonite. In the benzene sorption study, however, organo-bentonite proved to have a greater affinity for benzene over a broad range of concentrations. This apparent contradiction may be explained in terms of the sorption mechanisms of these respective minerals. In an investigation of benzene sorption on HDTMA-treated smectites, Sheng et al. (1996) observed adsorption isotherms with a double-sigmoid shape, which they attributed to dual sorption mechanisms. As was the case for previous studies of HDTMA-smectites (Boyd et al. 1988; Smith et al. 1990), Sheng et al. (1996) concluded that benzene is partitioned in the intercalate cations by solvation. Unlike previous studies, however, Sheng et al. further proposed that some of the benzene uptake by HDTMA-smectite is due to adsorption directly on the mineral surface. In this mechanism, the solvation of the intercalates by benzene results in a change in their orientation from a parallel to a more vertical position relative to the mineral surface. This change in orien-
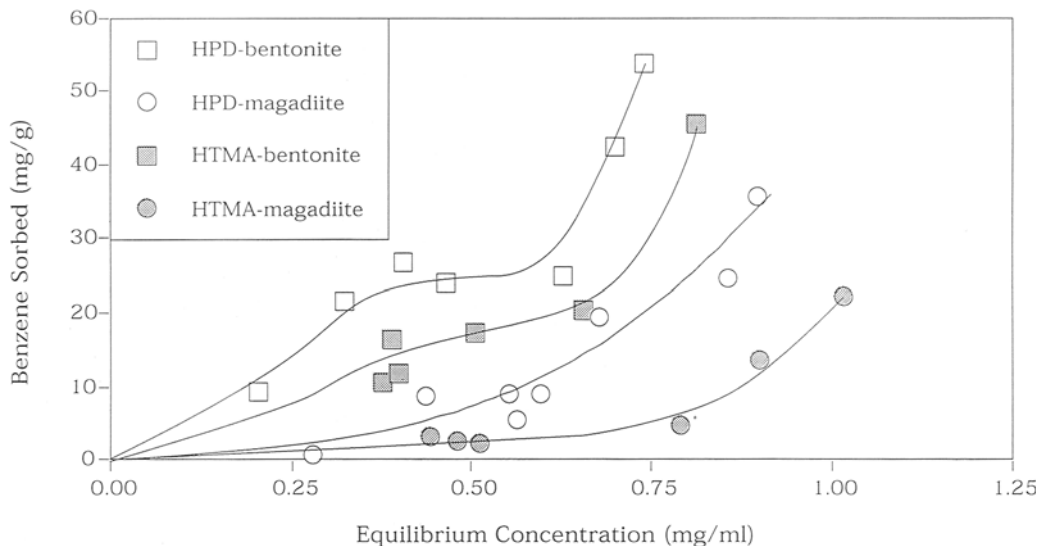
Figure 2. Adsorption of benzene from aqueous solution by HDTMA- and HPD-treated magadiite and bentonite.

tation allows for the adsorption of benzene molecules on the mineral surface in sites previously occupied by the intercalate cations.

In the present study, the double-sigmoid shape of the adsorption isotherms exhibited by the organo-bentonites is suggestive of the dual sorption mechanisms described by Sheng et al. (1996). Thus, the relatively high uptake of benzene exhibited by the organo-bentonites may be due to a combination of the partitioning of benzene in the organic intercalates and the adsorption of benzene on the mineral surface. The adsorption isotherms exhibited by the organo-magadiites are of type III (Gregg and Sing 1982). Isotherms of this type are consistent with a gradual increase in the solvency of the intercalates due to the partitioning of benzene in the organic phase (Sheng et al. 1996). The adsorption isotherms exhibited by the organo-magadiites do not, however, yield evidence of an adsorption mechanism on the mineral surface for benzene uptake. Although the intercalate cations in organo-magadiite are believed to have a nonparallel orientation (Lagaly et al. 1975a), the higher layer charge of magadiite would accommodate a tighter packing of intercalate cations, resulting in fewer sites on the mineral surface for adsorption of benzene. This model is in accord with explanations proposed for the decreased adsorption of NOCs in high- versus low-charged tetramethylammonium-treated smectites (Lee et al. 1990). The lack of an adsorption mechanism for benzene on organo-magadiite may simply result from steric hindrance to benzene adsorption at sites located directly on the mineral surface. Therefore, despite the greater CEC and *d*-spacing of the organo-magadiites, the absence of the adsorption mechanism for benzene uptake may ac-

count for its lower affinity for benzene relative to organo-bentonite.

Although magadiite appears to be less effective for the retention of benzene than the traditional toxic waste liner, bentonite, it should be noted that magadiite belongs to a broad class of layer silicates that include such minerals as kenyaite (Eugster 1967), silhydrite (Gude and Sheppard 1972), makatite (Sheppard and Gude 1970) and many others known only as synthetic products (reviewed by Frondel 1979). The ease with which these compounds are synthesized, compositionally altered (Eugster 1967; Lagaly et al 1975b) and intercalated with various organic cations (Lagaly et al. 1975a, 1975b) warrants further research into the role that these interesting minerals may play in the remediation of aqueous contaminants in nature.

ACKNOWLEDGMENTS

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