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INTERACTION BETWEEN ORGANIC AND INORGANIC POLLUTANTS IN THE CLAY INTERLAYER

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Abstract—A synergistic mechanism for the retention of organic and inorganic pollutants in clays is discussed in this paper. The mechanism of adsorption of cis- or trans-1,2-dichloroethylene vapor (CDE or TDE, respectively) by hydrated smectite clay (hectorite) exchanged with Pb^{2+}, Hg^{2+}, Cd^{2+}, Ca^{2+}, Ag^{+}, or Na^{+} has been investigated by simultaneously measuring chlorohydrocarbon uptake and water desorption isotherm and by recording the infrared (IR) spectrum of the adsorbed phase. Hydrated hectorite saturated with divalent cations adsorbs about 55% more CDE or 35% more TDE than those saturated with monovalent cations. The quantity of chlorohydrocarbon adsorbed is also a function of the hydration of the clay interlayer space. When dehydrated, hectorite does not adsorb CDE or TDE. Upon long outgassing at room temperature or even at 100°C, the characteristic IR bands of clays with adsorbed chlorohydrocarbon, although much weakened, are still observable. The ratio of the amount of water desorbed to the amount of chlorohydrocarbon adsorbed varied from about 0.22 to 0.34. A shift of the center of gravity of the hydration water OH stretching frequency towards a higher wavenumber and of the asymmetric CCl stretching vibration toward a lower frequency suggest that the formation of hydrogen bonds between CDE or TDE and water is the driving force for adsorption and that the cation-dipole interaction does not play a major role.

Key Words—BET, Chloroethenes, Chlorohydrocarbons, Contaminants, Dichloroethylenes, FTIR, Halohydrocarbons, Heavy metals, Hectorite, Isotherm, Pollutants, Smectite, Sorption, Toxicants.

INTRODUCTION

In terms of adsorption, the most active inorganic constituent of soils is the clay fraction. Clays not only have large surface areas, but also have mineral structures that bear negative charges that are balanced by exchangeable or charge-balancing cations. Among inorganic environmental toxicants, cations of heavy elements such as Cd, Hg, or Pb can easily exchange innocuous elements such as Na or Ca. In addition, clays can bind a large number of organic molecules because of their large specific surface areas and van der Waals, ion-dipole, and/or dipole-dipole interactions. These interactions can result in a synergistic effect whereby an inorganic pollutant is "clathrated" by the organic pollutant. The clays in soils are never saturated by heavy elements, but they are always hydrated.

The intermolecular interactions of organic pollutants with clay mineral surfaces can be expected to play a crucial role in the subsequent chemical/biological transformations, transport, and retention of these contaminants. This is especially true when considering volatile organic compounds for which diffusion in the vapor phase may be significant. Recently, Fourier Transform Infrared (FTIR) and Raman (Bowen *et al.*, 1988), FTIR/Gravimetric (Johnston *et al.*, 1992), and Diffuse Reflectance Infrared (Aochi *et al.*, 1992) spectroscopic techniques were used to investigate the interactions of dimethyl methylphosphonate (DMMP), water, and 1,2-dibromoethane (EDB) adsorbed on clay mineral surfaces, respectively. Bowen *et al.* (1988), having analyzed the IR spectral shifting of the DMMP vibrational bands after adsorption, suggested that the major interaction between the clay mineral and the DMMP molecule was an ion-induced dipole interaction of the phosphonate oxygen (P=O) with the interlayer cationic species and not through an intervening hydration sphere. Johnston *et al.* (1992) concluded that water molecules residing near the surface of montmorillonite were strongly influenced by the type of exchangeable metal cations present on the clay and by the overall water content. Aochi *et al.* (1992) reported that as the dielectric constant of the medium increases, the gauche conformation of EDB becomes more stable relative to the anti (i.e., dipole moment = 0) conformation due to its dipole moment effect. They indicated that the preference for the gauche conformer of EDB was consistent for pyrophyllite, smectite, and illite but not for kaolinite. They further suggested that the preferential retention of the gauche conformer of EDB may also depend on the surfaces exposed, the availability of micro- and mesopore spaces, and the interactive forces operating within those pore spaces. Consideration of dielectric field effects on conformational populations of 1,2-dihaloethanes was earlier advanced by Mizushima *et al.* (1949) and Mizushima (1954).

It has been well established that swelling clays such as montmorillonite adsorbed organic compounds into the clay interlayer spaces and that these substrates have been used in many studies of clay-organic complexes (Theng, 1974). Numerous reactions of clays with or-

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ganic substances have been reviewed by Rausell-Colom and Serratosa (1987). From all the previous and also the more recent investigations by Boyd *et al.* (1988), Zielke and Pinnavaia (1988), Sawhney and Gent (1990), Michot and Pinnavaia (1991), and Jaynes and Boyd (1991), it is apparent that the determination of the adsorption interactions of organic pollutants (e.g., halohydrocarbons or aromatic hydrocarbons) and clay minerals is an important factor in elucidating the fate of organic contaminants as they diffuse through soils.

Under laboratory conditions mimicking the natural environment, we have developed an idealized model to study the synergistic effect of the retention of an organic pollutant (e.g., chloroethene) by an inorganic pollutant (e.g., cadmium) in hectorite (analogous to montmorillonite). The clays have been fully loaded by either monovalent or divalent cations of heavy elements. If the mutual enhancement behavior of heavy-metal saturated clays with respect to the organic pollutant were similar to that of a calcium-saturated clay, then it will also be comparable to the behavior expected at intermediate compositions. The simultaneous adsorption of CDE or TDE and desorption of water have been measured and, in frequency domains where the typical vibrational bands of CDE or TDE and H_2O are observable, the infrared spectra have been recorded. The advantage of studying CDE and TDE is that it is possible to observe their vibrational CCl modes in spectral windows not obscured by clay vibrations.

The relative affinity of CDE or TDE and H_2O for cations of heavy elements and the structural modification undergone by adsorbed CDE or TDE with respect to their molecular configuration in the gas phase suggest that the interaction between the C–Cl bond and water belonging to the cation hydration shell plays a major role in the retention of chlorohydrocarbons.

The proposed idealized model system can only provide schematic phenomena of the chemical reactions being studied. Nevertheless, owing to the synergistic interaction between inorganic and organic pollutants, the results of the adsorption, retention, and chemical transformations of organic molecules in the clay interlayer predicted by this idealized model may be extrapolated to the important role of clay minerals in the natural system.

METHODS

Materials and reagents

Hectorite (SHCa-1, San Bernardino County, California) was obtained from the Clay Minerals Society Source Clay Minerals Repository. The carbonates in hectorite were removed by rapidly lowering the pH of a stirred aqueous slurry down to pH 3.5 with 0.1 N of HCl. As soon as the carbonates were decomposed, the pH was increased to about 7 by adding 0.1 N of NaOH while stirring and the residue was washed by centrifugation. The removal of the carbonates was monitored by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The residual carbonate content was less than 1%.

The clay fraction ($<2\ \mu m$) was exchanged repeatedly with 0.1 M solution of either $Pb(NO_3)_2$, $HgCl_2$, $CdCl_2$, $CaCl_2$, $AgNO_3$, or NaCl (all Baker's analytical grade) at $4 < pH < 7$ and the excess salt was removed by centrifugation. The cation-exchanged clay was then washed with deionized water until the excess Cl^- ions were no longer detectable by the $AgNO_3$ test. The cation exchange capacity of nearly carbonate-free hectorite is about 90 meq/100 g of the dehydrated weight of clay at room temperature. The cation-exchanged clay was then either freeze-dried for the adsorption studies or its aqueous slurry slowly sedimented to form self-supporting films for spectroscopic study.

Cis- and trans-1,2-dichloroethylene (CDE and TDE) were obtained from Fluka and used without further purification. CDE has a dipole moment of 1.90 Debye units (D), which is close to the H_2O dipole moment of 1.87 D. Because of its symmetry, the dipole moment of TDE should approach zero. However, a value of 0.70 D is reported in *Lange's Handbook of Chemistry,* edited by Dean (1985). The infrared spectra of CDE and TDE (Pouchert, 1970) are well known and their fundamental frequencies have been assigned to normal modes as described by Herzberg (1947).

Absorption apparatus

Figure 1 shows a schematic diagram of the volumetric-technique adsorption apparatus. It consists of a gas burette with 6 levels (V_1 to V_6) as well as a vial (v_D) filled with ~1 g $CaSO_4$ as desiccant, pretreated under vacuum at ~250°C before each experiment. $CaSO_4$ absorbs about 10% H_2O (w/w) with a residual H_2O vapor pressure of less than 0.1 Torr at room temperature (25°C ± 1°C). The accurately weighed clay powder, usually ~0.3 g, contained in the reactor column (v_R), was pretreated under vacuum at room temperature for exactly 3 hr before each adsorption experiment. There was some uncertainty in the amount of water remaining after this outgassing procedure since the dynamic residual pressure influenced water removal. Most of the loosely bound or physisorbed water molecules were removed, but the ones strongly coordinated to the exchangeable cations in the inner sphere coordination in the clay interlayer remained.

As the clay adsorbs organic molecules, water molecules may desorb from the interlayer. The adsorption apparatus, fitted with ChemClass℠'s teflon o-ring greaseless stopcocks and glass joint slightly greased with DuPont℠'s Krytox® fluorinated grease, was designed to measure the uptake of CDE or TDE and desorption of water molecules. The calculations used to simultaneously determine the chlorohydrocarbon adsorption

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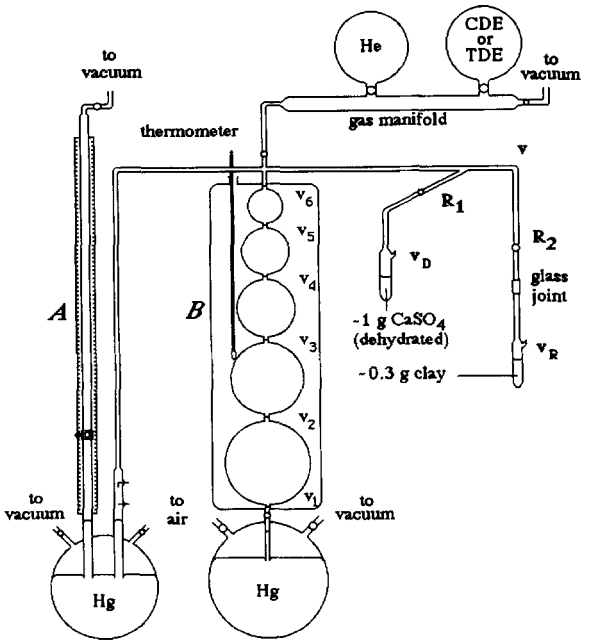


Figure 1. The volumetric-technique adsorption apparatus used to simultaneously measure the number of CDE or TDE molecules adsorbed and the number of water molecules desorbed: A) is a mercury manometer and B) a gas burette with 6 levels (v_1 to V_6), respectively. v represents the dead volume of the manifold in the system. The sample is in v_R. See text and appendix.

and water desorption isotherms are described in the appendix.

Infrared spectroscopy

The home-built IR cell was fitted with KBr windows and an oven that permitted outgassing the sample at higher temperature when needed. For the sake of comparison with the adsorption experiments, the clay film was also pretreated by outgassing at room temperature for exactly 3 hr. Therefore, the clay film in the IR cell and the clay powder in the adsorption apparatus were pretreated the same way so that the initial degree of hydration was as close as possible in both cases. The clay sample was then exposed to an increasing relative vapor pressure (P/P_o) of CDE or TDE. At each equilibrium pressure level, IR spectra were recorded using a Nicolet MX-1 FTIR spectrometer in the 4000–400 cm^{-1} spectral range in the absorbance mode. A total of 200 accumulations were performed for each IR spectrum with a maximal resolution of 2 cm^{-1}.

The self-supporting clay films weighed about 5 to 8 mg per cm^2. The integrated absorbance for each band using a constant wavenumber integration domain ($\Delta\nu$) was reported to 1 mg/cm^2 and expressed in arbitrary units (a.u.). The integrated absorbance (I) is proportional to the number of oscillators within the optical pathway (n) with the proportionality coefficient (ϵ) being the absorption coefficient or the specific absorbance:

$$I = \left(\int_{\nu_2}^{\nu_1} A\, d\nu - \int_{\nu_2}^{\nu_1} A_o\, d\nu\right) \Big/ m = n\epsilon$$

where A_o and A are the absorbances of the clay film before and after introduction of CDE or TDE, respectively, and m is the mass of the clay film. IR spectra of CDE or TDE in the gas phase were recorded by lifting up the sample holder containing the clay film from the IR beam at each equilibrium pressure. These spectra were subtracted from the spectra obtained while the clay film was in the beam; thus, the integrated signal was corrected by the absorbance of the clay film before adsorption.

In this study, the quantity of CDE or TDE adsorbed by the clay film in the IR cell was deduced from the adsorption isotherm obtained for the clay powder in the adsorption apparatus. This extrapolation is inevitably a source of error for the value of ϵ.

RESULTS

Qualitative analysis of the infrared spectra of adsorbed cis-1,2-dichloroethylene (CDE)

Figures 2 and 3 show stacked plots of infrared spectra of CDE adsorbed by the Cd and Ag-exchanged hectorites, respectively. These are IR spectra representative of the divalent and monovalent cation-exchanged clays, respectively. The clay bands are at 3677 cm^{-1} (octahedral OH stretching mode), 1200 to 900 cm^{-1} (SiO stretching mode), 680 to 611 cm^{-1} (octahedral stretching mode), and 550 to 450 cm^{-1} (SiO bending mode). The Pb-exchanged hectorite shows a broad band at about 1391 cm^{-1}, which has not been assigned. The hydration water OH stretching band extends from 3600 to 3150 cm^{-1}, and the H_2O bending mode is at 1631 cm^{-1}. The fundamental modes ν_1^{CH}, ν_2^{CC}, ν_9^{CHCl}, ν_{10}^{CCl}, and ν_{11} of CDE in the adsorbed phase at 3086, 1588, 1293, 843, and 702 cm^{-1}, respectively, are observable, although ν_{11} overlaps with the octahedral stretching band of the clay. The ν_2^{CC} band of CDE slightly overlaps with the H_2O bending mode.

In all the clay samples, regardless of the cation type, the fundamental modes of CDE in the adsorbed phase are always observed at exactly the same frequencies. The frequencies of CDE in the gas phase observed by us are the same as those in Herzberg (1947) within about 3 cm^{-1}. The ν_1^{CH} and ν_2^{CC} frequencies are essentially unchanged in the adsorbed and gas phases. The ν_9^{CHCl} (asymmetric CHCl bending mode) and ν_{10}^{CCl} (asymmetric CCl stretching mode) frequencies of CDE in the adsorbed phase are lowered by 10 and 14 cm^{-1} with respect to the gas phase, indicating that the adsorption process involves interaction of chlorine with its molecular environment, that is, either directly with the exchangeable cations or the water molecules hy-

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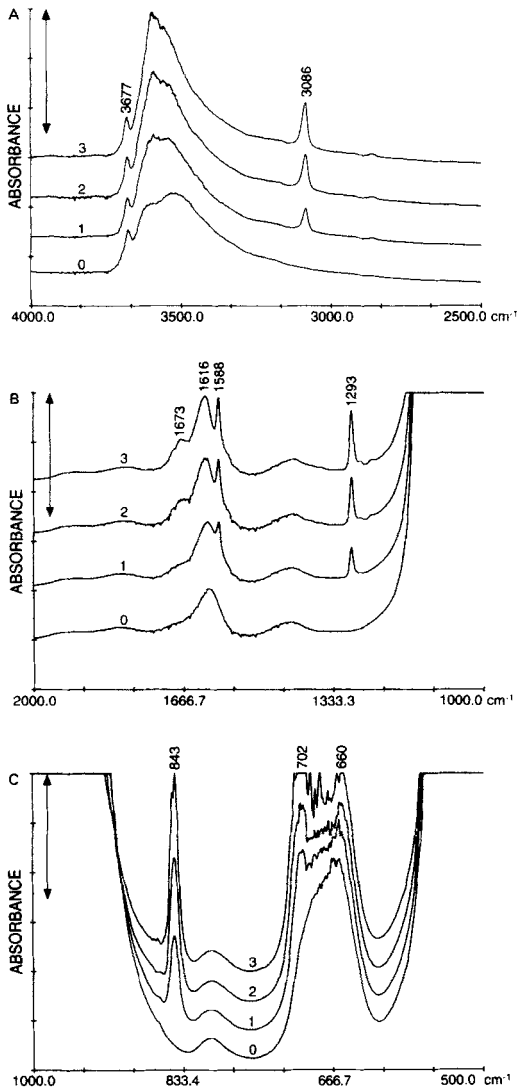


Figure 2. Stacked plots of A) IR spectra of CDE adsorbed by Cd-exchanged hectorite recorded between 4000 and 2500 cm^{-1}; B) IR spectra of CDE adsorbed by Cd-exchanged hectorite recorded between 2000 and 1000 cm^{-1}; and C) IR spectra of CDE adsorbed by Cd-exchanged hectorite recorded between 1000 and 500 cm^{-1}. [↕ = 1 absorbance unit; the number of CDE molecules adsorbed in mmol/g (n ads) from bottom to top is 0 = 0, 1 = 1.03, 2 = 1.46, and 3 = 1.88]

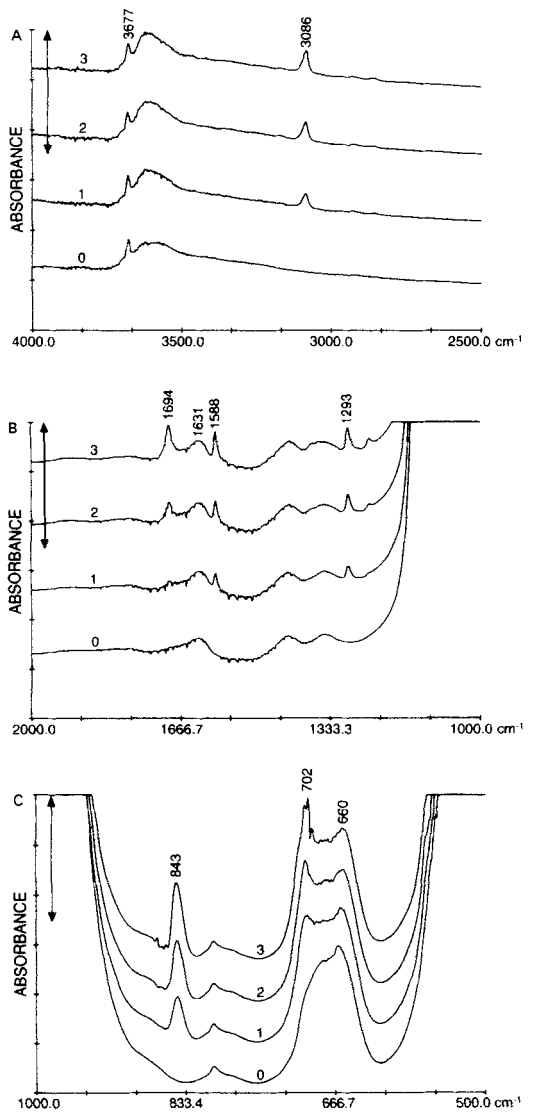


Figure 3. Stacked plots of IR spectra of A) CDE adsorbed by Ag-exchanged hectorite recorded between 4000 and 2500 cm^{-1}; B) CDE adsorbed by Ag-exchanged hectorite recorded between 2000 and 1000 cm^{-1}; and C) CDE adsorbed by Ag-exchanged hectorite recorded between 1000 and 500 cm^{-1}. (↕ = 1 absorbance unit; the number of CDE molecules adsorbed in mmol/g (n ads) from bottom to top is 0 = 0, 1 = 0.55, 2 = 0.92, and 3 = 1.24)

drating these cations. However, the fact that the frequencies obtained when comparing the fundamental mode frequencies of CDE in the adsorbed and gas phases do not depend on the nature of the exchangeable cation suggests that the main interaction is with the hydration water molecules. In fact, the shape of the corresponding hydration water OH stretching band changes as the number of adsorbed CDE molecules increases. In the starting clay material (i.e., prior to CDE adsorption), the spread of the hydration water OH stretching mode is considerably larger than in the clay having adsorbed a sizeable amount of CDE. In other words, the center of gravity of the hydration water OH stretching vibration shifts toward a higher wavenumber as the number of adsorbed CDE molecules increases. This is very apparent for the Cd-exchanged clay sample (Figure 2A) and for clays saturated with other divalent cations. For clays saturated with monovalent cations that have much less hydration water, this spectral modification is less apparent (Figure 3A). Normally, the hydration water OH stretching mode increases in frequency, whereas

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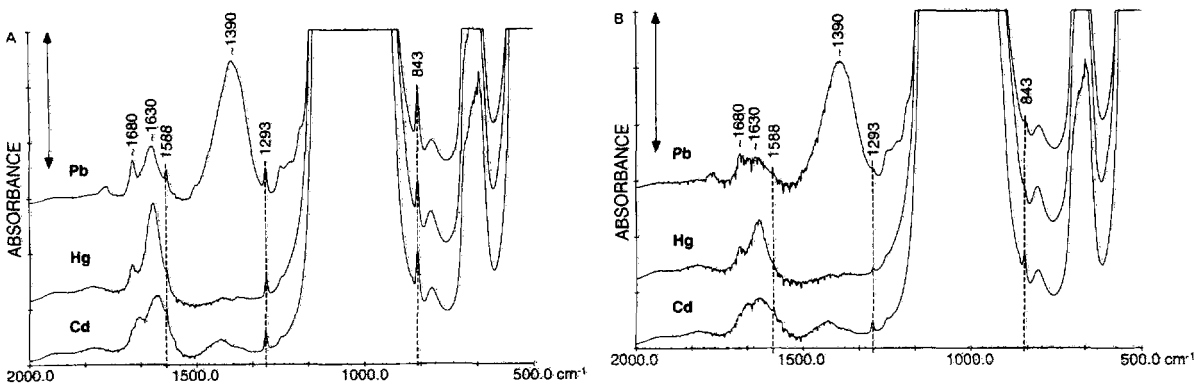


Figure 4. IR spectra of A) the Pb, Hg, and Cd-exchanged hectorites upon desorbing CDE under vacuum at room temperature for 5.5 hr; and B) the Pb, Hg, and Cd-exchanged hectorites upon desorbing CDE under vacuum at 100°C for an additional 4 hr. (↕ = 1 absorbance unit)

the water bending mode decreases in frequency as an OH group gets less hydrogen bonded (Pimentel and McClellan, 1960). If the CCl and the water OH interacts, the asymmetric CCl stretch should shift towards lower frequency with respect to the gas phase, while the OH stretch which is less hydrogen bonded to chlorine than to oxygen should shift toward higher frequency. Our main observations are in agreement with these predictions. Moreover, a weak interaction between CH_3CCl_3 and surface OH group on alumina has been assigned to hydrogen bonding by Ballinger and Yates (1992).

Upon increasing CDE adsorption, the water bending mode is surprisingly split into a doublet with the broad band initially at 1631 cm^{-1} (or at 1616 cm^{-1} for Cd-exchanged hectorite) and the new band at 1694 cm^{-1} (or at 1673 cm^{-1} for Cd-exchanged hectorite), which is about 60 cm^{-1} higher in wavenumber (Figures 3B or 2B). This band at 1694 cm^{-1} is not observed upon adsorption of TDE, as will be shown later. We do not offer an assignment for this band, but we note that on a Cu(II)-montmorillonite, Boyd and Mortland (1989) have observed the formation of carbonyl and/or carboxyl stretching bands between 1700 and 1750 cm^{-1} when TDE was refluxed over dehydrated clay.

It is interesting to compare the IR spectra obtained while desorbing CDE under vacuum at room temperature for 5.5 hr (Figure 4A) with those at 100°C for an additional 4.0 hr (Figure 4B), in order to verify if any chemisorbed CDE was left in the dehydrated clay interlayer. As shown in the stacked plots of infrared spectra in the frequency domain between 2000 to 500 cm^{-1}, CDE desorbs upon outgassing at room temperature (see the intensity of ν_{10}^{CCl} at 843 cm^{-1}), but it is not removed from the Pb, Hg, and Cd-exchanged hectorites. Accordingly, the H_2O bending mode at 1631 cm^{-1} and the band at 1694 cm^{-1} decrease in intensity. Heating the clay film at 100°C during outgassing substantially reduces the remaining CDE as well as the intensity of the H_2O bending mode at 1631 cm^{-1} and the band at 1694 cm^{-1}. The same observations were also made for the Ca, Na, and Ag-exchanged hectorites.

Qualitative analysis of the infrared spectra of adsorbed trans-1,2-dichloroethylene (TDE)

In view of the CDE adsorption findings, two possibilities exist for the adsorption mechanism: 1) TDE will not be adsorbed because of its much smaller dipole moment, in which case we will conclude that the main driving force for the CDE adsorption is the dipole-dipole interaction between the CDE and water molecules hydrating the cations; or 2) TDE adsorption will occur to a degree comparable with that obtained for CDE accompanied by a downward shift of the asymmetric CCl stretching mode. In such an event, we would conclude that the main driving force for CDE and TDE adsorption is hydrogen bonding between the CCl of chloroethenes and the OH of water molecules in the inner sphere coordination of the exchangeable cations.

Figure 5 shows the ν_9^{CH}, ν_{10}^{CHCl}, and ν_{12}^{CCl} fundamental modes of TDE in the adsorbed phase of the Cd-exchanged hectorite at 3086, 1202, and 808 cm^{-1}, respectively. The frequencies of TDE in the gas phase observed by us are the same as those in Herzberg (1947) within about 3 cm^{-1}. The asymmetric CHCl bending (ν_{10}^{CHCl}) and asymmetric CCl stretching (ν_{12}^{CCl}) frequencies of TDE in the adsorbed phase overlap partially with the clay bands. In all the clay samples, independent of the cation type, the fundamental modes of TDE in the adsorbed phase are always observed at the same frequencies. The ν_9^{CH} and ν_{10}^{CHCl} frequencies of TDE essentially do not change in the adsorbed and gas phases, while the ν_{12}^{CCl} (asymmetric CCl stretching frequency) in the adsorbed phase is lowered by 12 cm^{-1} with respect to the gas phase, as observed for CDE. The fact that the ν_{12}^{CCl} frequency at 808 cm^{-1} in the adsorbed phase is always exactly the same regardless of the nature of the exchangeable cations indicates that

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the adsorption process must involve interaction of chlorine with the water molecules hydrating the cations in the clay interlayer rather than directly with these cations. The main difference from the CDE case, shown in Figure 2, is the absence of splitting of the 1631 cm^{-1} band upon adsorption of TDE.

Degassing at room temperature for 5.5 hr decreased the amount of adsorbed TDE, but did not remove it completely from the Pb, Hg, Cd, Ca, Ag, and Na-exchanged hectorites. Accordingly, the H_2O bending mode at 1631 cm^{-1} decreased in intensity. Heating the clay film at 100°C for an additional 4.0 hr during degassing substantially reduced the remaining TDE as well as the intensity of the water bending vibration at 1631 cm^{-1}. Thus, the thermal behavior was the same as that observed in the CDE case.

In summary, the qualitative analysis of the IR spectra reveals that the main driving force for CDE and TDE adsorption is hydrogen bonding between the CCl of chloroethenes and the OH of water molecules hydrating the exchangeable cations in the clay interlayer. This interaction shifts the asymmetric CCl stretching mode towards a lower frequency. The center of gravity of the hydration water OH stretching vibration shifts toward a higher wavenumber. For clays saturated with monovalent cations having much less hydration water, this spectral modification is less pronounced. In general, the qualitative infrared study provides identical features for adsorbed TDE and CDE and similar modification of the OH stretch.

Quantitative analysis of the infrared spectra

The integrated absorbances (I) of the ν_1^{CH}, ν_9^{CHCl}, and ν_{10}^{CCl} modes of CDE or the ν_9^{CH}, ν_{10}^{CHCl}, and ν_{12}^{CCl} modes of TDE, divided by the masses of the corresponding clay films, have been plotted with respect to the number of adsorbed CDE or TDE molecules in order to determine their absorption coefficients, ϵ. The correlations between I and n ads (the total number of organic molecules adsorbed per unit mass) were generally quite good (i.e., correlation coefficient, $R^2 > 0.97$) and the absorption coefficients are shown in Tables 1 and 2. The absorption coefficients appeared to be systematically larger when CDE or TDE was adsorbed by clays saturated with divalent cations.

The average integrated absorbances of the OH region at every adsorption equilibrium pressure, A(OH) ($\Delta\nu$ between 3831 and 3149 cm^{-1} in Tables 1 and 2) was mostly contributed by the hydration water OH stretching vibration. It varied with cation type since water molecules remaining after the sample pretreatment were mainly the ones strongly coordinated to the cation. As illustrated in the CDE case (Figure 6), a reasonable correlation exists between A(OH) and the BET monolayer content of CDE or TDE adsorbed by the clay. These monolayer contents are obtained from the adsorption isotherms discussed in the next section. If

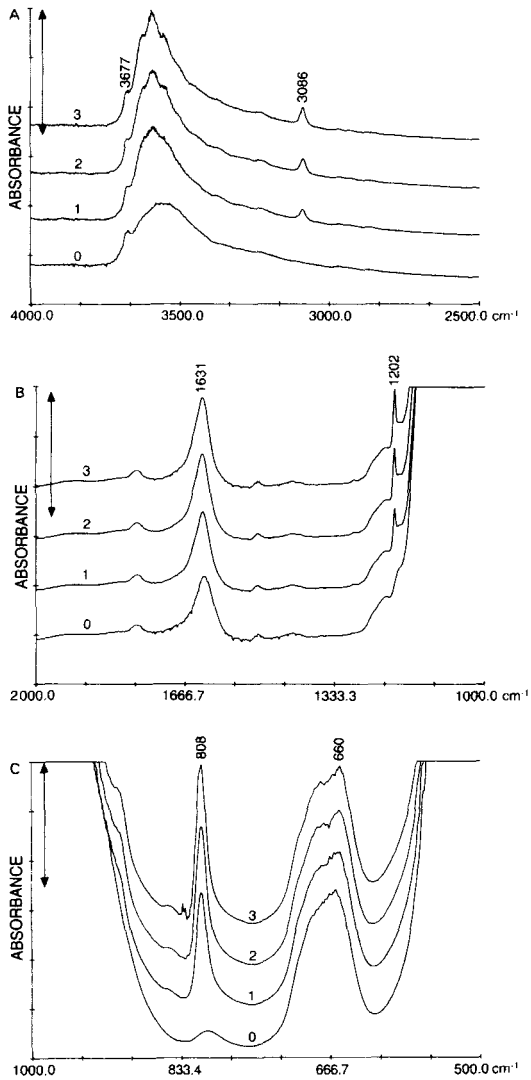


Figure 5. Stacked plots of IR spectra of A) TDE adsorbed by Cd-exchanged hectorite recorded between 4000 and 250 cm^{-1}; B) TDE adsorbed by Cd-exchanged hectorite recorded between 2000 and 1000 cm^{-1}; and C) TDE adsorbed by Cd-exchanged hectorite recorded between 1000 and 500 cm^{-1}. (1 = 1 absorbance unit; the number of TDE molecules adsorbed in mmol/g (n ads) from bottom to top is 0 = 0, 1 = 0.82, 2 = 0.99, and 3 = 1.15)

appreciable CDE or TDE and H_2O competition in the cation coordination shell had occurred, then we would not have observed this linear regression. Quantitative analysis of the IR spectra for TDE was affected by a higher experimental uncertainty due to the more serious overlapping between the clay bands and both the asymmetric CHCl bending (ν_{10}^{CHCl}) and CCl stretching (ν_{12}^{CCl}) vibrations.

CDE or TDE adsorption and H_2O desorption

CDE and TDE adsorption isotherms are shown in Figures 7A and 7B, respectively. Clays saturated with

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Table 1. Absorption coefficients (ϵ) of the CDE's ν_1^{CH}, ν_9^{CHCl}, and ν_{10}^{CCl} fundamental modes and integrated absorbances of the hydration water OH stretching band (A(OH)).

Clay	ϵ (ν_1^{CH}) (cm^{-1} mol^{-1})	ϵ (ν_9^{CHCl}) (cm^{-1} mol^{-1})	ϵ (ν_{10}^{CCl}) (cm^{-1} mol^{-1})	A(OH) (a.u.)
$\Delta\nu$	3135–3037 cm^{-1}	1314–1272 cm^{-1}	857–829 cm^{-1}	3831–3149 cm^{-1}
Na	0.49 ± 0.01	0.25 ± 0.02	1.10 ± 0.02	12.5 ± 0.3
Ag	0.48 ± 0.04	0.17 ± 0.01	0.90 ± 0.05	11.9 ± 0.5
Pb	0.66 ± 0.02	0.23 ± 0.01	1.00 ± 0.03	21.9 ± 1.9
Ca	0.60 ± 0.02	0.28 ± 0.01	1.10 ± 0.03	23.4 ± 1.6
Hg	0.77 ± 0.03	0.30 ± 0.06	0.97 ± 0.06	30.2 ± 1.5
Cd	0.78 ± 0.02	0.36 ± 0.01	1.40 ± 0.02	28.8 ± 1.9

$\Delta\nu$ is the integration domain.

divalent cations adsorb about 55% more CDE or about 35% more TDE than those saturated with monovalent cations. The adsorption power for both CDE and TDE decreases in the following order:

$$Hg^{2+} \simeq Cd^{2+} > Ca^{2+} \simeq Pb^{2} \gg Na^{+} > Ag^{+}.$$

When the order of CDE and TDE adsorption by clays saturated with divalent cations is compared to the corresponding absolute values of the enthalpies of hydration (Cotton and Wilkinson, 1972), the trend obtained is indeed consistent. The enthalpies of hydration of Hg^{2+}, Cd^{2+}, Ca^{2+}, and Pb^{2+} have absolute values of -1824, -1807, -1577, and -1481 kJ/mol, respectively, with an uncertainty of ~20 kJ/mol. These absolute values of the enthalpies of hydration are based on the assignment of -1091 ± 10 kJ/mol to H^+ (Halliwell and Nyburg, 1962). This correlation supports our observation that the quantity of chloroethenes adsorbed is a function of the degree of cation hydration in the clay interlayer space. However, the order of chloroethenes adsorption by clays saturated with monovalent cations is opposite of their corresponding enthalpies of hydration, which have absolute values of -406 and -473 kJ/mol for Na^+ and Ag^+, respectively, with an uncertainty of ~10 kJ/mol.

Table 3 contains the BET (Brunauer *et al.*, 1938) monolayer contents (n_m) of TDE and CDE used in Figure 6. The water desorption isotherms (the total number of water molecules desorbed per unit mass, n^w desorb) have also been measured per the method described in the Appendix. In all the clay samples, a linear relationship ($R^2 > 0.97$) exists between the number of adsorbed CDE or TDE and the number of desorbed water molecules. The proportionality coefficients, C, are shown in Table 3. Values obtained for C showed that about 0.32 or 0.37 mole of water was desorbed for each mole of CDE or TDE adsorbed, respectively, by clays saturated with monovalent cations, while the C values were about 0.22 for clays saturated with divalent cations. The important consequence of these observations is that while CDE or TDE molecules interact with water molecules in the inner sphere coordinations of the exchangeable cations as suggested by the IR study, they do not displace a significant number (i.e., <1%) of these water molecules. Otherwise, all the C values would approach 1, which they didn't. Probably, the water molecules which desorb upon CDE or TDE adsorption are loosely bound to the inner sphere coordinations of the cations. More water molecules are displaced during the CDE or TDE adsorption in clays saturated with monovalent cations than those saturated with divalent cations, since the C values for the former were on the average 30% larger than the latter (Table 3).

The comparison between the amounts of CDE and TDE adsorbed by the clay indicates that the adsorption of TDE was ~30% less extensive than that of CDE on clays saturated with divalent cations. However, clays saturated with monovalent cations possessed essen-

Table 2. Absorption coefficients (ϵ) of the TDE's ν_9^{CH}, ν_{10}^{CHCl}, and ν_{12}^{CCl} fundamental modes and integrated absorbances of the hydration water OH stretching band (A(OH)).

Clay	ϵ (ν_9^{CH}) (cm^{-1} mol^{-1})	ϵ (ν_{10}^{CHCl}) (cm^{-1} mol^{-1})	ϵ (ν_{12}^{CCl}) (cm^{-1} mol^{-1})	A(OH) (a.u.)
$\Delta\nu$	3135–3037 cm^{-1}	1216–1188 cm^{-1}	864–738 cm^{-1}	3831–3149 cm^{-1}
Na	0.33 ± 0.05	0.24 ± 0.04	1.75 ± 0.20	14.4 ± 0.4
Ag	0.34 ± 0.13	0.17 ± 0.06	1.38 ± 0.30	13.3 ± 1.8
Pb	0.44 ± 0.12	0.40 ± 0.08	2.93 ± 0.75	18.1 ± 1.3
Ca	0.39 ± 0.05	0.40 ± 0.05	1.86 ± 0.44	21.4 ± 0.5
Hg	0.40 ± 0.10	0.37 ± 0.03	2.26 ± 0.39	26.8 ± 1.7
Cd	0.37 ± 0.06	0.32 ± 0.04	2.53 ± 0.29	20.5 ± 1.1

$\Delta\nu$ is the integration domain.

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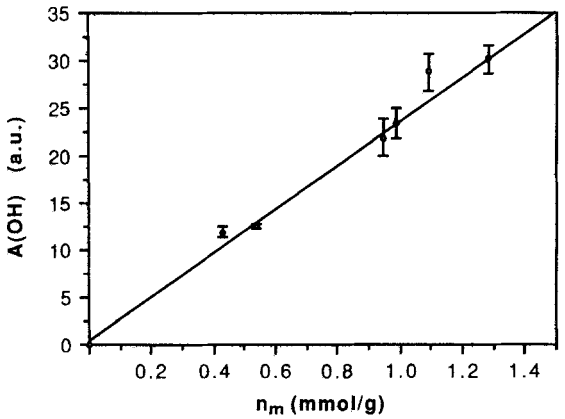


Figure 6. Linear correlation between the hydration water OH stretching integrated absorbance, A(OH), and the CDE monolayer content, n_m.

Table 3. BET monolayer contents (n_m) of CDE and TDE and proportionality coefficients (C) of the linear relationship n ads vs n^w desorb.

Clay	n_m (CDE) (10^{-3} mol g^{-1})	n_m (TDE) (10^{-3} mol g^{-1})	C (CDE)	C (TDE)
Na	0.54	0.54	0.326	0.393
Ag	0.43	0.44	0.310	0.341
Ca	0.99	0.69	0.209	0.219
Cd	1.09	0.80	0.185	0.182
Pb	0.95	0.74	0.248	0.219
Hg	1.28	0.80	0.236	0.243

See Figures 7A and 7B for the adsorption isotherms of CDE and TDE, respectively.

tially the same adsorption affinity toward both CDE and TDE. The amount of CDE or TDE adsorbed by the clay depends on the degree of hydration of the exchangeable cations in the clay interlayer. It is a well known fact that there are significantly more H_2O molecules in the clays saturated with divalent cations than the ones with monovalent cations (Grim, 1953). As expected, the clays saturated with monovalent cations (Na^+ or Ag^+) are less hydrated than those saturated with divalent cations (Hg^{2+}, Pb^{2+}, Ca^{2+}, or Cd^{2+}). The estimated 30% difference between the amounts of CDE and TDE retained by the clays saturated by divalent cations may be due to steric effects and/or to differences in their dipole moments. We may expect that the interactive forces between hectorite and molecules with a dipole moment (e.g., CDE) would be stronger than with TDE, resulting in greater retention of CDE. The preferential retention of bromohydrocarbon molecules with a dipole moment (e.g., the gauche conformer of EDB) during sorption/desorption in different clays with higher charge densities or effective dielectric constants suggested by Aochi *et al.* (1992) has been outlined earlier.

DISCUSSION AND CONCLUSIONS

Our findings suggest that the main driving force in the adsorption of chlorohydrocarbons by clays is the interaction between CDE or TDE and water molecules in the inner sphere coordinations of the exchangeable cations and that the cation-dipole interaction is a secondary effect. These conclusions are supported by results of the infrared spectroscopy and the volumetric adsorption studies. The CDE adsorption isotherms in Figure 7A show that the maximum values of adsorbed CDE at $P/P_o \simeq 0.7$ are approximately 2×10^{-3} and 1×10^{-3} mol/g for the clays saturated with divalent and monovalent cations, respectively. CDE could displace physisorbed water molecules which are loosely bound to the exchangeable cations into the vapor phase, by breaking hydrogen bonds between the water molecules

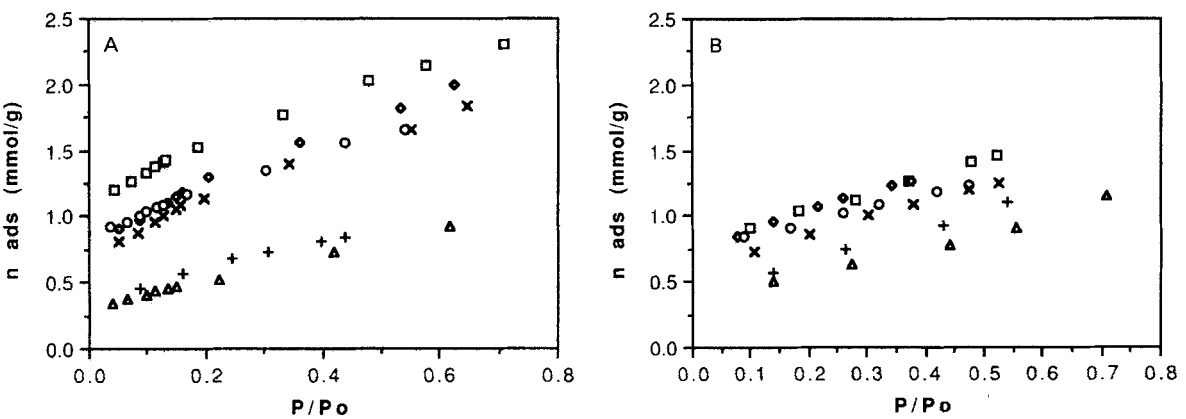


Figure 7. A) CDE adsorption isotherms at room temperature, where the adsorption power for CDE decreases in the following order: $Hg^{2+} \simeq Cd^{2+} > Ca^{2+} \simeq Pb^{2+} \gg Na^+ > Ag^+$. And B) TDE adsorption isotherms at room temperature. Note that the adsorption of TDE is ~30% less extensive than that of CDE on clays saturated with divalent cations. (□, ◇, ○, ×, +, and Δ denote Hg, Cd, Pb, Ca, Na, and Ag cations, respectively.)

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in the outer sphere coordination (i.e., the physisorbed H_2O molecules) and in the inner sphere coordination (i.e., the strongly coordinated H_2O molecules). Each CDE displaces only a small amount of water since most of the loosely bound water molecules in the clay interlayer have been removed during the sample pretreatment. In fact, the decrease in the percentages of hydration water (w/w) are only about 0.8% and 0.6% for the divalent and monovalent cation-exchanged clays, respectively. Considering that the total hydration water contents are on the order of 10%, these small decreases are not expected to affect significantly the intensity of the hydration water OH stretching and the H_2O bending vibrations at each equilibrium pressure. This is indeed consistent with our experimental results. On the other hand, if the adsorption driving force is the interaction between the water molecules hydrating the interlayer cations and CDE or TDE, then a linear correlation between the integrated absorbance of the hydration water OH stretching band, A(OH) and the BET monolayer content, n_m must exist and does, as seen in Figure 6.

It is our conclusion that clays saturated with divalent cations, such as Hg^{2+} or Cd^{2+}, adsorb more CDE or TDE than the monovalent cations, such as Na^+ or Ag^+, because the former cations have larger hydration shells than the latter. Since there are evidently twice as many monovalent exchangeable cations as divalent cations, the adsorption capacity of a Hg or Cd-exchanged clay towards CDE or TDE is per-cation about four times as large as that of a Na or Ag-exchanged clay. Therefore, the exchangeable cations in the clay interlayer play an indirect role in the sense that it is the size of their hydration shells that is important. If the asymmetric CCl stretching frequency was affected by the cation type, then a direct interaction could have been suggested; however, as emphasized earlier, this is not the case. The difference in the amounts of CDE and TDE retained by clays saturated with divalent cations may be caused by the presence of the effective dielectric constant in the medium or the charge effects on the surfaces of a smectite clay, the differences in the CDE/TDE dipole moments, and/or the steric effects.

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APPENDIX

To begin with, n_o molecules of the organic vapor are introduced in $(V_1 + v)$, where V_1 and v are the level 1 volume of the gas burette and the dead volume of the manifold in the system, respectively. After this introduction, v_R is opened to the system and the equilibrium pressure, P_1^{eq}, is measured. Equilibration time usually takes a few hours. Next, stopcock R_2 is closed and stopcock R_1 is opened (i.e., v_R is closed and v_D is opened). The mixture of organic vapor and water vapor is compressed into v_D by raising the level of mercury in the burette and then lowered back to the first level in which the pressure is now P_1^R. In the next stage, v_D is closed and v_R is opened and a new equilibrium pressure is obtained by lifting the mercury to level 2 in the gas burette. These manipulations are repeated up to the sixth level. Finally, with v_R and v_D closed, a new amount of organic vapor is introduced in the gas burette and the subsequent operations go on until the desired final level is reached in the same manner as after the first introduction of organic vapor.

We allow that P_{1i}^{eq} and P_{1i}^R are the pressures measured at any level i after the first introduction, while n_{o1} and n_{o2} are the first and second doses of organic vapor, respectively. At any level i, after the first introduction, the number of gaseous organic molecules remaining in the system is:

$$P_{1i}^R C_{1i}(V_i + v + v_D) + P_{1i}^o v_R C_{1i},$$

where $C_{1i} = (RT_{1i})^{-1}$, and $P_{1i}^o = P_{1i}^{eq} - P_{1i}^w$ is the partial pressure of organic vapor at equilibrium, and P_{1i}^w, the corresponding partial pressure of water. If n_{1i}^R and P_{1i}^o are:

$$n_{1i}^R = C_{1i}P_{1i}^o(V_i + v) + C_{1(i-1)}P_{1(i-1)}^R v_D$$

$$= C_{1i}P_{1i}^R(V_i + v + v_D) \quad \text{and}$$

$$P_{1i}^o = [n_{1i}^R - C_{1(i-1)}P_{1(i-1)}^R v_D]/C_{1i}(V_i + v),$$

respectively, then the total number of organic molecules adsorbed per unit mass is:

$$n_{1i}^o = [n_{o1} - (n_{1i}^R + P_{1i}^o v_R C_{1i})]/m + n_{1(i-1)}^o \text{ ads}/m$$

where m is the mass of clay powder in the system. The initial degree of hydration of the clay sample depends on the extent of outgassing before the start of each experiment (i.e., the sample pretreatment).

At any level i, the number of water molecules desorbed between step i and (i − 1) is:

$$n_{1i}^w = C_{1i}P_{1i}^w(V_i + v + v_R) - C_{1(i-1)}P_{1(i-1)}^w v_R$$

and the total number of water molecules desorbed per unit mass is:

$$n_{1i}^w \text{ desorb} = \sum_{i=1}^{i} n_{1i}^w/m.$$

After the second introduction of organic vapor in the burette, all the subscripts 1i switch into 2i and the same reasonings apply, except that the n_{o1} must be replaced by $(n_{o2} + C_{16}P_{16}^o v_R)$ and that the adsorption of organic vapor per unit mass becomes:

$$n_{2i}^o \text{ ads} = n_{16}^o \text{ ads} + [n_{o2} + C_{16}P_{16}^o v_R - (n_{2i}^R + P_{2i}v_R C_{2i})].$$

Accordingly,

$$n_{2i}^w \text{ desorb} = \sum_{i=1}^{6} n_{1i}^w/m + \sum_{i=1}^{i} n_{2i}^w/m$$

Note that $P_{2(i-1)}^R = P_{16}^R$ and that $P_{2(i-1)}^w = P_{16}^w$, while $P_{1(i-1)}^R = 0 = P_{1(i-1)}^w$ when i=1.

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