

DIMEPIPERATE ADSORPTION AND HYDROLYSIS ON Al^{3+} -, Fe^{3+} -, Ca^{2+} -, AND Na^+ -MONTMORILLONITE

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Abstract—The adsorption of the herbicide dimepiperate S-(α,α -dimethylbenzyl)-1-piperidinecarbothioate on homoionic Fe^{3+} -, Al^{3+} -, Ca^{2+} -, and Na^+ -montmorillonite was studied in aqueous medium. The adsorption is described well by the Freundlich equation. The adsorption capacity decreases in the order $Fe^{3+} > Al^{3+} > Ca^{2+} > Na^+$ clay. The dimepiperate adsorption from chloroform solution was also investigated by analytical, spectroscopic, and X-ray powder diffraction techniques. IR results suggest that the adsorption involves the interaction of the thioester carbonyl group of dimepiperate possibly with the surrounding water of metal ions. On Al^{3+} and Fe^{3+} clays, this interaction leads to hydrolysis of the thioester bond and formation of the thiol and carbamic acid derivatives that yield α -methylstyrene and piperidine, respectively.

Key Words—Adsorption, Dimepiperate, Hydrolysis, Infrared spectroscopy, Interlayer cations, Montmorillonite, Pesticides.

INTRODUCTION

The contribution of organic and mineral fractions to the adsorption of non-ionic organic molecules in soil has been the subject of several studies (e.g., Mortland, 1970, 1976; Gessa *et al.*, 1987; Senesi and Testini, 1982, 1984). Depending on the water content, both these constituents can play an important role in adsorption and retention processes. Under conditions of water saturation, the adsorption of an organic compound is generally dominated by its partitioning into soil organic matter. Conversely, in dry and subsaturated soils, the adsorption onto mineral surfaces is more important (Chiou *et al.*, 1979) because clay minerals can inactivate adsorbed pesticides by catalysing their decomposition (Crosby, 1976). In most cases, the degradation occurs through hydrolysis and the extent of the reaction is related to the nature of the exchangeable cations (Pusino *et al.*, 1988; Pusino and Gessa, 1990; Sánchez-Camazano and Sánchez-Martín, 1991).

Dimepiperate, S-(α,α -dimethylbenzyl)-1-piperidinecarbothioate (I) is new thiol-carbamate herbicide effective against weeds in rice paddies and on dry land (Ikeda, 1982). As it is relatively new, only limited information is available on its herbicidal activity and half-life in the field (Tanaka, 1984; Antonelli *et al.*, 1986) and the interaction mechanisms with soil colloids are still unknown. The aim of this work was to investigate the interaction between dimepiperate and homoionic montmorillonite. Therefore, the adsorption of the herbicide on Al^{3+} -, Fe^{3+} -, Ca^{2+} -, and Na^+ -montmorillonite from water was studied by analytical

(HPLC, GC) methods. The adsorption from an organic solvent was also studied by spectroscopic (IR) and X-ray diffraction measurements. It was observed that, depending on the acidic properties of the exchangeable cations, two different mechanisms may take place.

EXPERIMENTAL METHODS

Materials

Montmorillonite No. 25 (bentonite) from Upton, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used in this study. The $<2 \mu m$ fraction was obtained by sedimentation. The cation-exchange capacity (CEC) of the clay (sodium form), determined following literature methods (Hendershot and Duquette, 1986), was 90.2 meq/100 g. Al^{3+} -, Fe^{3+} -, Ca^{2+} -, and Na^+ -exchanged samples were prepared by immersing the clay into 1 N solutions of the corresponding metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until Cl^- free, and dried at room temperature. Dimepiperate ($C_{15}H_{21}NOS$) was supplied by Mitsubishi Petrochemical, Japan, as a waxlike solid with a solubility in water of $20 mg L^{-1}$ at $25^\circ C$ (Antonelli *et al.*, 1986).

Adsorption measurement

Batch distribution isotherms on Al^{3+} , Fe^{3+} , Ca^{2+} , and Na^+ clays were determined at $25 \pm 2^\circ C$. In general, duplicate samples of 50 mg of air-dried clay were equilibrated in centrifuge polyallomer tubes with 10 ml of aqueous herbicide solution. The dimepiperate concentrations before equilibration ranged from 5.46 to 54.55

μM and were below the solubility limit. The tubes were shaken (end over end) for 24 hr. Generally, 95% of the adsorption was found to occur within 5 h. After equilibrium was reached, the suspension was centrifuged at 20,000 rpm for 15 min. The supernatant was pipetted off and analysed immediately using high-performance liquid chromatography (HPLC). The amount adsorbed by clays was calculated from the difference between the initial and final concentrations of dimepiperate in solution. The pH of aqueous suspensions did not vary significantly in the adsorption experiments (4.5, 4.2, 6.2, and 7.0, for Al^{3+} , Fe^{3+} , Ca^{2+} , and Na^+ clays, respectively).

The adsorption studies were repeated by immersing air-dried self-supporting bentonite films in a ca. 2% solution of dimepiperate in CHCl_3 . After 24 h, the films were separated from the solution and washed with CHCl_3 to remove excess pesticide. After air drying, the films were examined by infrared spectroscopy (IR), whereas the equilibrium solution was tested by gas chromatography (GC).

Chromatographic analyses

High performance liquid chromatographic (HPLC) analyses were carried out using a Waters 510 liquid chromatograph equipped with a 250×4 mm i.d. $\mu\text{Bondapak}^{\text{C}}_{18}$ (10 μm) analytical column. A multi-wavelength Waters 490 programmable detector operating at 230 nm and a Waters Baseline 810 chromatography work station were also used. The mobile phase (1 ml min^{-1}) was composed of acetonitrile and water (70:30 by volume, pH 3). In these conditions, the retention time of dimepiperate was 9.4 min.

Gas chromatographic analyses were performed with a Hewlett Packard Series II 5890 chromatograph using a WCOT fused silica containing CP-Sil-8 CB and flame ionization detector (FID). The temperature was programmed from 160° to 250°C at 5°C min^{-1} ; the carrier gas was helium at a flow-ratio of 10 ml min^{-1} ; and the injector and detector temperatures were 200° and 260°C, respectively. The retention times of dimepiperate and α -methylstyrene (IV) were 16.5 and 4.4 min, respectively.

Physical measurements

IR spectra were recorded with a Perkin-Elmer 683 spectrometer over the range 4000–600 cm^{-1} (optical resolution, 2 cm^{-1}). The spectrum for dimepiperate was recorded from a KBr disk and that of piperidine from a thin film between NaCl plates. Differential spectra were obtained for herbicide- and piperidine-bentonite complexes using self-supporting films. An untreated montmorillonite film was placed in the reference beam so as to minimize interference from water; only the 2000–1200 cm^{-1} region was found to be reliable.

XRD data were obtained on a Philips PW 1730 instrument equipped with an Olivetti M-20 computer,

using CoK_α radiation, in the 2θ interval 2–17°. Oriented films were prepared by evaporating small volumes of clay suspensions (ca 2% wt.) on microscope slides. The analyses were carried out at room temperature on the samples both air-dry and heated at 100°C under vacuum for 5 hr. The samples were kept in a dry atmosphere during the analysis, being protected against rehydration by a Mylar plastic film covering the slide.

RESULTS

Adsorption from water

Figure 1 shows the adsorption isotherms of dimepiperate on Al^{3+} -, Fe^{3+} -, Ca^{2+} -, and Na^+ -montmorillonite. All the isotherms are of type "S" according to the classification of Giles *et al.* (1960). The S-shape of the curve is usually explained as due to competition with the solvent molecules for substrate sites. As is usual in pesticide adsorption studies, the empirical Freundlich relationship was used to evaluate the results ($r = 0.99$). The linear form of this equation is as follows:

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

where C_s is the amount ($\mu\text{mole}/100$ g) of pesticide adsorbed, C_e is the herbicide concentration (μM) in the solution at equilibrium, and K_f and $1/n$ are empirical constants. K_f is the amount of pesticide adsorbed for 1 μM equilibrium concentration and $1/n$ the slope. The values of K_f and $1/n$ are given in Table 1. Both the isotherms and values of K_f show that the adsorption capacity decreases in the order $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^+$, which is also the order of decreasing acidity of both interlayer and external solutions. This result may suggest that the extent of adsorption on clays depends on the polarizing power of the saturating cation on the coordinated water molecules. However, because of the rather low adsorption levels of the pesticide from aqueous solution, no evidence on the adsorption mechanism can be obtained by IR spectra. Moreover, no decomposition product was found by HPLC analysis of the equilibrium solution.

Adsorption from organic solvent

The adsorption of dimepiperate on clay from CHCl_3 was also studied. Neat dimepiperate yields an absorption at 1645 cm^{-1} due to the amide I band stretch (Bellamy, 1975). The clay water bending (ca. 1640 cm^{-1}) is found in the same region, and it could be not distinguished from 1645 cm^{-1} band of dimepiperate. However, clay-herbicide interaction is expected to affect the position of the latter band. Accordingly, if the absorption around 1640 cm^{-1} was minimized in the difference spectra of samples, positive peaks due to the adsorbed molecules were observed for the herbicide. The IR spectra of dimepiperate Ca^{2+} - and Na^+ -montmorillonite complexes (Figure 2) showed bands at 1620 and 1570 cm^{-1} , respectively. This indicates a perturbation

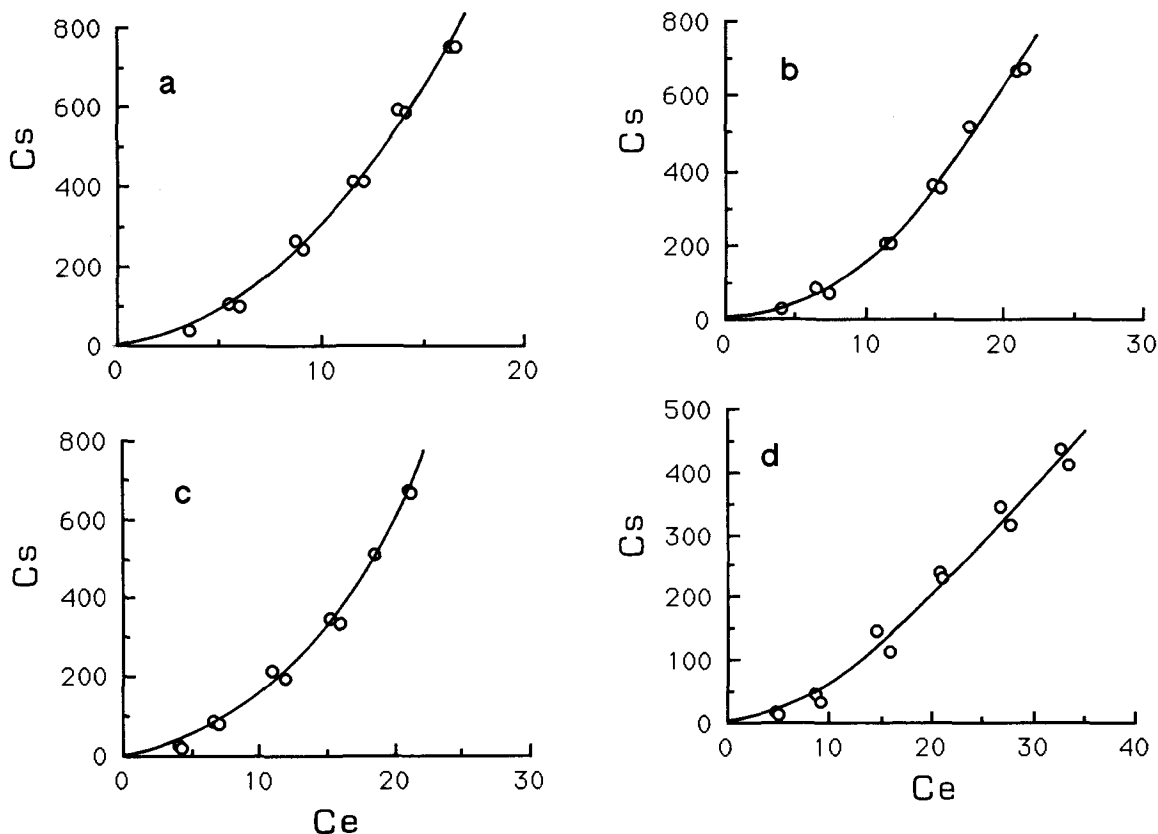


Figure 1. Adsorption isotherms of dimepiperate on montmorillonite: a) Fe³⁺, b) Al³⁺, c) Ca²⁺, and d) Na⁺ clays. C_e ($\mu\text{mole}/\text{l}$); C_s ($\mu\text{mole}/100\text{ g}$).

of the CO thioester group by the metal ions through direct bonds or, more probably, via hydrogen bonding involving residual water molecules linked to the cations. Such an interaction is expected to lower the force constant of the CO group and decrease the frequency value to a greater extent as the polarizing force (in this case, the ability to withdraw electrons from oxygen) of the metal ions increases. A similar behaviour was observed for the adsorption of a number of pesticides on clays (Fusi *et al.*, 1988; Micera *et al.*, 1988; Pusino *et al.*, 1989). IR spectra reported in Figure 3 suggest that a different mechanism takes place on Fe³⁺- and Al³⁺-montmorillonite surfaces. In particular, the spectra of Fe³⁺ and Al³⁺ complexes are very similar to each other and, over the range 1600–1200 cm^{-1} , exhibit bands at 1492, 1471, and 1455 cm^{-1} . These bands are com-

parable to those observed after the adsorption of piperidine on Al³⁺ clay. Moreover, unlike Ca²⁺ and Na⁺ samples, Fe³⁺ and Al³⁺ clays do not exhibit the band due to amide group. These observations suggest that, upon adsorption on Fe³⁺ and Al³⁺ clays, dimepiperate is decomposed into piperidine that remains adsorbed in the interlayer. Nevertheless, no inference can be made about the interaction mechanism(s). The chloroformic equilibrium solution was tested by GC to find the remaining breakdown product of the dimepiperate molecule. Under the working conditions reported in the experimental section, a chromatographic peak with a retention time of 4.4 min was found and attributed to α -methylstyrene by comparison with an authentic sample.

XRD results

The XRD d(001) values (Table 2) of untreated clays and those treated with dimepiperate in chloroformic solution indicate changes in interlamellar space of the phyllosilicate. In particular, the magnitude of d(001) increased for Na⁺ and Ca²⁺ clays kept at room temperature but decreased under the same conditions for the Fe³⁺ and Al³⁺ clays because of hydrophobic effects. Moreover, the collapse of the interlayer after heating under vacuum was lower than in the corresponding

Table 1. Freundlich constants (K_f and n) and correlation coefficient (r) for the adsorption of dimepiperate on montmorillonite.

Sample	K_f	n	r
Fe ³⁺	3.478	0.516	0.997
Al ³⁺	2.010	0.523	0.996
Ca ²⁺	1.789	0.516	0.994
Na ⁺	0.882	0.557	0.990

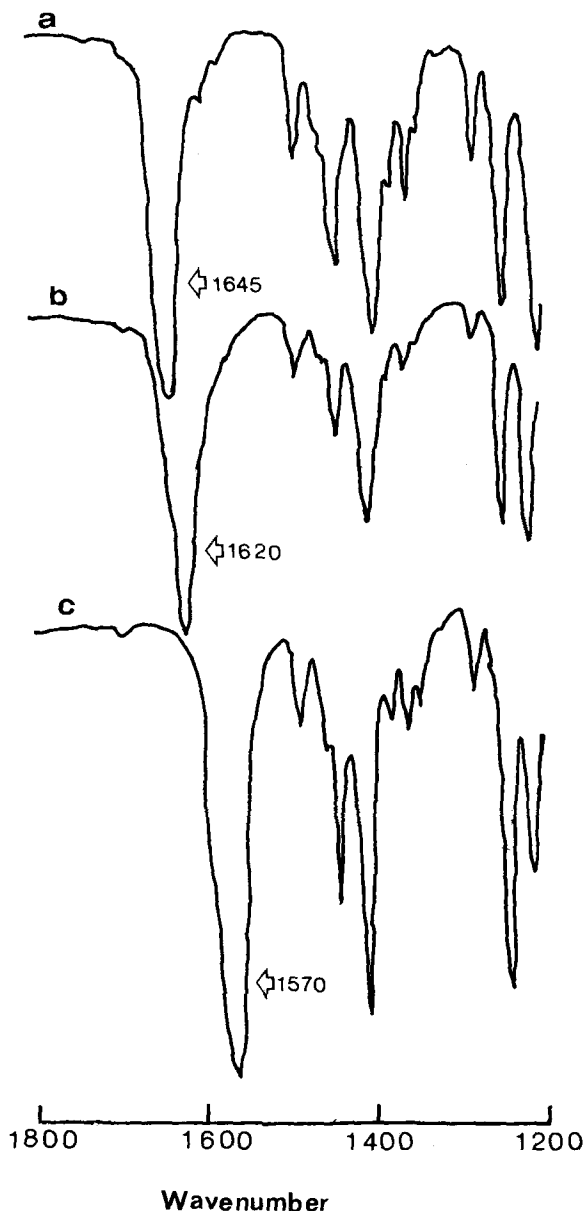


Figure 2. Infrared spectra of a) dimepiperate (KBr disk) and homoionic clays treated with dimepiperate, b) Na^+ , and c) Ca^{2+} . Spectra of clays were recorded as difference spectra with respect to those of untreated samples.

untreated samples. The larger increase of interlayer distance measured for Na^+ and Ca^{2+} clays (heated samples) treated with dimepiperate may be due to the bigger size of the intact pesticide molecule compared to that of piperidine formed on Fe^{3+} and Al^{3+} clays. It is also worthwhile to note that piperidine directly adsorbed on Fe^{3+} and Al^{3+} clays yields $d(001)$ values quite comparable to those measured after interaction of dimepiperate. From molecular modeling, we calculated that the hypothetical values for the intercalation of a monolayer of dimepiperate or piperidine with-

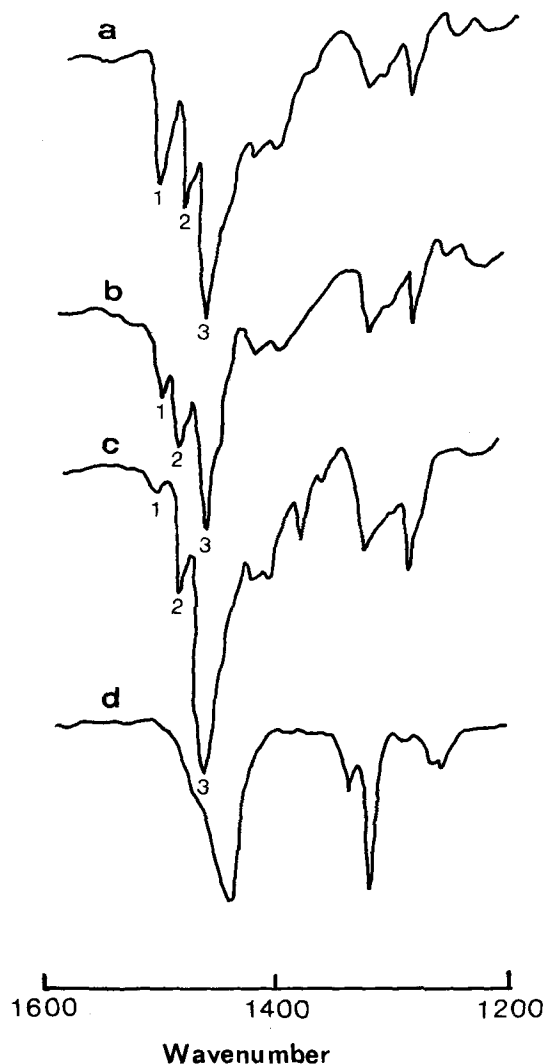


Figure 3. Differential infrared spectra of a) Fe^{3+} and b) Al^{3+} homoionic clays treated with dimepiperate; also c) Al^{3+} clay treated with piperidine. The spectrum of piperidine d) as a thin film is also shown. 1, 2, and 3 refer to absorption bands at 1492, 1471, and 1455 cm^{-1} , respectively.

in the silicate sheets are 13.9 and 12.5 Å, respectively. These values are generally consistent with the experimental data. The lower experimental value for the Na^+ -clay may be due to partial embedding of the methyl

Table 2. $d(001)$ values (Å) for homoionic bentonites untreated and treated with dimepiperate or piperidine.¹

Cation	Untreated		Dimepiperate		Piperidine
	25°C	100°C	25°C	100°C	100°C
Fe^{3+}	14.97	12.08	14.22	13.67	13.72
Al^{3+}	15.04	12.25	14.85	13.87	13.93
Ca^{2+}	14.48	12.15	14.81	14.65	—
Na^+	12.08	10.01	12.22	12.11	—

¹ Montmorillonite No. 25 from Upton, Wyoming.

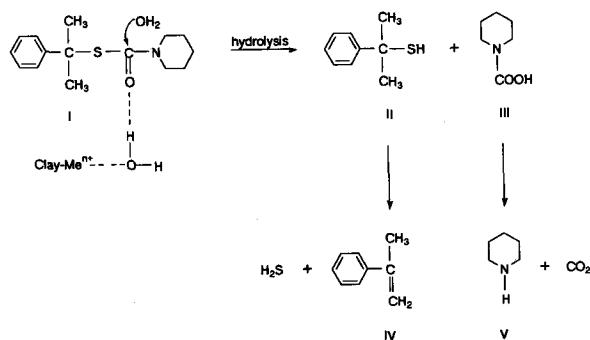


Figure 4. Proposed mechanism for hydrolysis of dimepiperate on Fe³⁺ and Al³⁺ clays.

hydrogens in hexagonal holes or to the low adsorption levels.

DISCUSSION AND CONCLUSIONS

The adsorption of dimepiperate from water on clays follows the Freundlich equation, although water may be competitive enough with the pesticide. Because of the low extent of adsorption in aqueous solution, no inference about the mechanisms can be made. However, IR results on clay-dimepiperate complexes obtained from organic solution distinguish at least two mechanisms, both related to the acidity of the system. The first one, acting in all clays, is the interaction of the thioester carbonyl group of dimepiperate with the metal ions (hydrated or not), as evidenced by the shift of CO stretch toward lower frequencies in the IR spectra of Ca²⁺ and Na⁺ samples. The second one, occurring only in Fe³⁺ and Al³⁺ clays, leads to a cleavage of the adsorbed pesticide molecule owing to a hydrolysis reaction. The reaction is made possible by the greater acidic properties of Fe³⁺ and Al³⁺ ions compared to Ca²⁺ and Na⁺ ions (see, e.g., pH of aqueous suspensions). According to the mechanism shown in Figure 4, the interaction enhances the electrophilic character of the carbonyl carbon and simultaneously weakens the C-S bond, facilitating the cleavage of the thioester bond by the nucleophilic attack of water. The hydrolysis appears to be the initial step leading to the thiol (II) and the carbamic acid (III). Neither of these intermediates was isolated, very likely because of their rapid decomposition. The unstable carbamic acid intermediate (III) underwent decarboxylation to give piperidine (V). On the other hand, the thiol (II) gave α-methylstyrene (IV) by elimination of hydrogen sulphide that was recovered in the equilibrium solution. A specific adsorption of the herbicide, such to favour the subsequent hydrolysis, is required in such a mechanism. This assumption agrees with both the IR and X-ray data, which indicate that piperidine remains adsorbed in the interlayer clay.

Although it cannot be proved that the same mechanisms may apply to the adsorption from water, a sim-

ilar behaviour, e.g., a decomposition reaction following adsorption, is expected in natural environment under dry conditions. Normal adsorption processes are usually investigated using quantities of water greatly in excess of the amount a field soil would experience, whereas most agricultural soils do not exhibit a state of total water saturation and experience cycles of wetting and drying. In dry conditions, pesticide interactions similar to those observed in organic solution can be an important factor in pesticide movement and persistence. This conclusion may be particularly valid for non-polar organic molecules that are only sparingly soluble in water.

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