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# INTERACTIONS OF ALACHLOR WITH HOMOIONIC MONTMORILLONITES[1]

M. BOSETTO, P. ARFAIOLI AND P. FUSI[2]

**The adsorption of the herbicide Alachlor on montmorillonite saturated with different cations ($Al^{3+}$, $Cu^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$, $Na^+$, $Li^+$, $Rb^+$, and $Cs^+$) was studied in aqueous suspension. Equilibrium adsorption isotherms at 5° and 22°C fit the Freundlich relationship. A correlation between adsorption and the polarizing power of the exchangeable cation was observed. A decrease in temperature from 22° to 5°C resulted in an increase in adsorption except for Al-, Rb-, and Cs-montmorillonite. The isosteric heats of adsorption were also determined. The interaction of Alachlor with homoionic montmorillonites was also studied by FT-IR spectroscopy in an organic solvent. The results indicated that the molecule is adsorbed on monoionic montmorillonite by a coordination bond, through a water bridge, between C—O groups and the exchangeable cation of the clay. Further, the coordination strength is directly correlated with the polarizing power of the cation. X-ray diffraction analyses showed that the herbicide was able to penetrate the interlayer space of montmorillonite saturated with polyvalent cations. On moderate heating (70°C for 6 h) Alachlor adsorbed on Al-, Cu-, Ca-, Mg-, and $NH_4$-clay is partially decomposed to 2-chloro-2′,6′-diethylacetanilide.**

Alachlor (2-chloro-2′,6′-diethyl-N-methoxymethyl acetanilide) is a pre-emergence herbicide used for weed control in soybeans, corn, and peanuts. This herbicide is used extensively in Italy in common agricultural practice. The adsorption of Alachlor and other acetanilide herbicides was positively correlated with soil organic matter and clay content and inversely with herbicidal activity (Ballard and Santelmann 1973; Parochetti 1973; Weber and Peter 1982; Peter and Weber 1985).

Ballard and Santelmann (1973) found that clay content had less influence on Alachlor activity than other soil properties. Eshel (1969) reported that clay had a high capacity to inactivate Alachlor. In another study (Weber and Peter 1982), the herbicide was adsorbed on a Ca-organic matter and a Ca-montmorillonite in similar amounts at low equilibrium concentrations. At high equilibrium concentrations, much higher amounts of Alachlor were adsorbed by Ca-montmorillonite than Ca-organic matter.

Degradation is a slow biological process for Alachlor and other acetanilide herbicides (Sharp 1988), and only small amounts were mineralized in surface soils (Novick et al. 1986). It has been found that microbial degradation was of greater importance than volatilization and leaching for acetanilide herbicides (Ballard and Santelmann 1973; Beestman and Deming 1974; Zimdahl and Clark 1982). Alachlor was also reported to be degraded by a soil fungus, *Chaetomium globosum* (Tiedje and Hagedorn 1975). Hargrove and Merkle (1971) found that Alachlor was degraded to 2-chloro-2′,6′-diethylacetanilide when incubated at 46°C in a fine sandy loam; the degradation was ascribed to acidic soil water film surfaces. The same compound was also identified as the degradation product of Alachlor adsorbed on silica gel (Handa et al. 1973).

In spite of all these studies, there is a lack of information about the mechanism of adsorption of Alachlor on specific clay minerals and on the effect of the exchangeable cations.

The aim of this study was to investigate Alachlor adsorption on homoionic montmorillonite and to determine the effect of the exchangeable cations and temperature on its adsorption. Furthermore, we wanted to establish the mechanism through which adsorption and degradation of the herbicide on homoionic clays take place.

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## MATERIALS AND METHODS

### *Materials*

Alachlor with a solubility of 242 mg $L^{-1}$ (at 25°C) was supplied by Riedel de Haen Co. (Germany). The purity (99%) was confirmed by melting point (39.5–41.0°C), infrared spectra, and elemental analysis.

The 2-chloro-2′,6′-diethylacetanilide was prepared by treating Alachlor with 5 *N* aqueous HCl and acetone (4:1 v/v) at 45°C. After 4 days, the acetone was evaporated and a white compound precipitated. The product was recrystallized from hot water. The melting point (133°C), the C, H, and N content, and the infrared analysis were in agreement with the expected values for acetanilide.

The <2-μm fraction of Upton, Wyoming montmorillonite $(Si_{7.82}, Al_{0.18})(Al_{3.04}, Fe_{0.32}, Mg_{0.64})\ O_{20}\ (OH)_4X_{0.76}$ in which the negative layer charge arises principally from isomorphous substitutions in octahedral sheet was used in this study. The sample was supplied by Ward's Natural Science Establishment, Rochester, New York. The clay was made homoionic with different cations: Al, Cu(II), Ca, Mg, Na, Li, K, Rb, Cs, and $NH_4$ by treating the <2-μm fraction three times with 1 *N* solution of the respective chloride salts. The excess electrolytes were removed by washing with deionized water and centrifuged until the supernatant solution gave a negative test for $Cl^-$. The sample was oven-dried at 40°C for 2 days and stored, until used, on $CaCl_2$. Samples were used within 2 weeks.

### *Adsorption-Desorption Measurements*

Adsorption isotherms at 5° and 22°C were made on suspensions obtained by adding 50 ml of aqueous Alachlor solution (concentration from 0 to 926.61 μmol $g^{-1}$) to 10 mg of homoionic clay. Samples were subjected to shaking in thermostatic baths for 18 h. This time was estimated to be sufficient (according to kinetic measurements) to reach the equilibrium. The suspensions were centrifuged at 30,000 *g*, and the equilibrium concentrations were determined in the supernatant by UV spectroscopy at 220 nm. The adsorption experiments were repeated three times for each concentration. It was ascertained that turbidity, especially due to the monovalent cation-montmorillonite particles, was completely removed by centrifugation and did not interfere with the readings. The amount of herbicide adsorbed at equilibrium was considered to be the difference between the amount of Alachlor initially present and that in the supernatant. The minimum detectable value for Alachlor was 0.5 μg $ml^{-1}$, and the analytical range was 5–50 μg $ml^{-1}$.

Desorption experiments were carried out in triplicate at 22°C as follows: after the initial adsorption, the herbicide equilibrium solution was removed and replaced with 20 ml of deionized water. Samples were equilibrated under continuous shaking for 18 h. Another 20-ml aliquot of dionized water was added after removing the supernatant by centrifugation. This procedure was repeated four times until no Alachlor was spectrophotometrically detected in the supernatant.

### *Infrared Analysis*

Thin self-supporting films of homoionic clays were prepared by placing a few milliliters of clay suspension (about 2% by weight) on a polyethylene sheet and allowing them to air dry. The films were peeled away and immersed for 96 h in an Alachlor-saturated $CCl_4$ solution. $CCl_4$ was used as solvent instead of water to avoid the dispersion of clay film. The films, once removed from the solution, were rinsed twice with $CCl_4$ and air dried.

Preliminary investigations showed that $CCl_4$ was not adsorbed on homoionic montmorillonite. Even if $CCl_4$ can influence the hydration status of the exchangable cations of the clay, the IR spectrum of the air-dried homoionic clay and the corresponding complex, after treatment with $CCl_4$, shows the typical band of water at about 1630 $cm^{-1}$. Since the Fourier transform infrared (FT-IR) technique was used, spectra subtractions were accurate and interference by water did not occur.

The FT-IR spectra were recorded at room temperature in the range of 4000–1200 $cm^{-1}$ using a model 1710 Perkin-Elmer spectrophotometer interfaced to a microcomputer and a digital plotter. Difference spectra were obtained by subtracting the spectra of the corresponding homoionic clays from the spectra of the clay-organic complexes. Absolute and difference spectra were also recorded in the 1200–600 $cm^{-1}$ range. These spectra are poorly defined and not

essential for elucidating adsorption mechanism and, therefore, are not shown here.

### *X-Ray Diffraction Analysis*

In the $2\vartheta$ interval from 3° to 15°, diffraction patterns of homoionic montmorillonite and their complexes with herbicides were obtained using a General Electric XRD-5 diffractometer and Co $K_\alpha$ radiations. The analyses were carried out at room temperature on samples air dried and heated for 18 h at 190°C. These samples were kept in a dry atmosphere and protected against rehydration by a Mylar plastic film covering the slide.

### *Gas-Chromatographic Analysis*

In order to identify Alachlor and/or its metabolites, gas chromatographic qualitative analyses of the acetonic extract of homoionic montmorillonite-Alachlor complexes (as self-supporting films) were carried out with a Carlo Erba model HRGC 5300 gas chromatograph equipped with a flame ionization detector (FID). Columns of borosilicate glass coils were packed with Anakrom Q (110–110 mesh), previously coated with 2% w/w SE 30 and its surface silanized, prior to use, by on-column injection of 4 × 50 ml each of hexamethyldisilazane (HMDS) and bis-(trimethylsilyl)trifluoroacetamide (BSTFA). Column temperature was programmed from 160°C to 250°C with a rate of 3°C $min^{-1}$, while detector and injector were both kept at 270°C. High purity dry nitrogen served as gas carrier.

## RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms at 22°C of Alachlor on homoionic montmorillonite. The attribution of these isotherms to the classes described by Giles (Giles et al. 1960) couldn't be the strictly correct one. On the other hand, the replications for each concentration gave very close values (±1%) in all cases. Nevertheless, at first sight, the Al-, Cu-, Ca-, Li-, and Cs-montmorillonite isotherms seems to be of the L type. In this case, the molecules of Alachlor most likely would be adsorbed flat and showing a minimum competition of solvent for sites on the adsorbing surface. Similar results have been reported for some pesticides adsorbed on clays (Haque and Sexton 1968; Tercè and Calvet 1978; Bansal 1983; Bansal and Prasad 1985; Maza et al. 1989; Dios Cancela et al. 1990). The L curve for Cu-montmorillonite is very close to C type as observed with some organophosphorous and carbamate insecticides adsorbed on different soils (Felsot and Dahm 1979). Further on Rb-montmorillonite, the isotherm could be of the $L_3$ type. The Mg- and $NH_4$-montmorillonite isotherms seem of the C type, suggesting a constant partition of solute between solution and adsorbent. This kind of curve was observed also for some pesticides (Haque and Coshow 1971; Van Bladel and Moreale 1974; Weber 1980). The Na- and K-clay isotherms appear to be of the S-type, indicating that in the initial part of the curve, the herbicide molecules strongly compete for adsorption sites with the solvent molecules. Esse (S) type isotherms were often observed with pesticides adsorbed on smectites (Haque and Coshow 1971; Bowman and Sans 1977; Tercè and Calvet 1978; Aly et al. 1980; Bansal 1983; Sanchez Martin and Sanchez Camazano 1984; Bansal 1985).

However, a mechanistic interpretation of the isotherms is not unique and is not necessarily the correct one in the present case. In fact, the adsorption of Alachlor on homoionic montmorillonite in aqueous solution at 22°C fits the empirical Freundlich relationship with a correlation coefficient ($r$) in the range 0.97–1.00. The linear form of this equation is

$$\log C_s = \log K + 1/n \log C_e$$

where $C_s$ is the amount of herbicide adsorbed ($\mu$moles $g^{-1}$), $C_e$ is the equilibrium concentration in solution ($\mu$mol $L^{-1}$), and K and 1/n are constants. The 1/n, K and $r$ values are reported in Table 1.

Table 1 indicates also a correlation (though not a perfect one) at 22°C between the polarizing power of the exchangeable cation saturating the clay and the adsorption strength (expressed as K). However, ionic size (namely steric factors and cation polarizability) is also important. At 5°C, steric effects seem to dominate (e.g., the effect of temperature on clay swelling or dispersion, or the effect of temperature on the conformation of adsorbed molecule in the vicinity of the surface cations). However, no good correlation between adsorption and the polarization power of the cation was observed for the pesticide Pirimicarb adsorbed on montmorillonite (Sanchez Camazano and Sanchez Martin 1986).

Further, it can be seen that the K value for

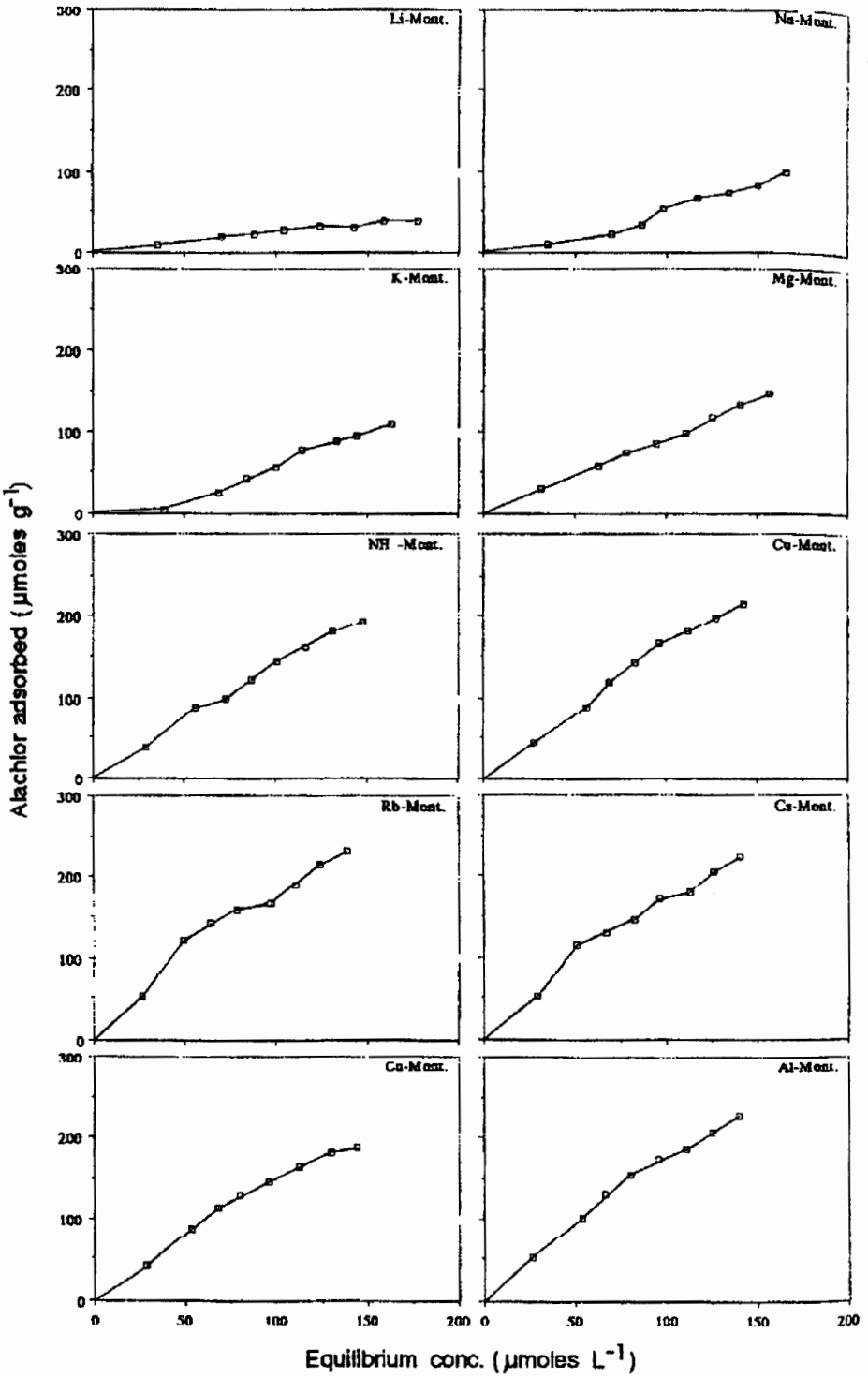



FIG. 1. Adsorption isotherms (22°C) of Alachlor on homoionic montmorillonites.

TABLE 1

*Freundlich constants (K and 1/n) on molar basis of Alachlor adsorbed on homoionic montmorillonite at 5° and 22°C and changes in enthalpy (ΔH) for $C_e$ = 120 μmol $g^{-1}$*

| Sample | K | | 1/n | | r | | ΔH |
|---|---|---|---|---|---|---|---|
| | 5°C | 22°C | 5°C | 22°C | 5°C | 22°C | (Kcal $mol^{-1}$) |
| Li | 1.042 | 0.483 | 0.70 | 0.85 | 0.96 | 0.99 | −1.21[a] |
| Na | 0.418 | 0.023 | 1.64 | 1.18 | 0.98 | 0.99 | −0.47 |
| K | 2.054 | 0.027 | 1.40 | 1.65 | 0.99 | 0.98 | −1.35 |
| Rb | 3.320 | 4.120 | 0.81 | 0.82 | 0.97 | 0.97 | +2.67 |
| Cs | 2.465 | 3.378 | 0.87 | 0.85 | 0.99 | 0.98 | +2.17 |
| $NH_4$ | 2.273 | 1.443 | 0.99 | 0.99 | 0.98 | 0.99 | −0.81 |
| Ca | 1.746 | 1.010 | 0.94 | 0.94 | 0.96 | 0.99 | −0.83 |
| Mg | 1.286 | 1.059 | 0.99 | 0.99 | 0.99 | 1.00 | −0.55 |
| Cu | 1.809 | 1.736 | 0.98 | 0.96 | 0.99 | 0.99 | −0.53 |
| Al | 0.115 | 3.034 | 0.88 | 0.85 | 0.99 | 0.99 | +2.02 |

[a] $C_e$ = 40 μmol $g^{-1}$.

the $NH_4$-system is similar to those shown by the clays saturated with divalent cations. The K values for the Cs-system is similar to that of Al-1; the highest K value was observed for Rb-montmorillonite. It is difficult to explain the relatively high values for $NH_4$-clay which, in general, behaves like K-systems and for Rb- and Cs-montmorillonite. In these latter cases, the cation size effect could be predominant. Both Rb and Cs cations in the unhydrated state are large enough to prevent the complete closure of the interlayer space when swelling minerals are dehydrated. Mooney et al. (1952) found that N-specific surfaces of Rb- and Cs-montmorillonite are larger than the surfaces of Li- and K-montmorillonite.

It can be seen also from Table 1 that a decrease in temperature from 22° to 5°C results in an increase in Alachlor adsorption except for Al-, Rb-, and Cs-montmorillonite. These data indicate that the adsorption process is endothermic for Al-, Rb-, and Cs-clays (K values increase with temperature) and exothermic in all other cases (K values increase while temperature decreases).

The isosteric heat of adsorption (changes of enthalpy) were determined from the isotherms at 5°C and 22°C applying the integrated Van't Hoff equation:

$$\Delta H_{iso} = R \frac{\ln C_{e1} - \ln C_{e2}}{1/T_1 - 1/T_2}$$

where R is the gas constant, and $C_{e1}$ and $C_{e2}$ are the equilibrium concentrations at temperatures $T_1$ and $T_2$. The $\Delta H_{iso}$ values, determined for a constant value of $C_e$ and assuming that the solvent-solute exchange is the same in all the systems, are reported in Table 1. The adsorption process for Alachlor adsorption by Al-, Cs-, and Rb-montmorillonite is endothermic while it is exothermic for all the other samples. It must be pointed out that the main contributions to the sign of $\Delta H_{iso}$ are: i) the solute adsorption on the surface of the adsorption and/or ii) the interaction of the adsorbed molecule with the exchangeable cation (exothermic processes) and iii) the breaking of the solvent molecules from the adsorbent surface and the interlayer expansion (endothermic processes) (Van Bladel and Moreale 1974; Sanchez Martin and Sanchez Camazano 1984).

The $\Delta H_{iso}$ values indicate that the interaction energy of homoionic montmorillonite with Alachlor in aqueous medium is not strong. In this case, we postulate a physical bonding by hydrogen bond (probably involving the C=O group of the molecule, as discussed below) or Van der Waals forces. Similar results were observed for some pesticides (Bansal 1983; Sanchez Martin and Sanchez Camazano 1984; Dios Cancela et al. 1990).

The desorption results are reported in Fig. 2. A recovery of only about 50% after several washings in distilled water is rather surprising. It is difficult to give an explanation of such a severe hysteresis occurring in all the investigated systems. Perhaps the centrifugation caused an irreversible fixation of the herbicide on clays. Similar results were observed for Oxamyl and Dimecron, for which it has been suggested that an appreciable adsorption of pesticide occurs by ionic interactions at crystal edge and crystal basal surface (Bansal 1983).

The interactions of Alachlor with homoionic montmorillonite were also studied in an organic solvent ($CCl_4$). Some of the main IR vibration bands of free Alachlor and herbicide-clay complexes are reported in Table 2. The FT-IR spectra of the Al-montmorillonite-Alachlor complex air dried and after heating at 70°C for 6 h are shown in Fig. 3.

A detailed study of the spectra of the complexes indicates that the stretching bands of C=O and C—N groups of the molecule undergo modification in comparison with those of pure Alachlor. Particularly, the C=O stretching band of the molecule (1692 $cm^{-1}$) shifts to lower fre-

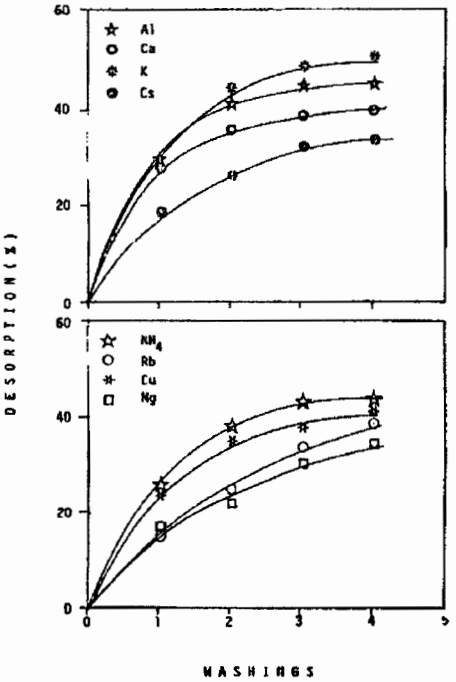



FIG. 2. Desorption (%) at 22°C of Alachlor adsorbed on homoionic montmorillonites by water washings.

TABLE 2

*FT-IR vibration bands ($cm^{-1}$) of air-dried Alachlor-montmorillonite complexes*

| Sample | ν C=O | ν C—N (anilidic) |
|---|---|---|
| Alachlor ($CCl_4$ solution) | 1692 | 1372 |
| Homoionic clay-Alachlor | | |
| Li | 1661 | 1387 |
| Na | 1672 | 1385 |
| K | 1671 | 1381 |
| $NH_4$ | 1660 | 1382 |
| Rb | 1669 | 1381 |
| Cs | 1667 | 1378 |
| Ca | 1651 | 1388 |
| Mg | 1651 | 1387 |
| Cu | 1658 | 1388 |
| Al | 1646 | 1387 |

quencies (1672–1646 $cm^{-1}$) as a consequence of adsorption, while the magnitude of this shift follows the order: trivalent > divalent > monovalent cation.

This behavior can be ascribed to ion-dipole interaction between C=O group and the exchangeable cation. As a consequence of this interaction, the double bond nature of C=O is reduced, and this results in an increased C—N (anilidic group) double bond. This is confirmed by the shift of the C—N stretching band (1372 $cm^{-1}$) toward higher frequencies (1378–1388 $cm^{-1}$).

Therefore, these results indicate that Alachlor is adsorbed on homoionic montmorillonite by a coordination bond, through a water bridge, between the C=O group and the exchangeable cation of the clay (Fig. 4). The coordination strength is directly correlated with the polarizing power of the cation. Results of this type have been reported for several organic compounds adsorbed on clays (Mortland and Meggitt 1966; Sanchez Camazano and Sanchez Martin 1986; Fusi et al. 1986; Fusi et al. 1989a and 1989b).

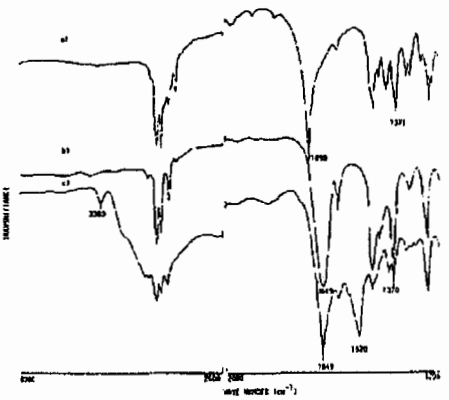
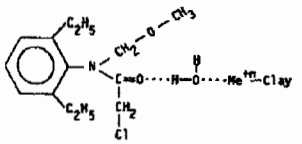


FIG. 3. (a) Infrared spectra of Alachlor in $CCl_4$ solution. (b) Differential infrared spectra of Al-montmorillonite-Alachlor complex at room temperature. (c) Complex "b" after heating at 70°C for 6 h and then cooled in air.



WHERE $Me^{n+}$ = $Li^+$, $Na^+$, $Cs^+$, $K^+$, $Rb^+$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Al^{3+}$.

FIG. 4. Suggested adsorption mechanism of Alachlor on homoionic montmorillonites.

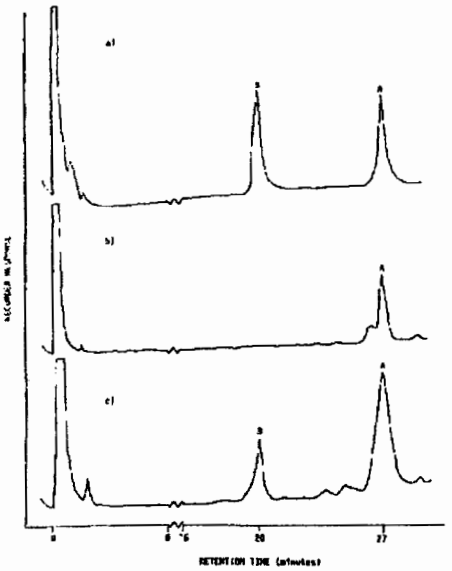


FIG. 5. Chromatograms from: (a) Hexane solution of A (Alachlor) and B (degradation products i.e., 2-chloro-2′,6′-diethylacetanilide); (b) Hexane extract of the Al-montmorillonite-Alachlor complex at room temperature; (c) Hexane extract of the Al-montmorillonite-Alachlor complex after heating at 70°C for 6 h, and then cooled in air.

Some significant changes occur in the IR spectra for Al-, Cu-, Ca-, Mg-, and $NH_4$-montmorillonite-Alachlor complexes when heated at 70°C for 6 h, while the spectra of Li-, Na-, K-, Rb- and Cs-complexes remain unchanged.

Two new bands appear at 3380 $cm^{-1}$ and 1520 $cm^{-1}$ (1538 $cm^{-1}$ for Cu-montmorillonite) that could be tentatively assigned to the stretching and bending vibration of a N—H group, respectively (Bellamy 1975). At the same time an attenuation of the intensity of the bands at about 1900 and 1460 $cm^{-1}$ (stretching and deformation vibration of CH) is observed. These features suggest the formation of the 2-chloro-2′,6′-diethylacetanilide as a degradation product of the Alachlor-clay complex. This compound was found also as a degradation product of Alachlor in a fine sandy loam soil incubated for 72 h at 0% of relative humidity and 46°C (Hargrove and Merckle 1971). The gas-chromatographic analysis of the acetonic extract of Al-, Cu-, Ca-, Mg-, and $NH_4$-montmorillonite complexes revealed, in fact, the presence of 2-chloro-2′,6′-diethylacetanilide (Fig. 5).

Therefore, these results suggest that Alachlor adsorbed on montmorillonite saturated by monovalent cations (except $NH_4^+$) is stable on heating, while if adsorbed on clay saturated by polyvalent cations, it undergoes a partial abiotic degradation to 2-chloro-2′,6′ diethylacetanilide. This behavior can be ascribed to the higher acidity, enhanced by heating, of the coordinated water (strongly polarized) of polyvalent cations in comparison with that of monovalent ones. Unique is the behavior of the $NH_4$-montmorillonite. However, $NH_4$-kaolinite was found to be fairly acid (to Hammet indicator) and to decompose Dieldrin (Fowkes et al., 1960). Further, the protonation of 3-aminotriazole adsorbed at the surface of $NH_4$-montmorillonite has been demonstrated (Russell et al. 1968).

The importance of the polarizing power of the exchangeable cation in the adsorption of Alachlor from $CCl_4$ is supported also by X-ray diffraction analyses (Table 3). The molecule is able to penetrate only the interlayer space of montmorillonite saturated with polyvalent cation. In fact, the heating at 190°C of the polyvalent clay-Alachlor complexes causes a reduction in the spacing (range 1.103–1.553 nm), but not the collapsed conditions (range 0.986–1.006 nm) as observed for heated untreated homoionic montmorillonite. The inability of Alachlor to intercalate the layer of Na-, K-, $NH_4$-, Rb-, Li-, and Cs-montmorillonite might be ascribed to the low polarizing power of the monovalent cations associated with the difficult penetration of a non polar solvent such as $CCl_4$ in the dense-packed

TABLE 3

*d(001) values (nm) for homoionic montmorillonites untreated and treated with Alachlor in $CCl_4$ solution*

| Sample | Untreated | | Treated | |
|---|---|---|---|---|
| | 25°C | 190°C | 25°C | 190°C |
| Li | 1.207 | 0.968 | 1.221 | 0.987 |
| Na | 1.266 | 0.959 | 1.266 | 0.959 |
| K | 1.179 | 0.986 | 1.152 | 1.026 |
| $NH_4$ | 1.115 | 1.069 | 1.069 | 1.047 |
| Rb | 1.058 | 1.047 | 1.069 | 1.047 |
| Cs | 1.140 | 1.115 | 1.140 | 1.115 |
| Ca | 1.530 | 0.996 | 1.654 | 1.530 |
| Mg | 1.486 | 1.006 | 1.654 | 1.553 |
| Cu | 1.192 | 0.986 | 1.266 | 1.103 |
| Al | 1.553 | 0.986 | 1.654 | 1.424 |

montmorillonite films. Similar results were observed for Carbaryl adsorbed on Na-montmorillonite (Fusi et al. 1986).

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