

INTERACTION OF CHLORDIMEFORM WITH CLAY MINERALS

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Abstract—The adsorption-desorption of the cationic pesticide chlordimeform from aqueous solutions on montmorillonite, kaolinite, illite, and vermiculite appears to be a cation-exchange process coupled with the coadsorption of neutral molecules and the extraction of Al from the structure of the mineral. Chlordimeform adsorption on montmorillonite, illite, and vermiculite by cation exchange is an irreversible process, whereas chlordimeform adsorbed on kaolinite is weakly bonded to the clay and easily removed by washing with water. X-ray powder diffraction and infrared spectroscopic data show that chlordimeform cations are adsorbed in the interlamellar spaces of montmorillonite at charge sites, lying in a flat position in contrast to kaolinite, illite, and vermiculite, where they adsorb on external surfaces or charge sites close to the crystal edges.

Key Words—Adsorption, Chlordimeform, Illite, Kaolinite, Montmorillonite, Pesticide, Vermiculite.

INTRODUCTION

The phenomenon of adsorption-desorption by clay minerals appears to be one of the most important factors affecting the fate and behavior of pesticides in soils (Bailey and White, 1970; Mortland, 1975). Because expanding layer silicates are negatively charged, cationic pesticides that are adsorbed by cation exchange ultimately reside in the interlayer space as exchangeable cations. Once adsorbed, a particular compound may be easily displaced, displaced with difficulty, or not at all. The last two cases are of special interest from the standpoint of bound or unavailable residues (White, 1976). This type of behavior has been shown for the cationic pesticides diquat and paraquat (Knight and Tomlinson, 1967; Weed and Weber, 1969; Hayes *et al.*, 1975).

Numerous studies on adsorption of organic cations (non-pesticides) by clays have been reviewed by Mortland (1970) and Theng (1974). Organic cations are adsorbed on clays by a cation-exchange reaction wherein electrostatic (coulombic) and van der Waals attractive forces play an important role (Hendricks, 1941; Grim *et al.*, 1947). The van der Waals forces are responsible for adsorption in excess of the cation-exchange capacity (CEC) of clays (Grim *et al.*, 1947). Vansant and Uytterhoeven (1973), studying adsorption of several organic cations on montmorillonite, reported that the amounts adsorbed were equal to or greater than the CEC depending on their pKa. While many studies have been carried out on the interaction of non-ionic pesticides with clays, the only cationic pesticides studied from the standpoint of their interaction with clays are diquat and paraquat (Weber, 1972; Green, 1974), both of which are divalent cations.

In this paper the adsorption-desorption of the cationic pesticide chlordimeform (N'-[4-chloro-2-methylphenyl]-N,N-dimethyl methanoimidamide hy-

drochloride) on montmorillonite saturated with Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, and Fe³⁺, and Na-kaolinite, K-illite, and Mg-vermiculite is reported. Iwan and Goller (1975) and Iwan *et al.* (1976) found that substantial amounts of chlordimeform added to soil were not degraded and postulated that the non-extractable portion of the pesticide was bound to soil constituents. However, no attempt has yet been made to elucidate the mechanism of chlordimeform retention in soils. Earlier studies on adsorption of chlordimeform by Na-, K-, Mg-, and Ca-montmorillonite (Perez Rodriguez and Hermosin, 1979) indicated a cation-exchange reaction as the fundamental interaction mechanism, although other mechanisms may be operable. The reversibility of pesticide adsorption by clays is very important from the point of view of unavailable residues in soils (White, 1976). Irreversible adsorption may produce "permanent" contamination and block an important portion of the CEC of the soils. Building on the work of Perez Rodriguez and Hermosin (1979), a more thorough study of the interaction mechanism between chlordimeform and soil clay minerals (montmorillonite, kaolinite, illite, and vermiculite) was undertaken.

EXPERIMENTAL

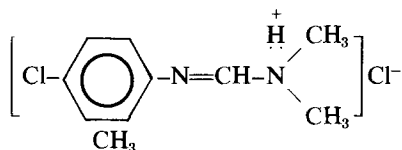
The clays used in this study were: Na-montmorillonite (Crook County, Wyoming, SWy-1) and kaolinite (well crystallized, Washington County, Georgia, KGa-1) both obtained from The Clay Minerals Society's Source Clays Repository; illite (Fithian, Illinois, API 35), obtained from Ward's Natural Science Establishment, Rochester, New York; and vermiculite from the Santa Olalla deposit in Huelva, Spain. Homoionic samples were prepared by saturating the natural clay with 1 N aqueous chloride solutions of the appropriate inorganic cation. The clay was washed by dispersing it with

Table 1. Adsorption-desorption data of chlordimeform on Na- and K-montmorillonite.

Adsorption isotherm data				Desorption data		
Chlordimeform equilibrium concentration (mmole/liter)	Chlordimeform adsorbed (mmole/g)	Cation released (meq/g)	Δ pH	Al extracted (μ eq/g)	With water: Chlordimeform desorbed (%)	With 0.05 N NaCl or KCl: Chlordimeform desorbed (%)
Na-montmorillonite						
0.0	0.15	0.20	2.3	1.6	3.6	4.0
0.8	0.64	0.65	1.6	1.7	9.3	8.6
5.1	0.92	0.76	1.4	2.5	—	—
11.4	1.11	0.96	1.3	3.0	11.8	10.8
20.9	1.15	0.88	1.4	4.0	—	—
39.0	1.16	0.98	1.8	3.8	12.8	12.6
46.5	1.14	0.98	1.9	3.8	—	—
K-montmorillonite						
0.2	0.47	0.38	1.3	2.3	3.3	3.1
1.9	0.61	0.47	0.9	2.5	21.7	22.9
5.4	0.94	0.80	0.9	2.6	—	—
10.6	1.04	0.91	1.1	2.9	21.7	21.1
21.2	1.09	0.91	0.6	3.1	—	—
31.2	1.12	0.91	0.8	3.0	19.7	23.5
46.5	1.15	0.91	0.9	2.8	25.2	26.0

distilled water until salt-free, air-dried, and ground to pass a AFNOR 20 sieve (mesh size of 0.08 mm).

Technical grade chlordimeform (99% purity) supplied by Shering Agro S.A. was used. This pesticide is soluble in water (50% by weight) and completely ionizes giving chlordimeform cation (CfH^+) and chloride anion. The molecular structure of chlordimeform hydrochloride (CfHCl) is shown below:



The adsorption isotherms of chlordimeform on the homoionic clays were carried out in triplicate by equilibrating 0.2 g of clay in 30 ml of aqueous solution of chlordimeform at 1 to 50 mmole/liter. Samples were shaken for 24 hr at 25°C. After equilibration, the suspensions were centrifuged and the supernatants analyzed spectrophotometrically by UV absorption at 240 nm to determine the chlordimeform concentration. The amounts of chlordimeform adsorbed were calculated from the difference in concentration before and after equilibration. The amounts of inorganic cations released from the clay during the adsorption and the pH of the suspensions and solutions were determined. The inorganic cation concentrations in solutions were determined as follows: Na^+ and K^+ by flame photometry, Mg^{2+} , Ca^{2+} , and Fe^{3+} by atomic absorption spectrophotometry, and Al^{3+} by the colorimetric method of Pritchard (1967).

Desorption studies were carried out by adding 30 ml of distilled water or 0.05 N salt solution (NaCl, KCl,

MgCl_2 , or CaCl_2) to 0.2 g of clay-pesticide from the adsorption experiments and equilibrating them for 24 hr at 25°C. After the suspensions had been centrifuged and analyzed, the amounts of desorbed pesticide were determined from the change in the concentration before and after equilibration.

The interplanar spacings for the homoionic clays and their respective chlordimeform complexes were determined by X-ray powder diffraction (XRD), using several orders of the 00 l reflections. The measurements were made by the Debye-Sherrer method on samples which had been saturated with chlordimeform, washed with water and air-dried, mounted in glass capillary tubes, and evacuated at 10^{-6} mm Hg before sealing the tubes. Samples were also examined as oriented film supported on glass slides (non-evacuated).

The infrared absorption (IR) spectra for the clays and clay-pesticide complexes were recorded from 4000 cm^{-1} to 400 cm^{-1} using a Perkin-Elmer double-beam spectrophotometer. Samples were examined as self-supporting films (Na-, Mg-, Ca-montmorillonite and their complexes) or KBr discs (K-, Al-, and Fe-montmorillonite; Na-kaolinite, K-illite, Mg-vermiculite and their complexes).

The CEC of the homoionic clays (Na-montmorillonite, Na-kaolinite, K-illite, and Mg-vermiculite) were determined by exchange with ammonium acetate at pH = 7.

RESULTS AND DISCUSSION

Adsorption-desorption studies

The chlordimeform adsorption data for the homoionic montmorillonites are summarized in Tables 1–3. The relationship between solute concentration at equilibri-

Table 2. Adsorption-desorption data of chlordimeform on Mg- and Ca-montmorillonite.

Adsorption isotherm data				Desorption data		
Chlordimeform equilibrium concentration (mmole/liter)	Chlordimeform adsorbed (mmole/g)	Cation release (meq/g)	Δ pH	Al extracted (μ eq/g)	With water: Chlordimeform desorbed (%)	With 0.05 N NaCl or KCl: Chlordimeform desorbed (%)
Mg-montmorillonite						
0.0	0.18	0.10	0.9	1.2	3.1	1.8
0.9	0.69	0.65	1.9	1.1	11.2	13.5
4.0	0.90	0.77	1.4	2.2	15.7	22.2
9.3	0.89	0.89	1.3	2.2	—	—
14.9	0.90	0.75	2.0	2.8	—	—
25.3	0.93	0.84	1.9	3.0	15.7	18.8
44.5	0.93	0.89	1.0	3.1	14.0	19.8
Ca-montmorillonite						
0.0	0.18	0.19	0.9	2.2	6.0	1.3
1.6	0.85	0.91	1.8	2.1	20.0	16.4
3.6	0.97	0.95	1.7	2.5	23.9	19.2
8.4	1.02	0.99	1.9	2.2	16.8	20.5
14.4	0.98	1.01	1.6	2.5	—	—
32.9	1.01	0.95	1.6	3.1	—	—
44.6	1.05	0.99	1.5	3.1	23.8	25.7

um and the amount removed from the solution defines the adsorption isotherms. The shapes of these isotherms were of "L" type according to the classification of Giles *et al.* (1960), as showed earlier for Na-, K-, Mg-, and Ca-montmorillonite (Perez Rodriguez and Hermosin, 1979). This type of isotherm indicates a specific adsorption on homogeneous sites and a high affinity of the solute for the adsorbent. The data of these isotherms fit the Langmuir equation which has been used to obtain the values of adsorption maximum, X_m , summarized in Table 4. The X_m values are very similar

Table 3. Adsorption-desorption data of chlordimeform on Al- and Fe-montmorillonite.

Adsorption isotherm data				Desorption data
Chlordimeform equilibrium concentration (mmole/liter)	Chlordimeform adsorbed (mmole/g)	Cation released (meq/g)	Δ pH	With water: Chlordimeform desorbed (%)
Al-montmorillonite				
0.1	0.29	0.21	-1.6	0.6
0.8	0.64	0.38	-1.2	5.6
5.2	0.62	0.40	-1.2	—
11.6	0.53	0.43	-1.2	—
21.2	0.81	0.48	-0.9	7.4
31.2	0.41	0.50	-0.7	17.0
37.7	0.69	0.39	-0.6	14.0
Fe-montmorillonite				
0.0	0.30	0.09	-2.1	0.0
1.5	0.54	0.28	-2.2	1.7
4.9	0.66	0.36	-2.3	—
11.6	0.53	0.33	-2.1	—
17.0	0.71	0.38	-2.0	7.0
29.7	0.68	0.37	-1.9	9.0
41.9	0.52	0.33	-1.8	17.3

to the CEC of montmorillonite (110 meq/100 g) except for Al- and Fe-montmorillonites which are smaller.

The exchangeable inorganic cations initially present in the montmorillonite were released to the solution during chlordimeform adsorption, and the amounts of the outgoing cations (Tables 1-3) were found to be equivalent to or slightly smaller than the amounts of chlordimeform adsorbed. At the same time, during the adsorption process on Na-, K-, Mg-, and Ca-montmorillonite, the pH of the suspension underwent a slight change (from 5.5-6.0 to 6.0-6.5), but the pH of the chlordimeform solution increased (Tables 1 and 2) from 4.0-5.0 to 6.0-7.0. In these cases, it was observed that Al^{3+} was released to the solution (Tables 1 and 2).

The pH of the suspensions for Al- and Fe-montmorillonite (4 and 3, respectively) were almost constant during chlordimeform adsorption, whereas the pH of the solution decreased from 4.0-5.0 to 2.0-3.0 (Table 3). These decreases of the solution pH are probably due to the acidic character of the clays; the largest decreases were observed for Fe-montmorillonite which was more acidic. The pH of an aqueous suspension (0.2

Table 4. Values of adsorption maximum, X_m , calculated from Langmuir equation.

Clay	X_m (meq/100 g)
Na-montmorillonite	114
K-montmorillonite	112
Mg-montmorillonite	93
Ca-montmorillonite	103
Al-montmorillonite	65
Fe-montmorillonite	66

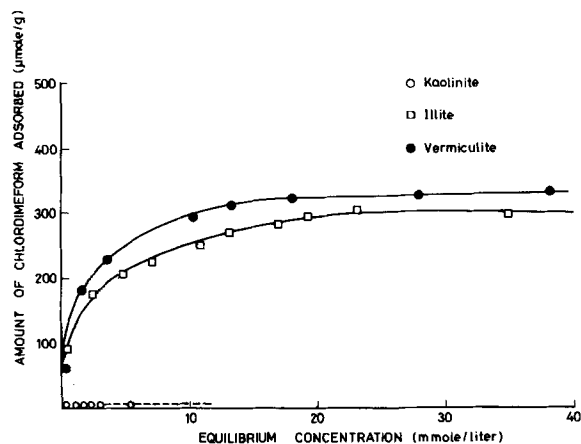


Figure 1. Adsorption isotherms of chlordimeform on (○) kaolinite, (□) illite, and (●) vermiculite at 25°C.

g of clay in 30 ml of distilled water) was 5.0 for Al-montmorillonite and 4.0 for Fe-montmorillonite.

These results indicate that the adsorption of chlordimeform from aqueous solution by montmorillonite is essentially a cation-exchange reaction between the initial exchangeable cations (X^{n+}) and the chlordimeform cations (CfH^+), that can be written as:



This reaction takes place in the interlayer space and on the external charged sites. As was predicted (Perez Rodriguez and Hermosin, 1979), additional reactions occur:

- (1) An exchange reaction between solution hydrogenium ions and the initial exchangeable cations, X^{n+} :



The protons for this reaction are provided by the solvent and/or the organic cation through hydrolysis. In some cases (Tables 1–3), the amount of the outgoing cation is greater than that of chlordimeform adsorbed. This process also contributes to pH changes.

- (2) An extraction of Al from the structure of the clay consumed protons producing an increase of the solution pH. This process would consume three protons for each Al released, but the change in the solution pH is also caused by the decrease of the chlordimeform concentration, by the hydrolysis of the released Al, and by the reaction shown by Eq. (2). For these reasons the changes of the solution pH and the amounts of the released Al are not uniform.
- (3) Non-cationic adsorption of the pesticide can be physical adsorption of neutral $CfHCl$ molecules or neutral Cf species. The $CfHCl$ species could be adsorbed by van der Waals forces on external and/

Table 5. Adsorption maximum values, cation released, and desorption percentages of chlordimeform on kaolinite, illite, and vermiculite.

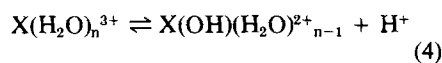
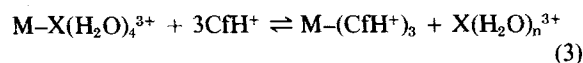
Clay	Chlordimeform adsorption maximum (mmole/g)	Cation released ¹ (meq/g)	Chlordimeform desorbed ¹ (%)
Na-kaolinite	0.01	0.01	90.0
K-illite	0.26	0.20	29.0
Mg-vermiculite	0.36	0.31	22.3

¹ Average values corresponding to the "plateau" points of the adsorption isotherm.

or internal surfaces. The Cf species could be co-adsorbed on internal and/or external surfaces associated with the organic cations (CfH^+) by sharing a proton (Mortland, 1970), or physically adsorbed by van der Waals forces. Regardless, the IR spectra showed only features corresponding to CfH^+ or $CfHCl$.

As described above, the behavior of chlordimeform interacting with montmorillonite corresponds with that proposed by Vansant and Uytterhoeven (1973) for alkyammonium cations with acidic character ($pK_a < 6$).

For Al- and Fe-montmorillonite the observed decrease of the solution pH after chlordimeform adsorption is due to the acidic character of these inorganic cations which hydrolyze after release to the solution. Also, these clays may be partially hydrogen-saturated due to hydrolysis of Al^{3+} and Fe^{3+} . Thus, the exchange process of chlordimeform would take place according to the following reactions:



and



As seen in Table 3, the difference between the amounts of chlordimeform adsorbed and the cations exchanged are much larger for Al- and Fe-montmorillonite than for other homoionic clays (Tables 1 and 2). This fact is attributed to the process described by Eq. (5) which does not take place in the other homoionic clays. The X_m values obtained from the Al- and Fe-montmorillonite isotherms (Table 4) are smaller than those for Na-, K-, Mg-, and Ca-montmorillonite due to the difficulty of exchanging Al^{3+} and Fe^{3+} and their hydrolysis products from the interlamellar exchange sites. From the X_m values (Table 4), the effectiveness of the chlordimeform cation in exchanging the inorganic cations decreases as follows: $Na^+ \sim K^+ > Ca^{2+} > Mg^{2+} > Al^{3+} \sim Fe^{3+}$.

The results of the desorption of chlordimeform adsorbed in montmorillonite are shown in Tables 1–3. The

Table 6. Cation-exchange capacities, adsorption maximum, and residual chlordimeform on clay minerals.

Clay	Chlordimeform adsorption maximum (meq/100 g)	CEC (meq/100 g)	Residual chlordimeform after successive washes ¹ (meq/100 g)
Montmorillonite	100.0	110	92.5
Vermiculite	36.0	126	23.0
Illite	25.0	35	9.8
Kaolinite	1.5	2	0.0

¹ The samples saturated with chlordimeform were washed until no further desorption occurred.

amounts of chlordimeform desorbed by washing with either water or salt solutions were equal (Tables 1 and 2) suggesting that the adsorption of chlordimeform by montmorillonite via cation exchange is an irreversible process. If this process were reversible, the amounts of chlordimeform desorbed by washing with aqueous salt solutions should be higher than those obtained with water. The desorption percentages obtained by both water or salt solutions were very low, about 10–25% as maximum values, which probably correspond to the chlordimeform being weakly bonded as neutral molecules or cations. The irreversibly adsorbed chlordimeform corresponds to the cations in the interlamellar spaces which are strongly bonded between the silicate layers by coulombic and van der Waals forces. This irreversibility may be associated with interlayer collapse upon adsorption, since the $d(001)$ for both air-dried and moist chlordimeform-montmorillonite complexes were equal.

The adsorption isotherms of chlordimeform on Na-kaolinite, K-illite, and Mg-vermiculite are shown in Figure 1. These isotherms are also of "L" type, according to Giles *et al.* (1960). The X_m values, the initial exchangeable cation released during adsorption, and the desorption percentages with water (as average values) of chlordimeform on kaolinite, illite, and vermiculite are summarized in Table 5.

The amounts of chlordimeform adsorbed on kaolinite are very small (Figure 1); the X_m value is slightly smaller than the CEC of this mineral but much lower than the X_m for the other clay minerals studied (Table 6). The amounts of inorganic exchangeable cation released from the clay during chlordimeform adsorption were equivalent to or slightly smaller than those of chlordimeform adsorbed. The desorption percentages obtained by washing the chlordimeform-kaolinite complex with water are very high, with almost all the chlordimeform adsorbed being removed (Table 5). These data suggest that the adsorption of chlordimeform on kaolinite is a cation-exchange reaction with chlordimeform cations, as well as an adsorption of some neutral molecules only on the external surface of the clay. The high desorption percentages indicate that

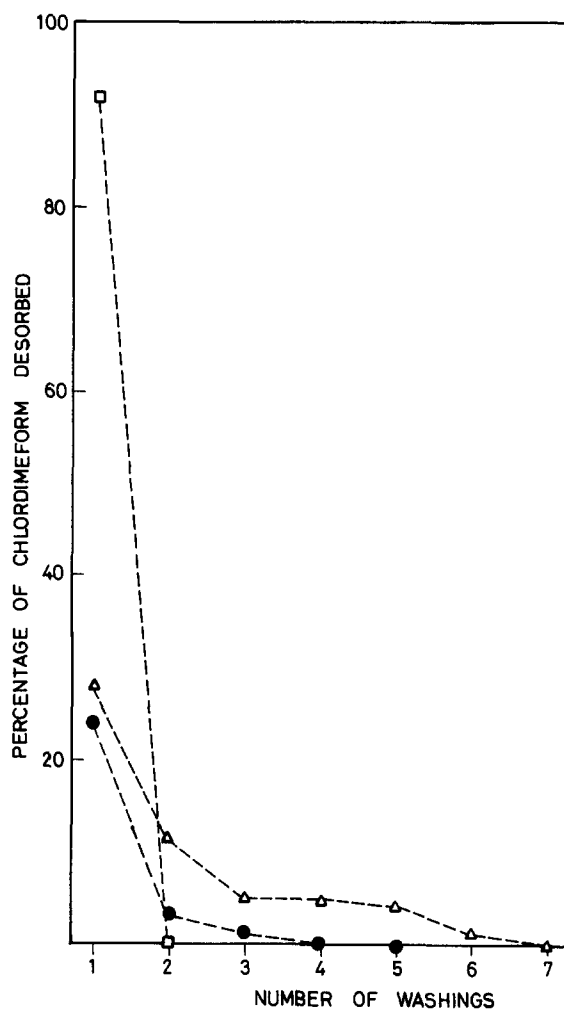


Figure 2. Desorption of chlordimeform by water washing the clay-chlordimeform complexes of (□) kaolinite, (△) illite, and (●) vermiculite.

the binding of the pesticide to the clay surface is very weak. Although a constant value, X_m , is reached at the "plateau" of the kaolinite isotherm, in this case there is not a total coverage of the surface, because from the surface area of this kaolinite ($13 \text{ m}^2/\text{g}$) and the adsorption maximum value ($14.7 \mu\text{mole}/\text{g}$), a coverage of $0.2 \text{ molecule}/100 \text{ \AA}^2$ can be calculated.

The adsorption of chlordimeform on illite and vermiculite is moderately high but lower than on montmorillonite. The X_m value for illite is similar to its CEC (Table 6) and, during the adsorption of chlordimeform, K^+ was released to the solution. The amount of outgoing K^+ was equivalent to or slightly smaller than the amount of chlordimeform adsorbed (Table 5). The adsorption data for vermiculite are similar to those for illite (Table 5); the adsorption maximum is slightly higher than that for illite but much lower than the corresponding CEC (Table 6). Although vermiculite is an expand-

Table 7. X-ray powder diffraction data of homoionic montmorillonites and their chlordimeform complexes.¹

Clay	Chlordimeform adsorbed (mmole/g)	d(001) (Å)	d(002) (Å)
Na-montmorillonite	0.00	11.3	—
	1.00	12.3	6.5
K-montmorillonite	0.00	11.2	—
	0.83	12.3	6.5
Mg-montmorillonite	0.00	14.5	7.5
	0.98	12.3	6.5
Ca-montmorillonite	0.00	14.5	7.8
	0.88	12.8	6.6
Al-montmorillonite	0.00	14.7	—
	0.77	12.8	6.6
Fe-montmorillonite	0.00	14.0	—
	1.04	12.8	6.6

¹ Lower data are for chlordimeform complexes.

ing mineral with high CEC and internal surface area, its adsorption of chlordimeform is much lower than that for montmorillonite. This suggests that the adsorption occurs only on the external surface and in interlayer spaces close to the crystal edges. The desorption percentages for illite and vermiculite (Table 5) are slightly higher than those for montmorillonite.

Thus, chlordimeform is adsorbed on illite and vermiculite by the same mechanisms described for montmorillonite; however the cation-exchange reaction does not take place on all charged sites, but only on those more available at the external surface and close to the crystal edges.

The desorption of chlordimeform adsorbed on the clay minerals was studied by successive washings with water of the chlordimeform-clay complexes. The percentage of chlordimeform rinsed out of the clay vs. the number of washings is plotted in Figure 2 for kaolinite, illite, and vermiculite. The data for montmorillonite were reported earlier (Perez Rodriguez and Hermosin, 1979). As was the case for montmorillonite, the percentage of chlordimeform desorbed decreased in the successive washes, and a point was reached after which no more chlordimeform was released (Figure 2). For kaolinite this point is prior to the second wash, since almost all chlordimeform adsorbed was removed in the first wash. For the other minerals when no more chlordimeform was released, different amounts of adsorbed pesticide remain (Table 6) which should correspond to the chlordimeform strongly bound to the clay surfaces as exchange cations.

It has been shown that the adsorption of numerous pesticides and organic compounds is limited in non-expanding minerals, taking place only on the external surfaces (Frissel and Bolt, 1962; Weber and Weed, 1968; Tomlinson *et al.*, 1969; Huang and Liao, 1970). Vermiculite usually exhibits an adsorption capacity similar

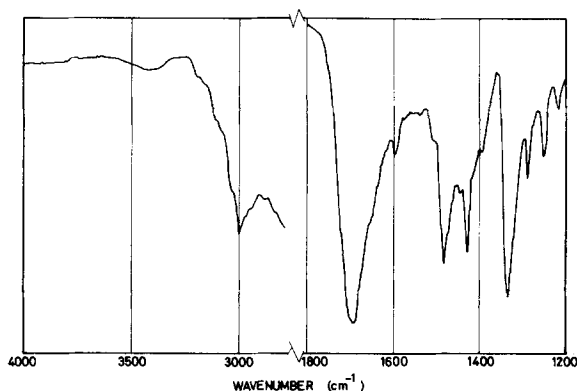


Figure 3. IR spectrum of chlordimeform hydrochloride in KBr disc.

to that of montmorillonite for organic compounds (Weiss, 1963; Johns and Sen Gupta, 1967; Rausell-Colom and Salvador, 1971; Loepfert *et al.*, 1979), but this capacity depends on the nature of the organic compound and generally requires more drastic conditions than montmorillonite (Lagaly and Weiss, 1969; Walker, 1975). It has been shown that some organic cations such as diquat and paraquat cannot displace magnesium cations from the interlamellar spaces of vermiculite (Hayes *et al.*, 1975) due probably to the high stability of the interlayer Mg-water sheet of this mineral (Mathieson and Walker, 1954). This may explain the weak adsorption of chlordimeform on vermiculite. It is postulated that initially chlordimeform cations are strongly bonded to the exchange sites close to the crystal edges, which may block the entrance of other cations into the interlamellar spaces.

X-ray powder diffraction (XRD) data

The values of d(001) spacings of the homoionic montmorillonites and the chlordimeform-montmorillonite complexes are listed in Table 7. The values of chlordimeform complexes of the different homoionic samples were 12.3 or 12.8 Å² which, according to Greener-Kelly (1955), indicate that the chlordimeform cations lie flat in the interlayer spaces with the plane of the aromatic ring parallel to the silicate layers.

The diffraction patterns of the chlordimeform-montmorillonite complex were also obtained for parallel oriented specimens (on glass slides) for both air-dried and moist samples (non-evacuated), which produced d(001) spacings of 14.8 and 15.2 Å, respectively. When the sample (oriented specimen or random powder in capillary tube) was heated at 110°C, taking precautions to avoid rehydration, a d(001) value of 12.8 Å² was found plus a rational series of reflections to d(004). The heated sample did not swell after either room exposure for several days or moistening with water.

The dimensions of the chlordimeform cation obtained from a scale model are: 17.5 × 4.5 × 4.4 Å³.

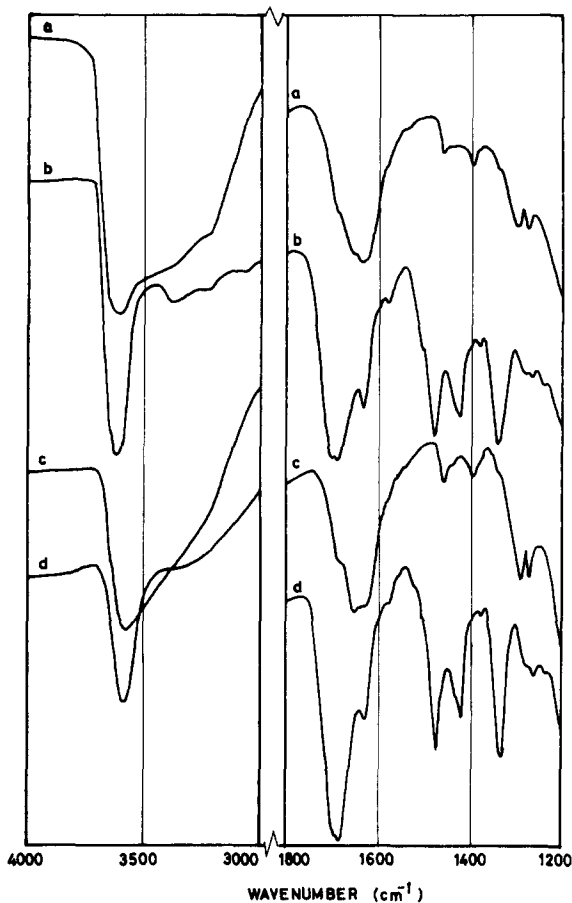


Figure 4. IR spectra of (a) Mg-montmorillonite and (b) its pesticide complex (films); (c) Ca-montmorillonite and (d) its pesticide complex (films).

Assuming a monolayer of chlordimeform cations to lie flat between the silicate layers, the value of the $d(001)$ spacing of the complexes should be $9.6 + 4.4 = 14.0 \text{ \AA}$, which agrees with the experimental values obtained for oriented samples (non-evacuated). The values of the

basal spacings listed in Table 7, as well as for the heated sample (110°C), are smaller because the vacuum and heating treatments remove the residual interlamellar water and the organic cations may approach the silicate layers more closely by coulombic and van der Waals forces, producing a "keying effect."

The $d(001)$ values obtained from air-dried and moist samples of the chlordimeform-montmorillonite complex were practically equal (14.8 and 15.2 \AA) indicating that chlordimeform cations collapse or fix the interlamellar spaces upon adsorption. Further expansion by water molecules is apparently restricted and, hence, the chlordimeform cation is essentially irreversibly adsorbed by montmorillonite. However, these forces were not sufficient to prevent expansion with glycerol.

Thus, XRD data suggest that a single layer of chlordimeform cations has been adsorbed in the interlayer region of the chlordimeform-montmorillonite complex in a parallel orientation. This orientation is favored because the surface area of a chlordimeform cation in that position (77 \AA^2) is practically equal to the equivalent area of montmorillonite (70 \AA^2) (Perez Rodriguez and Hermosin, 1979).

The basal spacings obtained for kaolinite, illite, and vermiculite (on evacuated powder samples) showed no change after chlordimeform adsorption. The chlordimeform-clay basal spacings were the same as those for the untreated clays (7.2 \AA for kaolinite, 9.9 \AA for illite, and 14.2 \AA for vermiculite), suggesting the absence of interlamellar adsorption. For vermiculite, the basal spacings would allow for interlayer adsorption, but this is very low when the small value of the X_m obtained from the adsorption isotherm is considered.

Infrared spectra

The infrared spectra (IR) of chlordimeform hydrochloride, clays, and pesticide-clay complexes are shown in Figures 3–5.

The chlordimeform-montmorillonite spectra (Figure 4 contains only the spectra of Mg- and Ca-montmoril-

Table 8. Infrared frequencies (cm^{-1}) of chlordimeform complexes¹ of montmorillonite, compared to the frequencies of chlordimeform hydrochloride.

Assignment	Chlordimeform hydrochloride	Chlordimeform complexes of montmorillonite saturated with different cations					
		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	Fe ³⁺
$\nu_{\text{C-H}}$	3000	—	—	—	—	—	—
$\nu_{\text{C-N}}$	1693	1695	1700	1692	1690	1700	1700
$\nu_{\text{C-C}}$ (aromatic ring)	1595	1580	—	1585	1590	—	—
	1509	1510	1510	1510	1510	1510	1510
	1482	1480	1480	1480	1480	1480	1480
$\nu_{\text{C-H}}$ (in H-CH ₃)	1429	1425	1430	1425	1425	1430	1430
$\nu_{\text{C-N}}$ (arom. amin.)	1335	1341	1345	1340	1340	1345	1345

¹ The amount of chlordimeform adsorbed and cation released are similar to those for the "plateau" points of each isotherm.

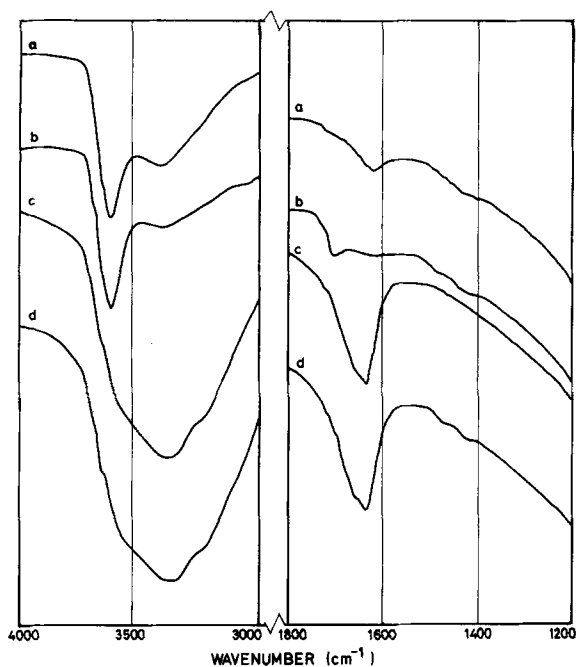


Figure 5. IR spectra of (a) illite, (b) illite-chlordimeform complex, (c) vermiculite, and (d) vermiculite-chlordimeform complex.

lonite because the spectra are basically equal for all homoionic montmorillonites) show large decrease of the absorption bands of stretching and bending modes of the water molecules associated with the exchangeable cations in the interlayer spaces, at 3420 cm^{-1} and 1650 cm^{-1} , respectively. The characteristic bands of the chlordimeform cation are present in the $1800\text{--}1200\text{ cm}^{-1}$ region, and their assignment and frequencies are summarized in Table 8 for chlordimeform hydrochloride and for chlordimeform-montmorillonite complexes.

These results suggest that (1) the water molecules associated with the inorganic exchangeable cations have been displaced by chlordimeform molecules to form a coordination complex with those cations, $X(\text{CfHCl})_m^{n+}$, in the interlamellar spaces, or (2) the inorganic exchange cations have been displaced with their hydration spheres from the interlamellar spaces by the chlordimeform cations which due to their size and hydrophobic nature, are not hydrated.

The first mechanism could explain the "weakly" adsorbed chlordimeform in addition to the physical adsorption. However, this mechanism is unlikely because the metal cation-chlordimeform interaction should produce changes in the IR patterns of the chlordimeform molecules, and these changes were not observed (Table 8). On the other hand, the large size of the chlordimeform molecule would make insertion into the coordination sphere of the exchangeable cations difficult for steric reasons.

The second mechanism is in accordance with the IR spectra as well as the adsorption-desorption and XRD data. The IR spectra of the chlordimeform-montmorillonite complexes show the characteristic bands of the chlordimeform cation which are listed in Table 8. The frequencies of the absorption bands for chlordimeform hydrochloride and chlordimeform adsorbed in montmorillonite are practically equal indicating that the pesticide is adsorbed as a cation in the interlamellar spaces by mechanism (2). According to Haque *et al.* (1970), the small shifts observed in the frequencies of the adsorbed chlordimeform, as compared to the free chlordimeform hydrochloride, result from the organocation-anionic clay surface interaction.

Figure 5 shows the IR spectra of illite, vermiculite, and their chlordimeform complexes after washing with water. The IR spectra of kaolinite and its complex are not shown because no difference was observed between them, indicating that no chlordimeform remained adsorbed after washing. The IR spectra for the illite and vermiculite complexes show that there is no interlamellar adsorption, since no changes in the stretching and bending frequencies of the interlayer water was observed. However, in these spectra small shoulders occur at 1700 , 1480 , and 1425 cm^{-1} which correspond to the chlordimeform adsorbed on the external surfaces of these minerals. The IR absorption bands of the chlordimeform adsorbed on illite and kaolinite are not as well resolved as those reported for the montmorillonite complex which may be due to the fact that KBr pellet method is not as sensitive a technique for surface chemistry studies by IR as self-supporting films. In addition, the amounts of chlordimeform adsorbed by illite and vermiculite were much smaller than those for montmorillonite.

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Резюме—Адсорбция-десорбция катионного пестицида, хлордиформа, из водяного раствора на монтмориллоните, каолините, иллите, и вермикулите является катионнообменным процессом, связанным с коадсорбцией нейтральных молекул и экстракцией Al из структуры минерала. Адсорбция хлордиформа на монтмориллоните, иллите, и вермикулите при помощи катионного обмена является необратимым процессом, тогда как хлордиформ, адсорбированный на каолините, есть слабо связанный с глиной и легко удаляемый при промывании водой. Результаты рентгеновской порошковой дифракции и инфракрасной спектроскопии показывают, что катионы хлордиформа адсорбируются в пространствах между тонкими пластинками монтмориллонита, в центрах заряда, расположенные плоско, в противоположности до каолинита, иллита, и вермикулита, в которых они адсорбируются на внешней поверхности центров заряда, в близости ребор кристалла. [E.C.]

Resümee—Die Adsorption-Desorption des kationischen Pestizides Chlordimeform aus wässrigen Lösungen an Montmorillonit, Kaolinit, Illit, und Vermiculit scheint ein Kationenaustauschprozeß zu sein, der gleichzeitig mit der Adsorption neutraler Moleküle und der Extraktion von Al aus der Mineralstruktur gekoppelt ist. Die Adsorption von Chlordimeform an Montmorillonit, Illit, und Vermiculit durch Kationenaustausch ist ein irreversibler Prozeß, während an Kaolinit adsorbiertes Chlordimeform nur schwach an den Ton gebunden ist und leicht mit Wasser ausgewaschen werden kann. Die Daten der Röntgenpulverdiffraktometrie und Infrarotspektroskopie zeigen, daß Chlordimeform-Kationen in den interlamellaren Zwischenräumen des Montmorillonites an Ladungsplätzen adsorbiert sind und in einer flachen Position liegen, während sie bei Kaolinit, Illit, und Vermiculit im Gegensatz dazu an äußeren Oberflächen oder an Ladungsplätzen nahe der Kristallkanten adsorbiert zu sein scheinen. [U.W.]

Résumé—L'adsorption-désorption du pesticide cationique chlordiméforme de solutions aqueuses sur la montmorillonite, la kaolinite, l'illite, et la vermiculite semble être un procédé d'échange de cations accouplé à la coadsorption de molécules neutres et à l'extraction d'Al de la structure du minéral. L'adsorption de la chlordiméforme sur la montmorillonite, l'illite, et la vermiculite par échange de cations est un procédé irréversible, tandis que la chlordiméforme adsorbée sur la kaolinite est faiblement liée à l'argile, et facilement enlevée par un lavage à l'eau. Les données de diffraction poudrée aux rayons-X, et de spectroscopie infrarouge montrent que les cations de chlordiméforme sont adsorbés dans les espaces interfeuilletés de la montmorillonite à des sites de charges, dans une position plate, contrairement à la kaolinite, l'illite, et la vermiculite, où ils semblent adsorber sur les surfaces externes ou sur des sites de charges près des bords des cristaux. [D.J.]