



The swelling of HDTMA smectites as influenced by their preparation and layer charges

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Abstract

Both aqueous and ethanolic solutions of hexadecyltrimethylammonium (HDTMA) bromide have been reacted with layer silicates of different charge. Layer spacings of the resulting intercalates vary with charge and are consistent with the intercalated HDTMA forming: monolayers of flat-lying molecules when layer charges, on a per unit cell basis, are $<0.5 e^-$; bilayers of flat-lying molecules for charges between 0.5 and $1.0 e^-$ and tilted paraffin-like arrangements for charges greater than $1.0 e^-$. Intercalation reactions carried out using aqueous solutions allow salt molecules to be coadsorbed with HDTMA cations. Coadsorption of salt molecules appears not to occur when intercalation reactions are carried out with ethanol. Leaching with ethanol removes salt molecules from intercalates produced in an aqueous medium. For smectites with charges $>0.5 e^-$, and for vermiculites, the intercalation of salt molecules from an aqueous medium leads to greater layer spacings than for intercalates formed in ethanol or leached with ethanol.

Toluene sorption isotherms show that toluene uptake from water by an intercalate is increased when it is formed from a highly charged smectite. Toluene uptake from water also increases when the intercalate contains HDTMA salt molecules. Layer spacings show that HDTMA intercalated layer silicates swell in the presence of neat toluene, and thus sorption from solution is also accompanied by interlayer expansion. Reactive barriers to contain BTEX pollutants ideally should be produced using a clay of the highest charge available, and should have been reacted with aqueous HDTMA. Washing is not necessary.

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1. Introduction

The intercalation of the cationic surfactant hexadecyltrimethylammonium (HDTMA) into swelling layer silicates has been studied in the context of the potential use of intercalated clays as sorbents for aromatic

hydrocarbons in environmental technology (Jaynes and Boyd, 1991; Bonczek et al., 2002). These previous studies have shown that the HDTMA enters clay interlayers both as cations, which replace inorganic ones, and also as coadsorbed salt molecules bound to the organic cations by van der Waals forces operating between the alkyl chains (Xu and Boyd, 1995a,b; Lee and Kim, 2002).

As shown for example by the work of Lagaly and Weiss (1969), who considered layer silicates with charges between 0.5 and $2.0 e^-$ per unit cell, interlayer

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organic species develop conformations with respect to the silicate layer planes according to the layer charge density. In clays with low charge densities ($<0.5 e^-$ per unit cell), the aliphatic chains of HDTMA are parallel to the layer planes and form monolayers up to charge densities commensurate with the area covered by the organic cation. Above $0.5 e^-$ per cell, bilayer configurations begin to form with the aliphatic chains remaining parallel to the layer planes. At still higher charge densities ($>1.0 e^-$ per cell), pseudotrimolecular or paraffin-like structures have been postulated (Lagaly and Weiss, 1969). The first three configurations have been associated with distinctive interlayer spacings of 13.6, 17.6 and 21.6 Å, respectively. Interlayer spacings given by the paraffin-like interlayer arrangements depend upon the packing density of HDTMA, which in turn influences the angle of rise of the aliphatic chains. Different spacings, including that usually associated with the pseudotrimolecular structure, can thus occur for paraffin-like arrangements. At transitional charge densities, interstratifications of the various structural configurations can occur (Xu and Boyd, 1995a; Bonczek et al., 2002).

The incorporation of salt molecules of the cationic detergent cetylpyridinium bromide by several cetylpyridinium exchanged vermiculites, with layer spacings of ≈ 30 Å, was shown by Slade et al. (1978) to result in an increase in layer spacings to ≈ 40 Å. X-ray single crystal diffraction photographs showed that ordered interlayer structures were present in both the 30 and 40 Å phases. Lee and Kim (2002) have reported that the incorporation of excess HDTMA molecules into a montmorillonite also resulted in an increase in its layer spacing, from ≈ 20 to ≈ 36 Å.

The interlayer structures of HDTMA clays can be expected to influence their effectiveness as environmental sorbents such as could be used to prevent or reduce the contamination of soils by the common constituents of petroleum products, such as benzene, toluene, ethylbenzene and xylene (BTEX hydrocarbons). For example, the removal of coadsorbed organo-salt molecules from HDTMA intercalated clays might increase their internal porosity leading to greater hydrocarbon uptake or, because of their lower carbon content, their reduced organophilicity may reduce the uptake.

The present paper reports on *d*-spacing measurements used to explore the effect of salt molecules and

toluene sorption by HDTMA intercalated smectites and vermiculites produced by reactions in water or in ethanol. Additionally, the sorption isotherms for toluene by a low- and a high-charged HDTMA intercalated smectite, both with and without coadsorbed salt molecules, are reported.

2. Materials and methods

Diocahedral and trioctahedral smectites, listed in Table 1, were converted to their Na-exchanged state by the usual methods of purification, exchange and dialysis (e.g. Gates et al., 2002). A portion of each purified smectite was Ca-saturated for analysis by X-ray fluorescence spectroscopy using the methods of Norrish and Hutton (1969). Structural formulae, on an ignited basis, were calculated from the percentage oxides using the program CLAYFORM (Bodine, 1987). The cationic charges per unit cell (22 oxygen equivalents) and the ratios of tetrahedral to total charges were calculated and are given in Table 1.

Preparation of HDTMA clays from the Na-exchanged materials was carried out by three different methods. Method 1 involved reacting with an excess of aqueous 0.01 M HDTMA–Br solution followed by washing with water until halide (Br) was not detectable with $AgNO_3$. Method 2 followed method 1 except that an ethanolic 0.01 M HDTMA–Br solution was used and washing was carried out with ethanol, again, until the washings were halide-free. Method 3 involved washing preparations from method 1 with ethanol; initially, the wash liquid contained halide, but with continued washing, halide became undetectable as excess HDTMA–Br was removed. Smectite samples were shaken at room temperature with the HDTMA solutions until the X-ray powder diffraction patterns of the products showed a rational series of 00/ reflections. Reaction times were about 4 days and solutions were replaced daily. In order to extend the layer charge range to low values, a series of reduced-charge montmorillonites (RCM) was used in this study (Madejová et al., 1996). These materials have some of their layer charge partially neutralized by the Hoffmann–Kleeman effect. In order to provide additional samples in the high layer charge range, two vermiculites, which had been analyzed by Norrish (1972), were Na-saturated and included in the suite of

Table 1

Relationship between cation exchange capacity, location of layer charge (X) and layer spacing ($d(001)$) of HDTMA layered silicates prepared in aqueous (method 1), ethanol (method 2), or water and ethanol (method 3) solvents

Sample	Lable	Smectite type ^a	Source ^b	CEC ^c	Tetra X / total X	$d(001)$ (Å)			
						H ₂ O prep	EtOH prep	H ₂ O prep, EtOH wash	Toluene solv ^d
JP210	R1	RCM	1	0.14	0.43	13.6	13.6		
JP160	R2	RCM	1	0.30	0.23	13.7	13.6		
JP135	R3	RCM	1	0.56	0.16	15.4	13.8		14.0 ²
JP130	R4	RCM	1	0.64	0.11			14.0	43.6 ¹
Binjour Plateau	S1	Sap	2	0.66	1.89			18.8	
SHCa-1	H1	Hect	3	0.68	0.00	18.0	15.6		33.4 ²
NAu-2	N1	Nont	3	0.72	0.63	18.5	17.1		37.5 ²
Sap E	S2	Sap	2	0.72	1.03	18.3	17.6		
JP120	R5	RCM	1	0.74	0.12	19.5	17.6		39.4 ²
JC Lane	M1	Mont	2	0.74	0.11			17.6	
SWy-1	M2	Mont	2	0.76	0.32	20.1	17.6		42.0 ¹ , 46.6 ²
SapCa-2	S3	Sap	2	0.78	0.95			19.7	
San Remo	S4	Sap	2	0.81	1.44			18.1	
Swansea	B1	Beid	2	0.82	0.63			18.3	
JP110	R6	RCM	1	0.86	0.09			17.6	
SBCa-1	B2	Beid	3	0.88	0.98	22.0	19.6		43.6 ²
JP105	R7	RCM	1	0.92	0.07			17.6	
Giralong	N2	Nont	2	0.92	0.74			18.9	
Burro Creek	S5	Sap	2	0.92	0.63			18.5	
NG-1	N3	Nont	2	0.96	0.92			20.5	
Jelšovy Potok	M3	Mont	1	0.98	0.05			17.6	
SAz-1	M4	Mont	3	1.00	0.05	27.3	17.6		42.7 ²
Mount Binjour 4a	B3	Beid	2	1.04	0.50	31.7	21.9		45.5 ²
Otay	M5	Mont	2	1.06	0.02	30.0		17.9	46.9 ¹
Drayton	B4	Beid	2	1.08	0.94	37.1	21.8		44.6 ²
Nyasaland	V1	Verm	2	1.24	2.46	29.3		26.3	44.6 ³
Taconite Harbor	S6	Sap	2	1.28	0.86	37.1	23.3		42.0 ²
Llano Stop 10	V2	Verm	2	1.50	1.42	29.6		25.8	44.8 ³

^a RCM= reduced charge montmorillonite; Sap= saponite; Hect= hectorite; Nont= nontronite; Mont= montmorillonite; Beid= beidellite; Verm= vermiculite.

^b Source 1, Madejová et al. (1996); source 2, CSIRO Land and Water Reference Mineral Collection; source 3, Source Clays Repository, The Clay Minerals Society (U.S.A.).

^c CEC is the cation exchange capacity expressed in electrons (e⁻) per O₂₀(OH)₄.

^d Superscript refers to method of preparation for the HDTMA samples: method 1 (water), method 2 (ethanol) and method 3 (water and ethanol wash).

samples reacted with HDTMA. The vermiculites were only reacted with aqueous HDTMA solutions, but at 40 °C under reflux for 2 weeks; the solutions being replaced every few days and finally portions of each sample were washed with water or with ethanol.

The HDTMA smectites were deposited from water or ethanol suspensions onto ceramic plates to produce orientated films for examination by X-ray powder diffraction. A Philips PW1710 powder diffractometer fitted with a 1° divergence slit, a graphite monochromator and a proportional counter was used to obtain

the diffraction patterns with Co K α radiation. For the HDTMA vermiculites, the 00 l reflections were obtained from 'rafts' of flakes, which had been gently pressed onto the plates. A 1/12° divergence slit was used. The swelling of the HDTMA intercalates upon sorption of toluene was measured by placing a pad of toluene-saturated cotton wool beneath the ceramic plates supporting the orientated films within the closed sample compartment of the diffractometer. Diffraction patterns showed that the toluene rapidly wicked into the samples through the ceramic plates.

Toluene absorption isotherms were measured at 21 °C by shaking 50 mg of clay with 10 ml aqueous toluene ($\approx 40\text{--}400\text{ mg l}^{-1}$) in closed glass tubes overnight. The unfilled volume of each tube was 26% of the total tube volume, but tests with a 4% unfilled volume showed that the effect on the sorption results was negligible. After the suspended solids were removed by centrifugation (10 min, 2700 rpm), the equilibrium concentrations of toluene in solution were determined by ultraviolet (UV) absorption at 267.4 nm. Blanks, without intercalates, were also prepared and analysed to correct the isotherms for evaporative losses.

3. Results and discussion

3.1. Layer charge–layer spacing relationships

Fig. 1 shows the layer spacings for the HDTMA smectites and vermiculites as a function of total layer charge. Vertical lines are used in Fig. 1 to emphasize

the differences in the layer spacings for samples prepared in water (method 1) and in ethanol (method 2). Preparations in water resulted in greater layer spacings than for those given by preparations in ethanol. The increases in layer spacings with charge include a step from 13.6 to 17.6 Å, which becomes obvious between 0.65 and 0.75 e^- . This step is associated with interstratifications of monolayer and bilayer arrangements of interlayer organic molecules (Lagaly et al., 1976; Bonczek et al., 2002). Above a layer charge of about 1.0 e^- , the HDTMA smectite samples prepared in ethanol show layer spacings which increased linearly with increasing layer charge. In this high layer charge region, the differences between the layer spacings given by preparations in water and ethanol may be between 10 and 15 Å for smectites, but for water-washed and ethanol-washed HDTMA vermiculites, the differences are only ≈ 3 Å. In comparison to smectites, vermiculites carry a greater proportion of their total layer charge in their tetrahedral sheets, which leads to a greater electrical field strength at the layer surface. For samples B4 and

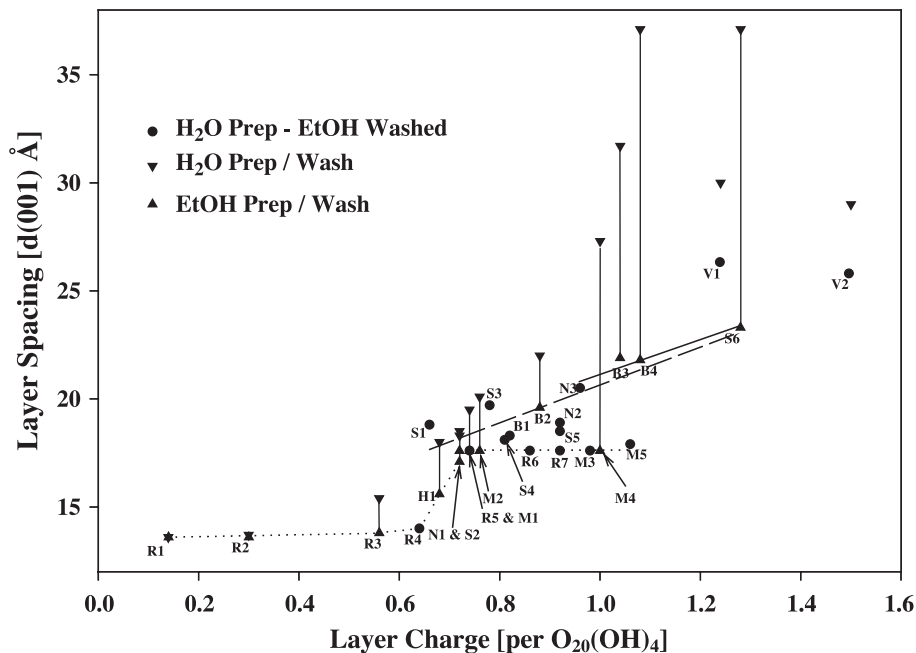


Fig. 1. Measured layer spacings for HDTMA smectites and vermiculites. Labels correspond to samples listed in Table 1. Vertical lines link spacings given by aqueous (method 1) and ethanolic (method 2) preparations. Solid line represents regression of layer spacings for HDTMA smectites with total layer charge $>0.95\ e^-$ per unit cell prepared in ethanol; dashed line represents regression of layer spacings for HDTMA smectites with total layer charge $>0.66\ e^-$ per unit cell, which fall above the monolayer–bilayer trendline (dotted line).

S6, the layer spacings for the water-washed preparations are $\sim 37 \text{ \AA}$, close to values observed by Xu and Boyd (1995a) for SAZ-1 and by Lee and Kim (2002) for a smectite from Korea.

Layer spacings for some samples (Fig. 1, filled circles) prepared in water and washed in ethanol (method 3) are greater than the 17.6 \AA spacing associated with bilayers. These samples all have a high ratio of tetrahedral to total charge (Table 1) and are saponites, beidellites or nontronites. Samples prepared by method 3 which fall on the monolayer–bilayer trend line (Fig. 1, dotted line) are montmorillonites with low tetrahedral to total layer charge ratios, or samples with low total layer charges.

All preparations in ethanol gave layer spacings which could be associated with structures classified as flat-lying monolayer (13.6 \AA), flat-lying bilayer (17.6 \AA), tilted paraffin-like ($>17.6 \text{ \AA}$) or interstratifications of these (Fig. 2). For smectites with the lowest charges ($<0.5 e^-$) produced by layer charge reduction, the layer spacings (13.6 \AA) are the same for products formed either in ethanol or in water. This is consistent with these materials having monolayers of flat-lying HDTMA cations in their interlayers. Apparently, sufficient space is available to incorporate some flat-lying salt molecules. The *effective* van der Waals thickness of HDTMA molecules in clay *interlayers* depends upon the orientation of the planes containing the zigzag chains of aliphatic carbons. With the planes parallel to the silicate surfaces, the effective thickness is 4.0 \AA , and $4.5\text{--}5.0 \text{ \AA}$ when perpendicular (MacEwen, 1948; Brindley and Hoffmann, 1962; Jordan, 1963). With the van der Waals thickness of the silicate layers of 9.6 \AA and the 4 \AA thickness for the parallel orientation of the zigzag planes, layer separations of 13.6 and 17.6 \AA result for flat-lying monolayer and bilayer configurations, respectively.

Above a layer charge of $0.55 e^-$, differences occur between the spacings obtained for materials produced in water or in ethanol. These differences probably result from disordered interlayer arrangements following the coadsorption of salt molecules. For example, cations and salt molecules forming a bilayer configuration interstratified with monolayer and/or paraffin type arrangements may cause some of these differences. Other differences may arise due to a proportion of the HDTMA molecules being oriented with the aliphatic carbon zigzag chains lying perpendicular to

the silicate surfaces so that the *effective* thickness of the molecule becomes 4.5 \AA . This, in combination with the layer thickness of 9.6 \AA , would result in bilayer spacings of $18.6\text{--}19.6 \text{ \AA}$.

Scale models show that a HDTMA cation, with its aliphatic zigzag plane perpendicular, covers an area of $(25.4 \times 3.4) + 2(3.4 \times 1.4) = 95.9 \text{ \AA}^2$, which is close to the 99.7 \AA^2 of Lagaly and Weiss (1969). The area of the base of a smectite unit cell is $5.3 \times 9.15 = 48.5 \text{ \AA}^2$ (Güven, 1988). Hence, in unit cells with a charge up to $0.5 e^-$ per unit cell, only one flat-lying HDTMA cation is necessary to balance the charge. For unit cells with charges between 0.5 and $1.0 e^-$, up to two HDTMA cations are required to balance the charge and hence bilayer structures occur. Bonczek et al. (2002) reported that the monolayer to bilayer transition for HDTMA-SWy-1 montmorillonite occurred when sufficient HDTMA was present to satisfy 70% of the CEC. This is equivalent to a layer charge of $0.53 e^-$, close to the value calculated above.

For smectites with charges greater than $1.0 e^-$ per unit cell, the interlayer organic moieties pack with a paraffin-like arrangement in which the aliphatic chains increase their angles to the silicate surfaces as the layer charge increases. Fig. 1 shows that an approximately straight line relates layer charge to spacing above a charge of $1 e^-$. If this line is projected backwards, it passes close to each of the set of lower charged ethanol-washed samples with high tetrahedral to total charge ratios (Table 1), possibly indicating that the organic molecules in these samples may also have tilted, paraffin-like arrangements. The layer charge, in governing the packing density, influences the angle of rise of the chains.

Vermiculites can have total layer charges equivalent to those of some smectites (e.g. Nyalaland vermiculite and Taconite Harbor saponite, Table 1), but vermiculites always have higher (about 2.1 times for these two samples) tetrahedral charges than smectites. However, most vermiculites have total charges above those of the highest charged smectites (e.g. Llano vermiculite Stop 10). Fig. 1 shows that the layer spacings associated with the water-washed HDTMA vermiculites ($\approx 29 \text{ \AA}$), containing removable salt molecules, are considerably less than those for the highest charged water-washed HDTMA smectites ($\approx 37 \text{ \AA}$). In the latter, the aliphatic chains of the salt molecules, and of the cations, possibly form

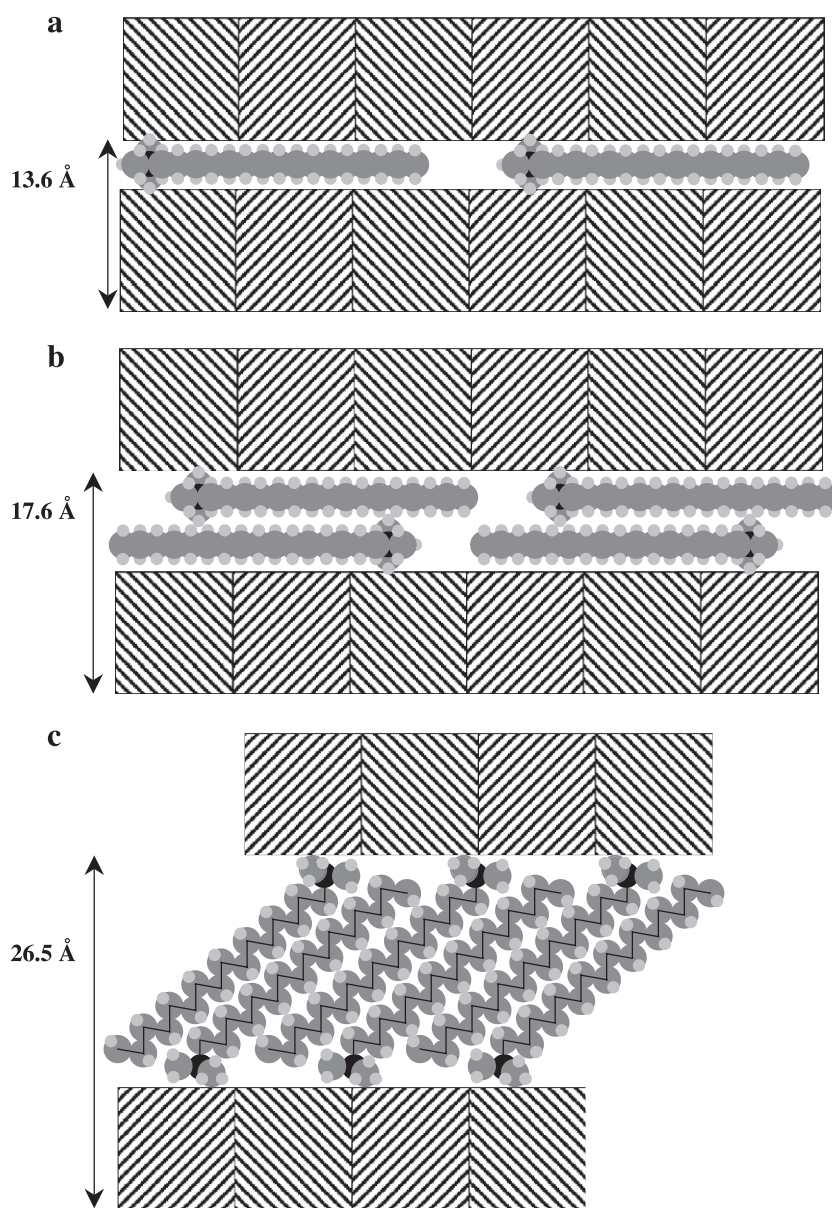


Fig. 2. Scaled representations of (a) monolayer, (b) bilayer and (c) paraffin-like interlayer arrangements for ethanol-washed HDTMA smectites and vermiculites. For scaling purposes, the vertical lines between the diagonally shaded blocks indicate a repeat distance along a unit cell dimension, b , of 9.2 Å.

bilayer paraffin-type structures with the aliphatic chains partially overlapping. These structures could be further supported by water molecules, removable on dehydration (Lee and Kim, 2002). In vermiculites, the attractive forces between the interlayer organic cations and the highly charged silicate surfaces are

greater than in smectites. Consequently, the repulsive forces between the halide ions of the salt molecules and the charged vermiculite surfaces, and between the head groups of the organic moieties, may be insufficient to overcome the attractive forces. Therefore, compared to smectites, a more limited expansion

occurs when salt molecules are incorporated into the paraffin-like structure in HDTMA vermiculites. In addition, the extent of the van der Waals interaction between the aliphatic chains of the organic cations and the salt molecules may also determine the resulting layer spacings. The balance of electrical forces in HDTMA clays which incorporate salt molecules is not well understood, and a contrasting case is provided by cetylpyridium vermiculite (Slade et al., 1978), which expands from ≈ 30 to ≈ 40 Å when salt molecules are incorporated. In both materials, the aliphatic chain lengths are the same, but the head groups differ both in size and electronegativity.

3.2. Toluene sorption

The sorption isotherms for toluene (Fig. 3) by the low-charged HDTMA smectite (SWy-1; M2) show that the aqueous preparation, i.e. material containing salt molecules, sorbs more toluene per given mass of organo-clay than the ethanol preparation. This effect is not as obvious for the high-charged HDTMA smectite (SAz-1; M4). The adsorption coefficients

(K) calculated from the adsorption isotherms for water-washed HDTMA, SWy-1 and SAz-1, are 75 and 223, respectively. For the ethanol-washed samples, the corresponding values are 59 and 210. In addition, the highly charged HDTMA smectite (SAz-1) took up substantially more toluene per unit of complex than the low-charged HDTMA smectite (SWy-1), whether ethanol-washed or not. For SAz-1, the higher layer charge results in a greater HDTMA content than for intercalates produced using SWy-1.

It is evident from Fig. 3 that the uptake of toluene increases when organic salt is present in the intercalate, as is also reflected by the K values being greater for the water-washed material. These results are broadly in agreement with those reported for BTEX molecules by Jaynes and Boyd (1991), Xu and Boyd (1995a,b) and Bonczek et al. (2002). However, the present data for toluene extends the absorption isotherm to higher equilibrium concentrations than those reported by Jaynes and Boyd (1991). At the higher concentrations an upward curvature of the isotherm for SWy-1 (M2) occurs, indicating that sorbed toluene may enhance further sorption. The present work also

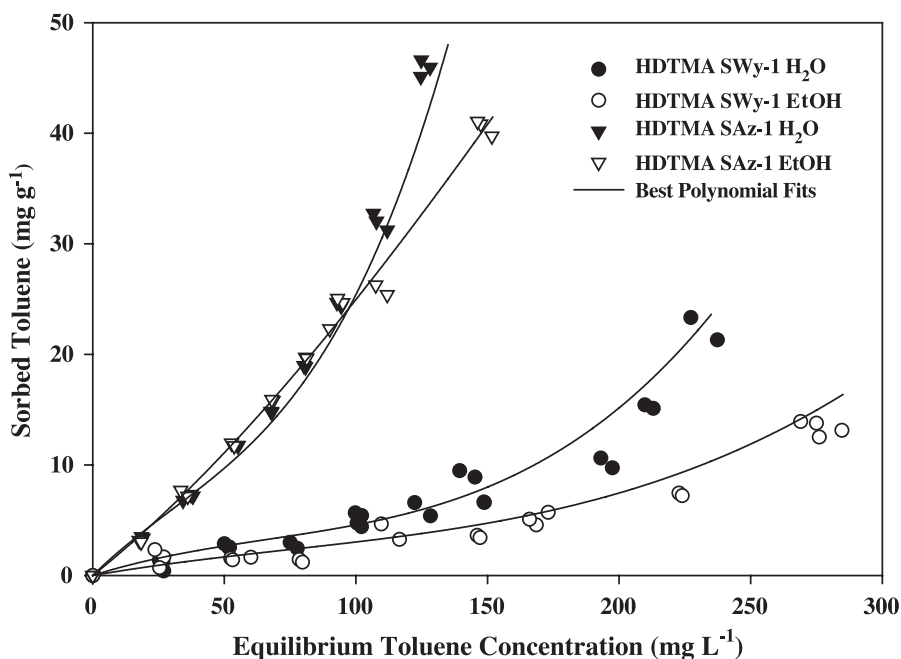


Fig. 3. Toluene sorption isotherms for aqueous (method 1) and ethanolic (method 2) preparations of HDTMA SWy-1 and SAz-1 montmorillonites.

shows that the removal of salt molecules with ethanol reduces the sorptive capacity of the SWy-1 complex, as reflected in the K values obtained. However, while the SAz-1 (M4) intercalates are better sorbers for toluene, the effect of salt in this material is not as obvious as it is for SWy-1 (Fig. 3). Clearly, high-charged clays should be used in combination with long chain alkylammonium complexes, such as HDTMA, to prepare modified clay barriers. Water washing of the product is sufficient and likely to be less expensive than ethanol washing.

3.3. Toluene induced expansion

The present sorption studies have demonstrated, as have those of Jaynes and Boyd (1991), that the uptake of toluene by HDTMA clays depends upon the preferential partitioning of toluene into the alkylammonium phase relative to the aqueous phase. This mechanism requires that space within the interlayers be available to accommodate the sorbed toluene; the extensive swelling of clays saturated with neat toluene (Table 1) shows that such space is indeed created. Note, however, that only the HDTMA smectites with flat-lying bilayers or tilted paraffin-type interlayer configurations swell to about 40–45 Å on sorbing toluene. Results for sample R3 indicate that HDTMA intercalates with flat-lying monolayer configurations do not swell in toluene. HDTMA smectites with layer spacings intermediate between those having monolayer and bilayer configurations swell only to 33–40 Å, as might be expected if interstratifications persist in the swollen material.

The interlayer space required for toluene sorption could possibly involve flat-lying aliphatic chains in bilayer configurations (e.g. Fig. 2b) tilting into open, paraffin-like bilayer configurations with toluene occupying the voids formed. For HDTMA vermiculites and high-charged smectites, the silicate layers with their attached HDTMA cations move apart resulting in bilayers of tilted molecules. These bilayers may eventually disorder if the swelling is great enough. Alternatively, if the orientations of the HDTMA cations remain flat-lying, liquid-like toluene may occupy the available interlayer space. In either case, the interlayer spacings are between 42 and 47 Å. Although Weiss (1963) and Lagaly (1976) studied the sorption of alcohols by alkylammonium intercalated

clays, the detailed mechanisms of toluene sorption are not necessarily those suggested above, but are currently being studied further by powder and transmission X-ray diffraction. In this context, it is interesting to note that positronium annihilation lifetime spectroscopy (Gates et al., 2003, CSIRO unpublished data) shows that when salt molecules are leached from an HDTMA vermiculite, its interlayer void volume increases.

4. Conclusions

This study has focused on how the incorporation of excess HDTMA-Br salt molecules influences the layer spacings and affects the sorptive capacity of the alkylammonium clay intercalates. Layer spacings of the resulting intercalates vary with charge, over a wide range of natural and charge-reduced materials, and are consistent with the intercalated HDTMA molecules forming flat-lying monolayers, flat-lying bilayers and tilted paraffin-like arrangements. It has also demonstrated that preparations of HDTMA smectites in aqueous solvents differ from preparations in nonaqueous solvents (ethanol); this corroborates the recent results of Lee and Kim (2002). Toluene sorption isotherms show that the uptake of toluene increases when organic salt is present in the intercalates, which is in agreement with the results of Jaynes and Boyd (1991). Uptake of neat toluene only occurs for HDTMA intercalates with bilayer and paraffin-like interlayer arrangements when the interlayers expand to give $d(001)$ values of between 33 and 45 Å.

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