# Behavior of the herbicide dimepiperate with homoionic clays in aqueous solution[*]

## Liu Weiping, Wang Qiquan, Shao Ying, Ji Jing

Department of Chemistry, Zhejiang University,
Hangzhou 310027, China

**Abstract**—— The adsorption of the herbicide dimepiperate with homoionic $Fe^{3+}$, $Al^{3+}$, $Cu^{2+}$, $Ca^{2+}$, $K^+$ and $Na^+$ saturated montmorillonite in aqueous solution was investigated. The adsorption to six homoionic clays was described well by the Freundlich equation. The adsorption capacity decreases in order to $Cu^{2+} > Fe^{3+} > Al^{3+} > Ca^{2+} > K^+ > Na^+$ clay and the same order of their acidities except for $Cu^{2+}$, because $Cu^{2+}$ has great catalytical ability. The kinetic of its hydrolysis was also studied. Among the six metal ions, $Cu^{2+}$ clay exhibited a particular affect of catalysis. The IR results suggest that only finding the adsorption of the hydrolytic product on $Cu^{2+}$ clay and dimepiperate on $K^+$, $Na^+$ clays, there being two compounds (dimepiperate and its hyrolytic product) adsorptions on $Fe^{3+}$ and $Al^{3+}$ clays.

**Keywords**:dimepiperate; montmorillonite; adsorption isotherm; adsorption mechanisms.

## 1   Introduction

With increasing use of herbicides in agriculture, studies on the behavior of these compounds in soil environment are becoming more and more important. As the adsorption of non-ionic organic molecules is concerned, organic and mineral fractions are among the most active soil components (Crosby, 1976; Gessa, 1987; Senesi, 1982). Adsorption of herbicides on soil from water is an important factor affecting their fate, biological activity, and persistence in soil. Depending on the water content, both constituents can play important role in adsorption and retention processes. In aqueous situation, the adsorption of pesticides is generally dominated by their partitioning into soil organic matter. Conversely, in dry and subsaturated soils, the adsorption onto mineral surface is more important (Chiou, 1979) because clay mineral can inactivate adsorbed pesticides by forming complex compound or catalyzing their decomposition (Crosby, 1976). In most cases, the exchangeable cations in clay minerals dominate the degradation occurring through hydrolysis and the mechanism of adsorption (Pusino, 1988; 1990; Sanchez-Camazano, 1991).

Dimepiperate, S-($\alpha$, $\alpha$-dimethylbenzyl)-1-piperidine carbothioate (1) is new thiolcarbamate herbicide effective against weeds in rice paddies and on dry land. By now, only a little information is available on its herbicidal activity and half-life in the field (Pusino, 1993). Its interaction mechanisms with soil colloids are still uncertain. Therefore, the present study was undertaken to learn the mechanism of interaction between dimepiperate and $Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Ca^{2+}$, $K^+$ and $Na^+$ saturated montmorillonite. The adsorption isotherms of herbicide on homoionic clays from water was studied by shaken-equilibration methods. The adsorption from an organic solvent was also studied by infrared spectroscopic (IR) measurements. It was observed that, depending on the acidic properties of the exchangeable cations and catalytical ability, some different mechanisms may take place.

## 2   Experimental methods

### 2.1   Materials

Montmorillonite (bentonite) from Lingan, Zhejiang Province, China, supplied by the Department of Geology, Zhejiang University, was used in this study. The $<2$ $\mu$m fraction was obtained by sedimentation. The cation-exchange capacity (CEC) of the clay (calcium form), determined following literature methods (Hendershot, 1986), was 82.2 meq/100g. Metal-exchanged samples were prepared by immersing the clay into 1 or 0.5 mol/L 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 at 25℃.

### 2.2   Adsorption measurement

Batch distribution isotherms on homoionic clays were determined at 25±2℃. Typically, triplicate samples of 50 mg of air-dried clay were equilibrated in centrifuge tubes with 5 ml of dimepiperate solution. The dimepiperate concentration before equilibration ranged from 5.23 to 52.30 $\mu$mol/L. The tubes were shaken (end-over-end) for 20h. Generally, 95% of the adsorption was found to occur within the first 5h. After equilibration, the suspension was centrifuged at 25000 r/min for 15 min. The supernatant was pipetted off and analyzed immediately using HPLC. The amount adsorbed by a clay was calculated from the difference between the initial and final concentrations of dimepiperate in solution.

The adsorption studies were repeated by immersing air-dried self-supporting bentonite films in a ca. 1% solution of dimepiperate in $CHCl_3$. After 24h, 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.

### 2.3   Hydrolysis measurement

Hydrolysis of dimepiperate on $Al^{3+}$, $Fe^{3-}$, $Cu^{2+}$, $Ca^{2+}$, $K^+$ and $Na^+$ saturated montmorillonite was also studied. Batch hydrolysis curves were determined at 25±2℃. In general, duplicate samples of 50 mg of air-dried clay were shaken in a 50 ml conical flask with 35 ml 55.5 $\mu$mol/L of aqueous dimepiperate solution in dark room. After different time, 2 ml sus-

pension was centrifuged at 30000 r/min for 20 min and analyzed immediately using HPLC to determine the concentration of residual pesticide.

## 2.4  Chromatographic analyses

High performance liquid chromatographic (HPLC) analyses were carried out using a Shimadzu LC-4A liquid chromatograph equipped with a $250 \times 4$ mm i. d. $\mu$Bondapack $C_{18}$ (10 $\mu$m) analytical column. A multiwavelength Shimadzu SPD-1 detector operating at 230 nm and Shumadzu C-R1B integrator system were also used. The mobile phase (1 ml/min) was composed of acetonitrile and water (70:30 by volume, pH 3). Under these conditions, the retention time of dimepiperate was approximately 9.0 min.

## 2.5  Physical measurements

IR spectra were recorded with a Shimadzu IR-470 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. Different spectra were obtained for dimepiperate and piperidine-bentonite complexes using self-surporting films. An untreated montmorillionite film was placed in the reference beam so as to minimize interference from water, only the $2000 - 1200$ cm$^{-1}$ was found to be reliable.

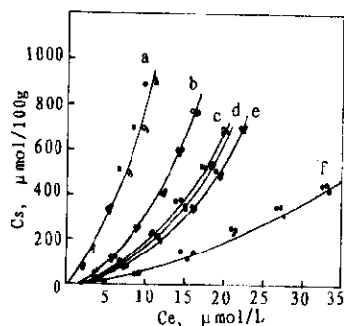# 3  Results

## 3.1  Adsorption from water



Fig. 1  Adsorption isotherms of dimepiperate on montmorillionite: (a) $Cu^{2+}$, (b) $Fe^{3+}$, (c) $Al^{3+}$, (d) $Ca^{2+}$ (e) $K^+$ and (f) $Na^+$ clays

Fig. 1 shows the adsorption isotherms of dimepiperate on metal-clays. All of the isotherms are of type "S" according to the classification of Giles *et al.* (Giles, 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:

$$\log Cs = \log Kf + 1/n \log Ce ,$$

where $Cs$ is the amount ($\mu$mol/100g) of pesticide adsorbed, $Ce$ is the herbicide concentration ($\mu$mol/L) in the solution at equilibrium, $Kf$ is the amount of herbicide adsorbed at 1 $\mu$mol/L equilibrium concentration and $1/n$, the slope. The values of $Kf$ and $1/n$ are given in Table 1.

Both the isotherms and values of $Kf$ show that the adsorption capacity the decreases in order of $Cu^{2+} > Fe^{3+} > Al^{3+} > Ca^{2+} > K^+ > Na^+$, which is also the order of decreasing acidity of both interlayer and external solutions: $Fe^{3+} > Al^{3+} > Cu^{2+} > Ca^{2+} > K^+$, $Na^+$, except for $Cu^{2+}$. While $Cu^{2+}$ is most famous for its great catalytical ability, it might be adsorbing extent by catalyzing adsorption reactions, such as decomposition, hydrolysis or simple physical adsorption. This result may suggest that the extent of adsorption on clays depends on the polarizing power and catalytic ability of the saturating cation on the coordinated water

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

| Sample | $Kf$ | $n$ | $r$ |
|---|---|---|---|
| $Fe^{3+}$ | 3.26 | 0.514 | 0.991 |
| $Al^{3+}$ | 1.94 | 0.521 | 0.993 |
| $Cu^{2-}$ | 34.86 | 0.684 | 0.990 |
| $Ca^{2+}$ | 1.69 | 0.519 | 0.991 |
| $K^+$ | 1.40 | 0.523 | 0.996 |
| $Na^+$ | 0.872 | 0.539 | 0.984 |

molecules. However, because of the rather low adsorption levels of the pesticide from aqueous solution, no evidence of the adsorption mechanism can be obtained by IR spectra. Moreover, no decomposition product was found by HPLC analysis of the equilibrium solution.

### 3.2 Adsorption from organic solvent

The adsorption of dimepiperate on clay from $CHCl_3$ was also studied. The main distinguishable feature of pure dimepiperate is the occurrence of a strong absorption at 1645 cm$^{-1}$ due to the amide band stretch (Bellamy, 1975). The clay water bending (ca. 1640 cm$^{-1}$) was found in the same region, which could not be distinguished from 1645 cm$^{-1}$ band of dimepiperate. However, clay-herbicide interaction is expected to affect the position of the amide band stretch. The IR spectra of dimepiperate $K^+$, $Ca^{2+}$, and $Na^+$ clay complexes (Fig. 2) exhibited strong bands at 1622, 1620 and 1570 cm$^{-1}$, respectively, indicating a perturbation of the CO thioesteral group caused by the metal ions through directed binds or, more probably, via hydrogen bonding involving residual water molecules linked to the cations. Such an interaction is expected to decrease the frequency and strength of CO group band to a greater extent as the polarizing forces (in this case, the ability to withdraw electrons from oxygen of CO group) of the metal ions increase. A similar behavior was observed for the adsorption of a number of pesticides on clays (Micera, 1988).

IR spectra reported in Fig. 3 indicated that the adsorption mechanism of $Fe^{3+}$, $Al^{3+}$ clay is quite a different one. Although the spectra of $Fe^{3+}$ and $Al^{3+}$ complexes also showed bards around 1595 cm$^{-1}$ which suggested the interaction between metal ions and CO thioesteral group of dimepiperate, the bands are rather weak. However, the spectra of the two complexes exhibit very similar to each other and, over the range 1600—1200 cm$^{-1}$, bands at 1492, 1471 and 1455 cm$^{-1}$. These bands are comparable to those observed after the adsorption of piperidine on $Fe^{3+}$, $Al^{3+}$ clay, respectively. These observations sug-
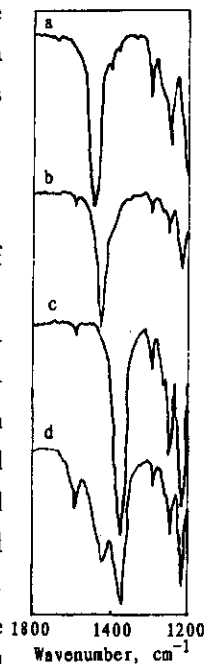


Fig. 2   Infrared spectra of (a) dimepipertate (KBr disk) and homionic clays treated with dimepiperate: (b) $K^+$, (c) $Ca^{2+}$, and (d) $Na^+$

1600    1400    1200
Wavenumber, cm$^{-1}$

Fig. 3   Different infrared spectra of (a) $Fe^{3+}$, and (b) $Al^{3+}$ homoinic clays treated with dimepiperate; also (c) $Al^{3+}$ clay treated with piperidine

gest that upon absorption on $Fe^{3+}$ and $Al^{3+}$ clays, dimepiperate is decomposed into piperidine to a great extent, and that piperidine remains adsorbed in interlayer.

According to the adsorption upon $Cu^{2+}$ clay, IR spectra (Fig. 4) showed that both adsorption methods take great effect. The dimepiperate $Cu^{2+}$ clay complex yield a medium adsorption at 1580 cm$^{-1}$ and also showed bands at 1492 (w). 1471 (w) and 1450 cm$^{-1}$(m) which are similar to those of piperidine $Cu^{2+}$ clay complex spectra.

It should be noted that the $Na^+$, $Ca^{2+}$, $K^+$ and $Cu^{2+}$ samples also showed particular strong bands at 760 cm$^{-1}$. To discuss it, we studied the IR spectra of piperidine and piperidine $K^+$, $Ca^{2+}$, $Na^+$ and $Cu^{2+}$ clay complexes (Fig. 5). Neat piperidine yielded a group of sharp, strong bands at 2730—2930 cm$^{-1}$ due to Vas $NH^{2+}$ or Vs $NH^{2+}$ but no absorption around 760 cm$^{-1}$, while piperidine metal-clay complexes exhibited strong absorption at 760 cm$^{-1}$ and much weaker absorption at 2730—2930 cm$^{-1}$. On the contrary, according to the piperidine $Al^{3+}$, $Fe^{3+}$ clays, no absorption around 760 cm$^{-1}$ is observed but the strong absorption around 2800 cm$^{-1}$. All these suggested that another adsorbing mechanism shows up. The particular strong absorption at 760 cm$^{-1}$ could be explained to be the result of reaction between the piperidinic nitrogen and metal ions, such as complexation reaction or simple polar effection.

## 3. 3   Hydrolysis of dimepiperate

Fig. 6 shows the hydrolysis curves of dimepiperate in six metal-clays. Pesticide on $Cu^{2+}$ clay exhibited a conspicuous hydrolysis effection, following that was $Fe^{3+}$ clay. It seemed that other metal ions had no particular affection on hydrolysis. Among the six metal ions, $Cu^{2+}$ is well-known by its catalytic ability, while $Fe^{3+}$ clay is the most acidic metal-clay. Therefore, the hydrolysis of dimepiperate most likely depends on the catalytic ability and acidity of the saturated ions.



1800    1600    1400    1200
Wavenumber, cm$^{-1}$

Fig. 4   Infrared spectra of (a) dimepiperate (KBr disk) and $Cu^{2+}$ clay treated with (b) piperidine and (c) dimepiperate

# 4   Conclusion

IR results on clay-dimepiperate complexes obtained from organic solution indict at least three mechanisms. One is the interaction of the thioester carbonyl group of dimepiperate with the metal ions (hydrated or not). The second one, leads to a cleavage of the adsorbed pesticide molecule owing to a hydrolysis reaction. This mechanism has a competitive effect to the last one. Spectra of ions, which have strong hydrolysis reaction, and clay complexes show rater weak peaks at-
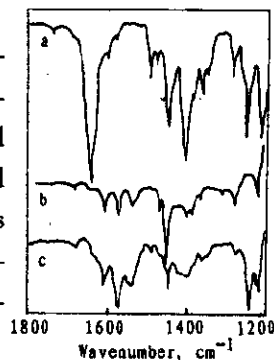
Fig. 5　Different infrared spectra of (a) K$^+$, (b) Ca$^{2+}$, (c) Na$^+$, and (d) Cu$^{2+}$ clays treated with piperidine. The spectrum of (e) piperidine as a thin film is also shown
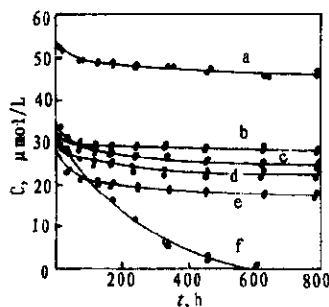


Fig. 6　Hydrolysis of dimepiperate on montmorillionate; (a) Na$^+$, (b) K$^+$, (c) Ca$^{2+}$, (d) Al$^{3+}$, (e) Fe$^{3+}$, and (f) Cu$^{2+}$ clays

tributable to the former mechanism. The hydrolysis reaction is made possibly by the acidic and catalytical properties of metal ions, so only spectra of more acidic M-clay, such as those of Fe$^{3+}$, Al$^{3+}$ and Cu$^{2+}$ exhibit the absorptions caused by the cleavage of adsorbent. Even among these three samples, as Cu$^{2+}$ is well-known to be responsible for acidic property weaker than Al$^{3+}$ and Fe$^{3+}$ ions, its clay complex shows a little weaker absorption attributable to the hydrolysis than the two others, but shows a much strong band due to the former mechanism according to the competitive effect. The third mechanism is the reaction between metal ions and piperidinic nitrogen. This reaction could presumably be the complexation reaction or simple polar effection.

Although it cannot be proved that the same mechanism may apply to the adsorption from water, a simple behavior, 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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