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## Effects of surface charge and particle morphology on the sorption/desorption behavior of water on clay minerals

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### ABSTRACT

*In situ* DRIFT spectroscopy is used in the current study to follow sorption/desorption of water vapor on several clay minerals that vary in surface charge and morphological character. Spectra of the dried sorbents indicate the significant effect of those factors on both liquid and vapor phase water remaining within the particles. Changes in the IR bands recorded during exposure to water vapor at 50% RH confirm the assignment of those bands to water. They also indicate that the dynamics of liquid phase sorption/desorption for all the sorbents investigated is consistent with the concept of capillary condensation within nanometer scale pores that was advanced in previous studies conducted with 1,2-dihaloethanes. The intraparticle accumulation of the vapor phase water, however, was found to be profoundly affected by both surface charge and particle morphology. These differences are attributed to the high polarity and hydration capabilities of water molecules. Band area changes documented during a second sorption/desorption cycle are nearly identical to those occurring during the first with regard to both timing and extent. They also confirm that some liquid phase water is retained by the sorbents even after five days of desorption and amounts of sorbed vapor phase water increase over the course of the experiments.

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### 1. Introduction

In 1990, Sawhney and Gent [1] investigated sorption of both 1,2-dibromoethane (EDB) and trichloroethylene (TCE) from the vapor phase onto columns packed with clay minerals. They reported remarkably high quantities of EDB sorbed after 16 h of sorption: 9% for Clay Spur montmorillonite, 6% for Fithian illite, 5% for Georgia kaolinite, and 3% for pyrophyllite by weight. No correlation could be found between the sorbed quantities and BET determined surface areas. These investigators also found that desorption proceeded much more slowly than sorption and substantial amounts of chemical were retained after a 24 h desorption period that followed 1 h of sorption: 34%, 19%, 56%, and 6% of sorbed quantities for kaolinite, montmorillonite, illite, and pyrophyllite, respectively. Similar results were found with TCE as the sorptive chemical. Desorption profiles for both chemicals were fitted to a two compartment model comprised of fast and slow desorbing components which led to the conclusion that the chemicals had diffused to and were retained within intragregate micropores. This conclusion had earlier been suggested by Steinberg et al. [2] after extensive analysis of soils that had retained substantial amounts of EDB 19 years after their

last treatment with the chemical. Our DRIFT experiments were initiated in order to understand these significant sorbed quantities and the reasons for the long term retention.

The DRIFT technique developed allows *in situ* monitoring of the status of sorbed chemical as a function of time during both sorption and desorption. Initial investigations with clay minerals were interpreted in the context of rotational conformer populations of dihaloethanes [3,4]. Onsager [5] proposed that molecules possessing a dipole moment experience a loss of potential energy compared to a vacuum state when transferred to a medium with a higher dielectric constant. Of the two stable conformers for dihaloethanes, only the gauche conformer possesses a dipole moment. The DRIFT spectra provided evidence that compared to bulk values, gauche conformer populations for the sorbed chemical were enhanced relative to the anti conformer. For three of the clay minerals, the expected enhancement of gauche conformer populations as a function of surface charge was in the order expected with illite > smectite > pyrophyllite. Kaolinite, which has nearly zero charge, unexpectedly showed preferential retention similar to illite. It was concluded from this result that preferential retention of the gauche conformer and long term retention of the chemical may not only be a function of layer charge but also the surfaces exposed and the manner in which the intraparticle micro- and mesoporosity is arrayed.

In later studies, evidence was presented for the development of intraparticle sorbed liquid and vapor phase dihaloethane on both clays and soils: neither the extents nor the rates of accumulation

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**Table 1**  
Layer charge characteristics of clay minerals.

Clay mineral	Octahedral charge	Tetrahedral charge	Layer charge	Reference
Low defect kaolinite, KGa-1, GA	+0.11	−0.17	−0.06	Source clays data sheet
High defect kaolinite, KGa-2, GA	+0.16	0.00	+0.16	Source clays data sheet
Macon, GA kaolinite, API #4	−0.03	−0.31	−0.34	Kerr et al. <sup>a</sup>
Clay Spur, WY montmorillonite, API #26	−0.53	−0.33	−0.86	Earley et al. <sup>b</sup>
Cheto, AZ montmorillonite SAz-1	−1.08	0.00	−1.08	Source clays data sheet
Otay, CA montmorillonite SCA-3	−1.29	−0.19	−1.48	Source clays data sheet
Fithian, IL illite, API #35	−0.17	−1.34	−1.51	Couch and Grim <sup>c</sup>
Silver Hill, MT illite, 1Mt-1	−0.44	−1.23	−1.68	Source clays data sheet

<sup>a</sup> [51].

<sup>b</sup> [52].

<sup>c</sup> [15].

for the two sorbed phases were the same. Most importantly, it was demonstrated that IR bands attributed to sorbed vapor phase chemical continue to increase in intensity even as liquid phase chemical is desorbing [6–8]. Our interpretations of these results are further tested here with water vapor as the sorptive chemical. The earlier results are relevant to those presented here because sorption from the vapor phase is a function of partial pressure and depends primarily on sorbent porosity. It is predicted by the Gurvitsch rule that pore volumes of chemicals sorbed on a given sorbent from the vapor phase should be similar even though the chemicals vary widely in physicochemical properties. Sorptives shown to follow this rule include water, benzene, CCl<sub>4</sub>, n-hexane and ethanol which provides strong evidence for capillary condensation in porous particles [9]. The rule was applied recently in estimating micropore volumes of water and TCE sorbed onto multiple sorbents including two of the clay minerals used in the current study [10,11]. Water is unique, however, in its ability to form strong hydrogen bonds between its own molecules and spheres of hydration about metallic cations. Because of its high polarity, it is also more likely to interact with the surfaces it encounters than most volatile organic chemicals and can thus act as an even more sensitive molecular probe of sorbent characteristics.

The layer silicates used in the current study are comprised of two basic structural units. The first is a sheet of silica tetrahedra in hexagonal arrays interconnected by shared oxygens. The second is a sheet principally of Al and/or Mg cations in octahedral coordination with OH anions. Kaolinites are comprised of 1:1 layers of each type of sheet and are thus classified as 1:1 layer silicates. Both montmorillonites and illites are comprised of 2:1 layers in which the Al/Mg octahedral layer is sandwiched between two layers of silica tetrahedra. Isomorphic substitution occurs in both types of layers: the extent, location, and the charge of substituting cations are responsible for surface charge which is compensated by cations located on the layer surfaces [12]. Sposito et al. [13] emphasized the importance of layer charge and surface characteristics in understanding the behavior of aluminosilicate clay minerals with regard to both hydrophilic and hydrophobic sorptive chemicals.

None of these clays, however, are found in natural deposits as single units; always as aggregated particles that are very stable under a wide range of conditions and retain sufficient order to allow characterization by X-ray diffraction analysis. The morphological character of these aggregate units is a function of both the parent material and the physicochemical environment existing during the formation process. Those factors determine the chemical composition, extent and location of isomorphic substitution, and also the growth mechanisms active during development.

Chemical analyses of kaolinites indicate very little isomorphic substitution and close to zero surface charge. The two kaolinites used in the current experiments are similar in their chemical composition and layer charge but differ in their degree of crystallinity: one is described by the Clay Minerals Society as highly ordered and the other as disordered. Electron micrographs (SEM)

of highly ordered kaolinites reveal crystals with well defined hexagonal edges, approximately 0.05–2 μm thick, 0.3–4 μm in diameter. Edges for disordered kaolinite are less well defined; particles tend to be smaller and thinner. SEMs shown by Grim [12] comparing that of a well-crystallized kaolinite to one of a poorly crystallized one illustrate this point particularly well. The degree of crystallinity may be a factor in the continuity of the pores that comprise the intraparticle pore network and also the degree of pore size variation along the length of the pore.

In general, illites are observed to form small, irregular aggregate structures with diameters approximately 0.1–0.3 μm. The layers comprising the aggregates are tightly held together by interlayer cations, usually K<sup>+</sup>, and are not easily separated. Much of the layer charge is a consequence of isomorphic substitution in the tetrahedral layer and thus is close to the clay surface (Table 1, [12]). Gaudette et al. [14] concluded that X-ray diffraction scans and sorption behavior of Cs<sup>+</sup> on multiple illites were best explained by the “core-rind” or “frayed-edge” hypothesis in which aggregates are comprised of a crystalline core encased within a shell of less ordered, more diffuse material. The core is considered to be much less accessible to external cations while the surfaces of the outer material are more available to cation exchange. Sorption studies reported by Couch and Grim [15] of boron on illites were also consistent with this hypothesis and similar ideas were advanced by Jackson [16]. It is reasonable to conclude from these studies that chemicals in solution can readily access the diffuse regions of the aggregates but access to the core is slower and much more limited.

In contrast to the illites, the primary source of layer charge for montmorillonite clays is substitution in the octahedral layer (Table 1). Total layer charge is generally higher than that of kaolinites but less than for illites. Interlayer cations of montmorillonite clays are more easily exchangeable than those associated with illites [12]. Grim and Guven [17] have proposed that montmorillonite clay aggregates fall into distinct categories defined by the growth mechanisms operating during their formation processes. Otay-type clay particles have developed under rapid growth conditions that favor the formation of clustered globular aggregates predicted to have the potential to trap both liquids and gases. The Otay clay used in the current study has a total layer charge comparable to the illites but differs in the location of the charge. Slower growth conditions favor lamellar structures resulting from a layer-by-layer growth process and are commonly observed with Wyoming-type clays. Many such clays are known to swell substantially upon immersion in water. Aggregates of Cheto-type clays are described as “mossy” in character and appear to be composed of tightly curled fibers. These are less easily dispersed. We investigate here whether differences in surface charge and morphological character of clay minerals affect their sorption/desorption behavior with a polar sorptive chemical, water.

Many investigations dealing with the sorption of water on clay minerals have been conducted in the past. Several factors may have contributed to differences in the spectra shown here

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