

MONOLAYER TO BILAYER TRANSITIONAL ARRANGEMENTS OF HEXADECYLTRIMETHYLAMMONIUM CATIONS ON Na-MONTMORILLONITE[†]

JAMES L. BONCZEK*, W. G. HARRIS AND PETER NKEDI-KIZZA

Soil and Water Sciences Department, University of Florida, P.O. Box 110290, Gainesville, FL 32611-0151, USA

Abstract—A low-charge Na-montmorillonite (SWy-2) was exchanged with hexadecyltrimethylammonium (HDTMA) at levels equal to 20, 40, 60, 70, 80, 90, 100, 150 and 200% of the cation exchange capacity (819 mmol(+)/kg) to determine the nature of adsorption and the ionic composition of the clay interlayers. In contrast with earlier work with smaller aliphatic cations, which suggested random interstratification of interlayers occupied by either organic or metallic cations, there was no evidence of cation segregation into homogeneous interlayers. Instead, X-ray analysis indicated that the organic cations assumed two dominant configurations which were roughly equivalent in prevalence at ~70% coverage of the CEC. Below 70% exchange the organocations existed predominantly in heterogeneous monolayers with Na⁺, attaining basal spacings of between 1.41 and 1.44 nm which were sensitive to changes in relative humidity. Relative humidity effects indicated that Na⁺ and HDTMA occupied functionally discrete domains within the interlayer as shown by the free interaction of water and a neutral organic solute, naphthalene, with Na⁺ and HDTMA, respectively. At greater levels of HDTMA exchange (up to 100% of the CEC), the organocations assumed a predominantly bilayer configuration. Transition to a fully-developed bilayer indicated by a 1.77 nm *d*-spacing at 100% coverage was gradual, suggesting some interstratification of the monolayers and bilayer configurations between 70 and 100% exchange. Sorption of naphthalene to the organoclays within this range of coverage was well correlated with clay organic carbon content, consistent with relatively unimpeded interlayer access of neutral organic molecules.

Key Words—Basal Spacing, Hexadecyltrimethylammonium, HDTMA, Organoclay, Sorption.

INTRODUCTION

Organoclays are synthesized from the exchange of resident metallic cations on clay surfaces by organic alkylammonium cations. Replacement of hydrated alkaline or alkaline earth cations strongly enhances the hydrophobicity of the clay interlayers, making them excellent sorbents for neutral hydrophobic compounds (Boyd *et al.*, 1988; Jaynes and Boyd, 1991). Thus, organoclays have been proposed as components in a variety of waste-containment barriers to inhibit the migration of toxic organic contaminants.

Organoclays are characterized as either adsorptive or organophilic depending upon the size of the alkyl substituents on the organocations, and the nature of their interaction with neutral hydrophobic compounds. Adsorptive clays result from exchange with quaternary ammonium ions of the general form [(CH₃)₃NR]⁺, where *R* represents a relatively short hydrocarbon substituent group. Due to their relatively small size, these cations function as props or ‘pillars’ in the interlamellar region, exposing siloxane surfaces to direct interaction with neutral hydrophobic compounds. Organophilic clays are produced from exchange with relatively long-chain alkylammonium cations (*R* ≥ 12),

which, upon adsorption, can form a hydrophobic partition medium within the clay interlayer, and function analogously to a bulk organic phase such as octanol or hexane. The conformation and thus the ultimate sorptive characteristics of this interlayer partition phase are strongly dependent on the size of the alkyl substituent, particularly in relation to the charge density of the clay. Some typical alkylammonium cations used in the synthesis of both types of organoclays are shown in Figure 1.

To create either species of organoclay, exchange with the alkylammonium cation is normally taken to completion, resulting in total coverage of the exchange complex to facilitate maximum sorption of hydrophobic organic compounds. The amount of exchange, however, can be tailored to specific objectives. For instance, it has been shown that clays partially exchanged with hexadecyltrimethylammonium (HDTMA) cations can maintain an organophilic character in proportion with their fractional coverage of the exchange complex, within certain limits (Boyd *et al.*, 1988). However, the physical arrangement of the organic cation within the interlayers at partial coverage, which partly determines these limits, is less well understood.

The majority of work related to the conformation of adsorbed interlayer alkylammonium cations has focused on relatively short-chain varieties like trimethylammonium (TMA), trimethylphenylammonium (TMPA), or a number of primary to quaternary amines (Jaynes and Boyd, 1990; Lee *et al.*, 1989; McBride and Mortland,

* E-mail address of corresponding author: bonczek@gnv.ifas.ufl.edu

[†] Florida Agricultural Experimental Station
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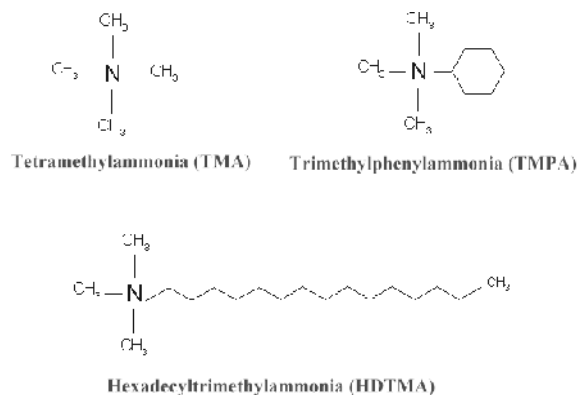


Figure 1. Three types of alkylammonium cations used in the synthesis of organoclays.

1975; Theng *et al.*, 1967). At maximum adsorption on smectite clays, these organocations are arranged in monolayers. At fractional levels of adsorption, however, the organic and metallic cations tend to segregate into randomly interstratified layers dominated by a single species.

McBride and Mortland (1975) reported that at <55% of the CEC, both TMA and TMPA organosmectites exhibit random interstratification of interlayers dominated by either organic or metallic (Cu^{2+}) cations. At up to 100% coverage, however, the basal spacings in these clays maintained a single value that was indicative of organic monolayers with no evidence of interstratification. This suggests that the organic and metallic cations coexisted in the same interlayers, and that basal spacings were fixed by the alkylammonium ion. Further, when clays exchanged between 55 and 100% of the CEC were equilibrated at two levels of hydration there was a fairly constant difference in interlayer spacing. This implies that interlayer hydration (presumably due to Cu^{2+}) still could impact on *d*-spacing, and that the effect was not necessarily dependent on the absolute amount of Cu^{2+} in the system, but merely its presence. Some elasticity of interlayer spacings of moist and oven-dried primary to quarternary adsorptive clays was also noted by Theng *et al.* (1967).

Less is known about the nature and conformation of intercalated long-chain alkylammonium cations on partially exchanged organophilic clays. Depending on the charge density of the clay and the proportion of the CEC occupied, long-chain alkylammonium cations can conceivably adopt monolayer, bilayer, pseudotrimolecular, or paraffin-type arrangements (Figure 2). Boyd *et al.* (1988) reported basal spacings consistent with random interstratification of Ca^{2+} and bilayer HDTMA interlayers for partially exchanged montmorillonite. However, exchange was performed at only three levels: 35, 70 and 100% of the CEC. Alternatively, transitional monolayer-to-bilayer arrangements have been reported for high-charge smectites (Lagaly, 1982; Lagaly *et al.*, 1976).

The purpose of the present study was to examine intercalation of HDTMA cations on a typical low-charge Na-smectite (SWy-2) to determine the nature of adsorption and the ionic composition of the interlamellar region. Clays were exchanged at levels between 20 and 200% of the CEC, and basal spacings were determined at two relative humidities. The effect of hydration lent additional insight into the makeup and properties of the interlayer volume that otherwise could not be determined. The migration of water into the interlayer established the role and location of Na^+ remaining on the exchange complex following adsorption of varying levels of HDTMA. To determine the analogous properties of the organic phase, the sorption of naphthalene, a neutral hydrophobic compound, was employed.

MATERIALS AND METHODS

Materials

Na-montmorillonite (SWy-2) was obtained from the Source Clay Repository of the Clay Minerals Society (Columbia, Missouri). Reagent-grade hexadecyltrimethylammonium chloride and naphthalene were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). Naphthalene is a weakly soluble (31.7 mg/L), neutral, hydrophobic ($\log K_{ow} = 3.37$) compound, which exhibits linear sorption on HDTMA montmorillonites at levels below ~20% of its solubility (Jaynes and Boyd, 1991; Nzengung *et al.*, 1996). Sorption is believed to be characterized by hydrophobic partitioning of the sorbate into the organic phase created by HDTMA, since naphthalene has very little affinity for Na-montmorillonite. It is useful, therefore, as a probe compound in the assessment of the organophilic character of partially and fully exchanged clays.

Preparation of organoclays

Organoclays were prepared from the wet-sedimented fraction obtained from the specimen clay as described by Nzengung (1996). The <2 μm fraction was washed three

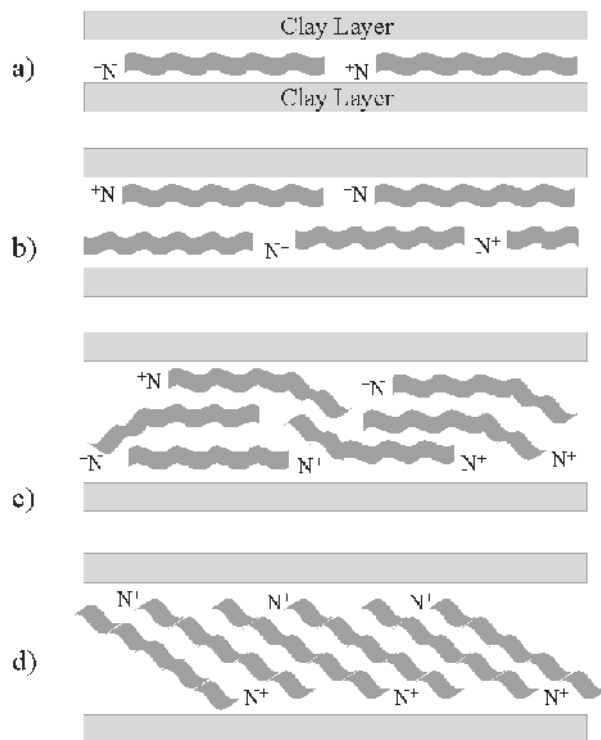


Figure 2. Potential conformations of interlayer cations (after Lagaly, 1982): (a) monolayer (1.37 nm), (b) bilayers (1.77 nm), (c) pseudotrimolecular layer (2.17 nm), (d) paraffin complex (>2.2 nm).

times with a 0.1 M NaCl solution, and then rinsed with deionized water. The CEC of the resultant Na-montmorillonite was determined by ^{45}Ca exchange, and was equal to 819 mmol(+)/kg. The Na-clay suspensions containing 25 g of clay were treated with solutions containing HDTMA equal to the desired coverage of the CEC (20, 40, 60, 70, 80, 90, 100, 150 and 200%) and allowed to incubate overnight. The resulting organoclays were then centrifuged, washed thoroughly, and freeze dried. Organic carbon contents of the organoclays were calculated from the amount of HDTMA adsorbed at each level. Adsorbed HDTMA was determined as the difference between the amount initially in solution, and that remaining following equilibration. The clays were stored in a desiccator over P_2O_5 until used.

X-ray analysis

Dried organoclays deposited on low-background quartz-crystal X-ray diffraction mounts were equilibrated over a large quantity of a saturated CaCl_2 solution in a desiccator to establish the relative humidity of 40%. To ensure constant humidity during the analysis, a constant-humidity 'chamber' with a Mylar window for beam passage was constructed around the diffractometer stage, and fitted with a digital hygrometer (Harris *et al.*, 1992). Triplicate X-ray scans were made between $40 \pm 2\%$ relative humidity and $97 \pm 1\%$ relative humidity. Small differences in the thickness of the

mounts, as well as swelling of the mounts due to hydration, changed the angle of the beam relative to the sample. Therefore, corrections were made in the diffraction peaks, when necessary, based on the known position of a slight quartz peak that was observed in each sample. Samples were scanned at $2^\circ 2\theta \text{ min}^{-1}$ using $\text{CuK}\alpha$ radiation.

Naphthalene sorption

Equilibrium sorption of naphthalene from aqueous solution on all clays was examined by batch method at a single initial concentration of 5 mg/L. The solution:clay ratio was 100:1. Clay was weighed into 15 ml glass centrifuge tubes and the naphthalene solutions added. The tubes then were shaken at ambient temperature (25°C) for 24 h (Nzengung *et al.*, 1996). Equilibrium solutions were obtained by centrifugation at 1200 g for 15 min. Naphthalene concentrations were determined by high-performance liquid chromatography (HPLC) using ultraviolet detection, a C-18 column, and a 60:40 acetonitrile:water mobile phase. Sorbed naphthalene was determined as the difference between the amounts added to each tube and that remaining in the equilibrium solution. The sorption coefficient, K_d , was computed from the equation $S = K_d C$, where S is the amount sorbed to the clay (mg/g), and C is the equilibrium solution concentration of naphthalene (mg/mL).

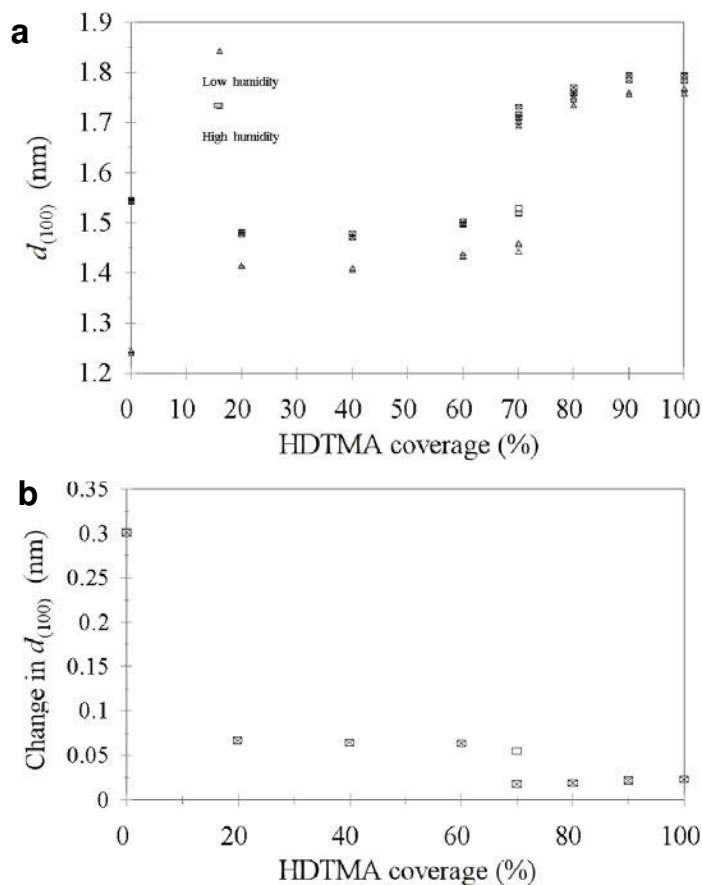


Figure 3. (a) Basal spacings of partially-exchanged organoclays at two relative humidities; and (b) the change in d -spacing with hydration. Open symbols indicate two diffraction peaks.

RESULTS AND DISCUSSION

Basal spacings at low relative humidity

The HDTMA cations typically take up a bilayer configuration in low-charge smectites at 100% coverage of the CEC. Evidence of interstratification of these bilayers with Na^+ interlayers has been reported for clays partially exchanged with HDTMA (Boyd *et al.*, 1988), but basal spacings from progressive coverage of Na-montmorillonite by HDTMA in the present investigation could not be reconciled with a construct based upon segregated, randomly interstratified Na^+ and HDTMA interlayers. Basal spacings in such a case would necessarily reflect the proportions of the interlayers exclusively occupied by each cation. In effect, with each increment of coverage, HDTMA would occupy progressively greater numbers of randomly distributed interlayers, increasing the resultant d -spacings accordingly. The present data, however, suggest that adsorbed HDTMA assumed two dominant configurations within the interlayer volume at low (<70%) and high (>70%) coverages (Figures 3 and 4).

Between 20 and 60% coverage, the magnitude and relative constancy of d_{001} suggest that HDTMA and Na^+

exist within the same interlayers, and basal spacing was governed largely by monolayer coverage of the alkylammonium cation. In other words, there was no evidence for significant random interstratification of homogeneous Na^+ and HDTMA layers. Measured d -spacings were somewhat greater than the 1.34 nm calculated for monolayer HDTMA-smectite, given silicate sheet and alkyl chain thicknesses of 0.94 and 0.40 nm, respectively. Basal spacings were also greater than those observed previously for dehydrated, fully-exchanged monolayer n -alkylammonium-montmorillonite samples (Laird *et al.*, 1989). However, in the present case, water was not excluded from the interlayer, which remains relatively hydrophobic at low HDTMA loadings. This could cause the alkylammonium carbon tails to gravitate away from the Na- and water-populated surface to produce the measured spacings.

Exchange beyond 60% showed a developing bilayer arrangement for HDTMA, terminating at the characteristic d -spacing of 1.77 nm for a nominal 100% coverage (Lagaly *et al.*, 1976; Nzungung *et al.*, 1996; Theng *et al.*, 1967). A transition between the two principal arrangements was also indicated (Figure 4). Initialization of the

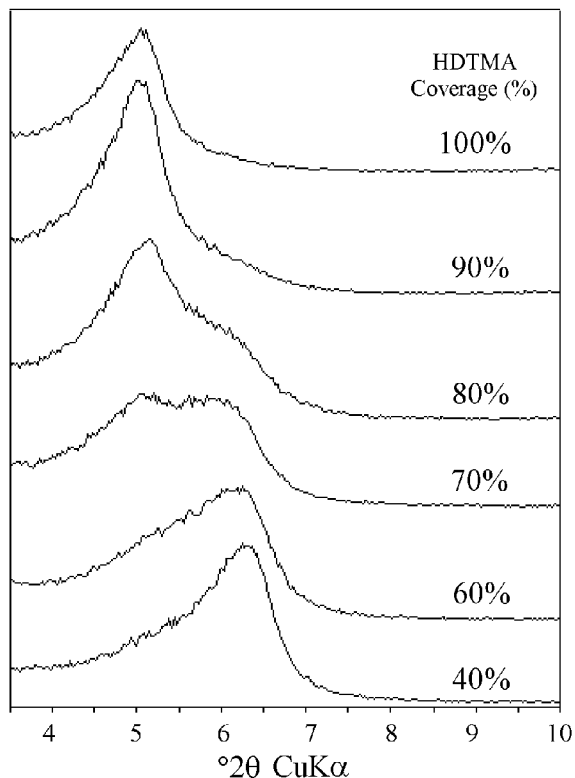


Figure 4. XRD traces for six different coverages of organoclays.

transition to a bilayer configuration is observable in the low-angle peak broadening for the 60% organoclay, which suggests the incipient development of a bilayer phase. An increase in the position of the primary peak to 1.47 nm also suggests some potential random interstratification of the two principal phases, as do the two peaks of relatively equal intensity at the 70% coverage. Neither of these peaks precisely corresponds to the monolayer or the bilayer spacings, but instead appear to be shifted toward an intermediate position between the two. With still greater HDTMA loading between 80 and 100% coverage of the CEC, the dominant arrangement was bilayer. However, weak, high-angle 'shoulders' on both peaks which correspond roughly to the monolayer d -spacing indicated that some residual monolayer phases persisted. Not until 100% coverage did the diffraction peak resolve to a single, discrete peak at 1.77 nm which is indicative of an exclusively bilayer arrangement.

The overall transition may reflect the adsorption characteristics of HDTMA. At low surface loadings, the adsorption process is driven primarily by electrostatics augmented by Van der Waals' interactions of the carbonaceous alkyl chains with siloxane surfaces. With increased loadings, however, adsorption shifts to a more dominantly hydrophobic process involving associations between the alkyl chains of resident and incoming cations. This fundamental change in sorption character, and the resultant reorientation of interlayer cations is

ordinarily attributed to steric constraints. These, in turn, are dictated by the relative planar areas of the alkylammonium cations and the charged sites on the smectite surface in an interlayer volume fully occupied by alkylammonium cations (Olis *et al.*, 1990; Stul and Mortier, 1974). When the area of the alkylammonium cation exceeds the area available per charged site, the ions are obliged to assume an alternative configuration within the interlayer.

Basal spacings at still greater coverages of 150 and 200% of the CEC increased to 1.86 nm and 2.08 nm, respectively. At these levels of HDTMA uptake, sorption was probably driven solely by hydrophobic interactions among the carbonaceous portions of HDTMA. Accommodation of the organic cation in the uncharged, strongly hydrophobic interlayer space, which would cause the expansion, is difficult to envision. However, although the cation remains charged, it may not be sufficiently hydrated to obviate the potentially powerful interactions among the aliphatic portions of the adsorbed species. Further, charged alkylammonium cation heads can protrude from the interlayer space at high adsorption levels. The increase in d_{001} , therefore, may be due to swelling of the interlayers in a manner similar to that documented for the absorption of organic solvents by HDTMA organoclays (Nzengung *et al.*, 1996), rather than a conformational shift. Adsorption beyond the CEC may also have involved HDTMA-chloride ion pairs, or aggregation of organic cations at the clay surface (Rytwo *et al.*, 1991). Interaction of the carbon chain with adsorbed HDTMA on external surfaces or crystal edges is also conceivable, but would not lead to increased d -spacings.

Overall, the data demonstrate that the orientation of interlayer cations is contingent upon their absolute numbers and their density, in conjunction with their planar areas relative to those of the charged sites on montmorillonite. In effect, there must first be sufficient numbers of the alkylammonium cations to support the formation of a bilayer, and second, their density must exceed a critical level to induce reorientation to their ultimate bilayer configuration.

Hydration of clay interlayers

Hydration of the organoclays provided additional clues to the potential makeup of the interlayer volume. Figure 3 indicates the change in d -spacing with clay hydration. The impact of hydration was uniform within the ranges of predominance for monolayer and bilayer coverage, suggesting that overall ordering of Na^+ and HDTMA within the interlayers remained similar, although the relative proportions of each cation did not.

Sodium ions are responsible for interlayer expansion due to hydration at low HDTMA coverages. Thus, given almost uniform response to hydration, expansion of the interlayers depended on the presence, rather than the amount of Na^+ . Furthermore, water was apparently able

to migrate unimpeded into the interlayer space, regardless of coverage, suggesting pervasive, contiguous domains of Na^+ within the interlayers. In essence, the two 'phases', dominated by either HDTMA or Na^+ , although not segregated into discrete interlayers, nonetheless functioned independently.

At >60% coverage, clay expansibility decreased in conjunction with the apparent change in configuration, rather than the amount, of HDTMA in the interlayers. The almost uniform response to hydration above 60% exchange also suggests that expansion was dictated by a similar mechanism among these higher-coverage clays. The source of the interlayer expansion is uncertain. The structure of water in an interlayer partially occupied by organic cations is not known, and thus its impact on interlayer expansion is unpredictable. The expansion did not depend strongly on the relative amounts of metallic or organic cations on the exchange sites, so it appears that expansibility upon hydration was controlled by either one cation or the other. If Na^+ hydration dictated the expansion, then the structure of water molecules was fundamentally different than for lower HDTMA coverages. For example, with 80% coverage, *d*-spacing increased from 1.74 to 1.76 nm upon hydration. However, the basal spacing for the hydrated, fully-expanded Na^+ interlayer was only 1.54 nm which is too small to yield the observed spacings. A possible alternative explanation may be that hydration of HDTMA, itself, caused the interlayer expansion. The aliphatic hydrocarbon 'tail' of HDTMA is hydrophobic (Figure 1), but the polar nitrogen 'head' admits the potential for hydration and consequent expansion of the interlayers.

Naphthalene sorption

It is apparent that below full saturation of the exchange complex with HDTMA, the majority of organic and metallic cations do not segregate into discrete interlayers as has been demonstrated for short-chain alkylammonium cations (Mortland, 1970; McBride

and Mortland, 1975). However, indirect observations of the access of water to polar regions in the interlayer space of partially-exchanged clays discussed above, as well as the separation of the interlayers themselves, suggest that they do tend to segregate within the same interlayers, and function largely independently with respect to water. This begs the question of whether organic compounds can access the organic domains as readily.

Sorption of naphthalene to the partially exchanged clays provided an affirmative, although qualified, answer. Figure 5 compares the partitioning coefficients (K_d) of naphthalene for all of the organoclays discussed above, based on organic carbon content. The straight line through the data was derived from linear regression of the K_d values for the 80, 90 and 100% coverages where bilayers and consequently a more stable partitioning phase, was better developed. Despite some potential sharing of the interlayer space between Na^+ and HDTMA, as suggested by hydration of the clays, the K_d values were highly linear in this region.

Sorption appeared to decline with excess coverage by HDTMA in amounts equal to 150 and 200% of the CEC. Neutral hydrophobic compounds sorbed on HDTMA smectites tend to augment the sorptive capacity of organoclays for other, or the same neutral compounds (Traina and Onken, 1991; Sheng *et al.*, 1996). However, polar or charged groups on alkylammonium cations which were sorbed beyond the CEC and were unbalanced by charges on the clay surface may have diminished the hydrophobic character of the interlayer and thus limited the uptake of naphthalene.

At <80% coverage, partitioning of naphthalene into the organic phase also appeared to decline. Either the monolayer conformation of the organic cations within the interlayer, or the presence of water and Na^+ in close proximity to the organic domains may have reduced K_{oc} compared with organoclays dominated by bilayers. There was, however, a gradual increase in naphthalene sorption as HDTMA occupancy increased and bilayers

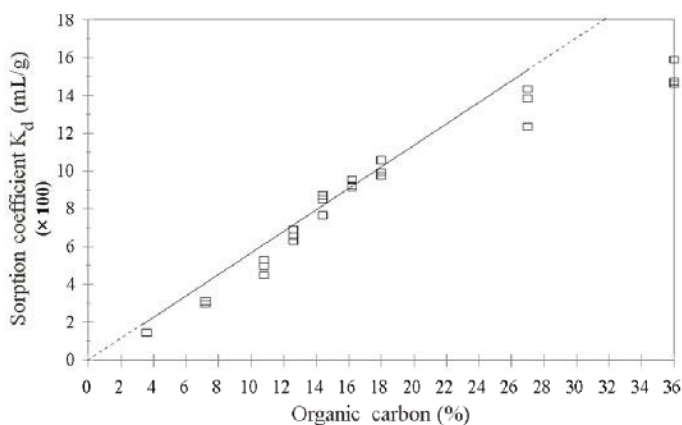


Figure 5. Naphthalene sorption on the full range of organoclays.

began to develop. Thus, sorption to the 70% organoclays (at the midpoint of the transition between monolayers and bilayers) approached levels achieved for the 80, 90 and 100% organoclays.

Note that while naphthalene sorption as indicated by K_{oc} declined below 80% coverage, expansion due to hydration was essentially uniform. Sorption appeared to be more susceptible to potential influences from the polar domains within the interlayer. Still, this is consistent with the proposed composition of the interlayer. Expansion was not contingent upon hydration of all interlayer Na^+ ions, but K_{oc} values do derive from the number of interlayer HDTMA aliphatic substituents accessed, as well as their conformation. As coverage increased, potential interference with sorption from proximate hydrophilic domains within the same interlayer apparently declined.

CONCLUSIONS

Overall, the results from both X-ray analysis and sorption of naphthalene are internally consistent. Heterogeneous monolayers and bilayers with Na-dominated clay interlayers depend upon surface coverage by HDTMA. However, despite this heterogeneity, Na^+ and HDTMA apparently occupy functionally discrete domains which are reflected in the response of the clays to the sorption of naphthalene, and to hydration.

Intercalation of the alkylammonium cations was apparently governed by fundamentally different processes at low and high surface coverages. Electrostatics augmented by Van der Waals' interactions of the alkyl hydrocarbon chains with siloxane surfaces apparently dictated adsorption at lower surface densities. At greater loadings, adsorption shifted to a more dominantly hydrophobic process involving associations between the alkyl chains of resident and incoming cations.

The true character of these processes might best be assessed with thermodynamic techniques, spectroscopy, or correlation of surface charge density with the planar area of a number of organic cations (or the number or carbon atoms in the alkyl substituents). Regardless of the particular technique, it is necessary to address the specific mechanisms and the adsorbate or adsorbent properties controlling the conformation and distribution of the interlayer cations.

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