

INTERACTION OF THE HERBICIDE ACIFLUORFEN WITH MONTMORILLONITE: FORMATION OF INSOLUBLE Fe^{3+} , Al^{3+} , Cu^{2+} , AND Ca^{2+} COMPLEXES

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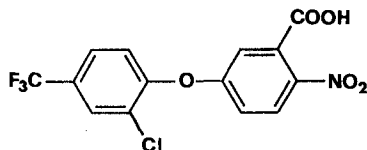
Abstract—Analytical, spectroscopic, and X-ray powder diffraction techniques were used to investigate the adsorption of the herbicide sodium acifluorfen (acifluorfen = 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid) from aqueous solution onto Cu^{2+} -, Al^{3+} -, Fe^{3+} -, and Ca^{2+} -saturated montmorillonite. As indicated by infrared and electron spin resonance spectra, which are coincident with those of the corresponding solid metal complexes, and by the basal spacings, which are the same for all the samples, acifluorfen extracted the exchangeable ions from the clay interlayer and precipitated them on external surfaces. The process involved the replacement of sodium as the saturating ion and was due to the formation of insoluble complexes between the herbicide and polyvalent metal ions.

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

INTRODUCTION

The fate of pesticides in soil is governed, to a large extent, by their adsorption on soil components. In this connection, clay minerals are among the most active soil components (Mortland, 1976; Crosby, 1976). Depending on the interaction mechanisms, the adsorption process may produce relevant effects on the interlayer metal ions. For example, saturating ions can lose exchangeability, e.g., due to the irreversible adsorption of pesticides as protonated species (Gessa *et al.*, 1987). On the other hand, pesticides having binding sites, once adsorbed into the interlayer, can coordinate to the metal ions and alter their chemical form and exchangeability. Metal ions forming neutral complexed species are replaced as saturating cations, e.g., by protons or protonated molecules, and therefore diffuse freely into solution (Micera *et al.*, 1988; Pusino *et al.*, 1989). Moreover, immobilization and mutual inactivation of both metal ions and pesticides are expected if insoluble complexes form.

Sodium-acifluorfen, the sodium salt of 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid,



is a herbicide widely used for selective postemergence control of broadleaf weeds in large-seed legume crops. Because of its wide use, satisfactory information is

available on the bioactivity of this herbicide (Duke *et al.*, 1984; Kenyon *et al.*, 1988; Willingham *et al.*, 1989), but not on its interaction with the soil components. The present study was therefore undertaken to investigate the interactions between sodium acifluorfen and Fe^{3+} -, Al^{3+} -, Cu^{2+} -, and Ca^{2+} -saturated montmorillonite.

EXPERIMENTAL

Materials

Montmorillonite No. 25 (bentonite) from Upton, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used in this study. The $<2\text{-}\mu\text{m}$ size fraction was obtained by sedimentation. The cation-exchange capacity (CEC), as determined by literature methods (Hendershot and Duquette, 1986), was 90.2 meq/100 g. Fe^{3+} -, Al^{3+} -, Cu^{2+} -, and Ca^{2+} -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. Sodium acifluorfen ($\text{C}_{14}\text{H}_6\text{ClF}_3\text{NNaO}_5$) was supplied by Rhône-Poulenc AG Company, USA, as a yellow hygroscopic solid.

The Fe^{3+} , Al^{3+} , Cu^{2+} , and Ca^{2+} complexes of acifluorfen were prepared by mixing aqueous solutions of sodium acifluorfen (1.5×10^{-3} mole in about 5 ml) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5×10^{-3} mole in about 2 ml), respectively. The precipitates obtained were filtered, washed first with water and then with absolute ethanol, and finally air-dried. Microanalytical (C, H, and N) and thermogravimetric data for the complexes are given in Table 1.

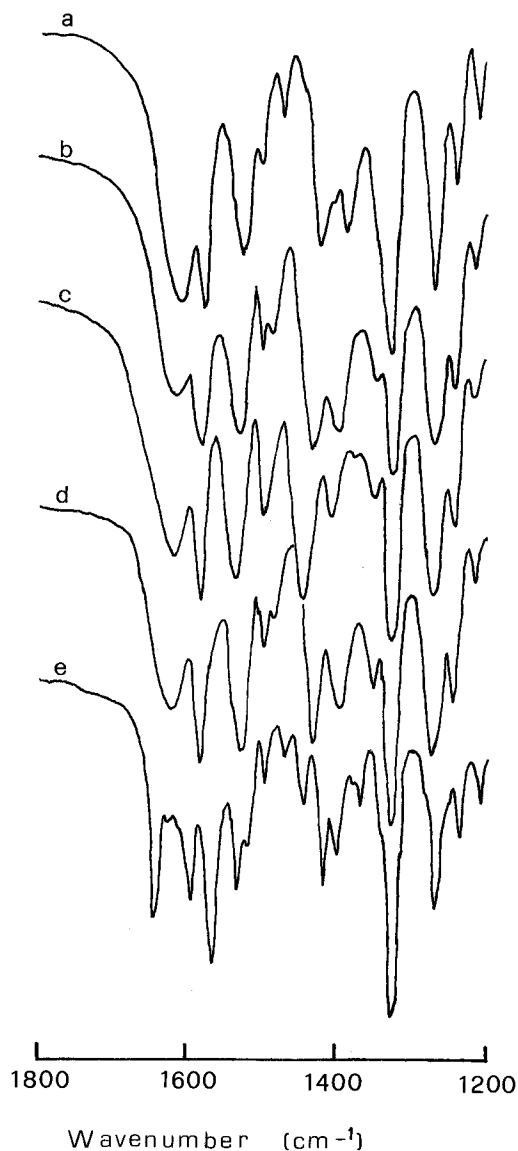


Figure 1. Infrared absorption spectra (KBr disks) of the (a) Na^+ salt, and the (b) Fe^{3+} , (c) Al^{3+} , (d) Cu^{2+} , and (e) Ca^{2+} complexes of acifluorfen.

Adsorption of the herbicide

The herbicide was adsorbed onto the montmorillonite samples by immersing 50 mg of clay in a 2% solution of sodium acifluorfen in water. After 24 hr, the clay was separated from the solution by centrifugation and washed twice with water to remove the excess pesticide. The samples were then slurried in 10 ml of distilled water: 5 ml was pipeted onto polyethylene sheets and the remaining 5 ml was pipeted onto glass slides to obtain air-dried clay films suitable for infrared (IR) and X-ray powder diffraction (XRD) analysis, respectively.

Solubility measurements

Solubilities were measured by equilibrating 100 mg of each solid complex with 10 ml of water, with stirring, for 24 hr at $25 \pm 0.1^\circ\text{C}$. After centrifuging at 50,000 g for 30 min, 5-ml aliquots of the supernatant solutions were withdrawn, acidified to pH 3, and analyzed for acifluorfen by high-performance liquid chromatography (HPLC) and for metal ions by spectrophotometric or titrimetric methods (Bandemer and Schaible, 1944; Chenery, 1948; Hildebrand and Reilly, 1957; Nebesar, 1964). All the experiments were performed in triplicate.

Analyses and spectroscopic measurements

HPLC analyses were carried out using a Waters 501 liquid chromatograph equipped with a 250×4 mm i.d. Lichrosorb RP 18 analytical column ($5 \mu\text{m}$), a Waters detector operating at 225 nm, and a Waters 740 data module. The mobile phase (1 ml/min) was composed of acetonitrile + water (70 + 30, by volume, pH 3.0). The retention time of acifluorfen, as the free acid, was 5.48 min. Sodium was analyzed with a Corning 410 flame photometer. IR spectra were recorded with a Perkin-Elmer 683 spectrophotometer. Spectra for the sodium salt and the metal complexes of acifluorfen were obtained using KBr disks, whereas those for the pesticide-clay complexes were recorded using self-supporting films. Electron spin resonance (ESR) measurements at the X-band were carried out at room temperature using a Varian E 9 spectrometer. Microanalyses (C, H, and N) were made using a Perkin-Elmer 240 analyzer. Thermogravimetric measurements were made with a Perkin-Elmer TGS 2 apparatus at the heating rate of $5^\circ\text{C}/\text{min}$ under a nitrogen flow. XRD data were obtained at 25°C on a Philips PW 1730 diffractometer equipped with an Olivetti M-20 computer, using $\text{CoK}\alpha$ radiation.

RESULTS AND DISCUSSION

Metal complexes of acifluorfen

The elemental analyses of the complexes of acifluorfen with copper and calcium, listed in Table 1, were consistent with a ligand-to-metal molar ratio of 2:1, whereas those of iron and aluminum complexes indicated the presence of three deprotonated ligands per metal ion. The IR spectra of all complexes (Figure 1 and Table 2) exhibited two bands in the ranges $1605\text{--}1645 \text{ cm}^{-1}$ and $1385\text{--}1405 \text{ cm}^{-1}$; these bands were assigned to the ν_{as} (COO) and ν_{sym} (COO) stretches, respectively, indicating metal-bound carboxylate groups.

A precise description of the structure was possible only for the copper compound, inasmuch as the ESR spectrum ($g_{\parallel} = 2.36$, $g_{\perp} = 2.08$, and zero-field splitting $D = 0.34 \text{ cm}^{-1}$) was clearly indicative of a dinuclear complex of copper(II) acetate-type (Brown and Chidambaram, 1973). In this type of complex the two

Table 1. Analytical data and proposed stoichiometry for complexes of acifluorfen.¹

| Complex | C (%) | H (%) | N (%) | H ₂ O ² (%) |
|--|---------------|-------------|-------------|-----------------------------------|
| Ca(C ₁₄ H ₆ ClF ₃ NO ₃) ₂ ·2H ₂ O | 42.16 (42.17) | 2.07 (2.02) | 3.42 (3.51) | 4.5 (4.52) |
| Cu ₂ (C ₁₄ H ₆ ClF ₃ NO ₃) ₄ ·4H ₂ O | 41.22 (40.97) | 1.94 (1.96) | 3.38 (3.41) | 4.5 (4.39) |
| Al(C ₁₄ H ₆ ClF ₃ NO ₃) ₃ ·2H ₂ O | 43.48 (44.06) | 1.98 (1.94) | 3.57 (3.67) | 3.0 (3.15) |
| Fe(C ₁₄ H ₆ ClF ₃ NO ₃) ₃ ·2H ₂ O | 42.16 (42.98) | 1.78 (1.89) | 3.46 (3.58) | 3.0 (3.07) |

¹ Calculated values in parentheses.² Thermogravimetric determination.

metal ions, lying at a distance as short as 2.6–2.7 Å from each other, are bridged by four carboxylate groups of the ligands. This finding was confirmed by the preliminary results of a single crystal X-ray diffraction study, which, although still in progress in this laboratory, substantiated such a structural arrangement in the solid complex. Similar dimeric structures have been previously observed in the solid state for the copper(II) complexes of other carboxylic pesticides, e.g., fluazifop and diclofop (Micera *et al.*, 1988; Pusino *et al.*, 1989).

Adsorption of sodium acifluorfen on clays

The IR spectra of Fe³⁺-, Al³⁺-, Cu²⁺-, and Ca²⁺-clays treated with sodium acifluorfen showed bands attributable to the ν_{as} (COO) and ν_{sym} (COO) modes of carboxylate groups, which exhibit metal-dependent shifts compared with those of the sodium salt. Thus, the interaction between acifluorfen and the clay led to the formation of carboxylate complexes. Noticeably, the IR frequencies of the carboxylate groups were exactly the same as those for the metal complexes precipitated from aqueous solution. In addition, an ESR spectrum of the dinuclear type was observed for the copper(II) clay after interaction with acifluorfen. All these findings suggest that, rather than being adsorbed in the interlayer, the complexes were precipitated on the outer surfaces. In fact, usually, metal complexes formed in the interlayer adopt a structure somewhat different from that in the solid state. For example, Micera *et al.* (1988) and Pusino *et al.* (1989) showed that, because of hydrogen bonding with water molecules, the IR bands of carboxylate groups undergo detectable shifts in the interlayer and, insofar as copper(II) complexes are concerned, those formed in clays are monomeric.

Table 2. Infrared spectroscopic absorptions (cm⁻¹) of carboxylate groups for metal complexes of acifluorfen.¹

| Metal ion | ν_{as} | ν_{sym} |
|------------------|------------|-------------|
| Na ⁺ | 1605 | 1385 |
| Al ³⁺ | 1612 | 1405 |
| Fe ³⁺ | 1615 | 1395 |
| Cu ²⁺ | 1620 | 1395 |
| Ca ²⁺ | 1645 | 1400 |

¹ ν_{as} and ν_{sym} = carboxylate antisymmetric and symmetric stretches, respectively.

The d(001) values of the treated samples (Table 3), as measured by XRD analysis, indicate that the dimension of the interlayer space was almost the same for all the samples and about equal to the value typical of a Na-montmorillonite. Moreover, this interlayer space was too narrow to intercalate the bulky dimeric complexes formed by copper(II) with the herbicide. These data rule out the possibility that acifluorfen occupied the intermellar space of the phyllosilicates, which likely accommodated only hydrated sodium ions. Analyses for sodium supported this conclusion. In fact they showed that, on treating a Cu-montmorillonite sample with an amount of Na-salt of acifluorfen equivalent to the CEC, the supernatant was completely depleted in sodium. In contrast, on treating the clay with NaCl, 59.45% of the ion remained in solution.

The mechanism that is consistent with all the results is that the sodium replaced the saturating metal ions and the metal ions were then complexed by the acifluorfen and precipitated on outer surfaces of the clay. The low solubility of the complexes formed was therefore the driving force of the whole process.

The solubility products were roughly evaluated by HPLC analysis of the pesticide and spectrophotometric or titrimetric determination of metal ions. HPLC, which can measure concentrations of acifluorfen as low as 10⁻⁶ M, failed to detect the herbicide in water after equilibration with the Fe and Al complexes for 24 hr. Thus, assuming that the stoichiometry of the solution complexes was the same as that in the solid state, the solubility products were probably <3 × 10⁻²⁴ M. This evaluation was confirmed by titrimetric and spectrophotometric analysis for metal ions. The same analytical procedure allowed values of about 1.5 × 10⁻¹⁹ M

Table 3. Basal spacings of homoionic bentonites untreated and treated with sodium acifluorfen.¹

| Cation | d(001) (Å) | |
|------------------|------------|---------|
| | Untreated | Treated |
| Fe ³⁺ | 15.10 | 12.65 |
| Al ³⁺ | 15.19 | 12.70 |
| Cu ²⁺ | 12.44 | 12.61 |
| Ca ²⁺ | 14.96 | 12.75 |
| Na ⁺ | 12.41 | 12.53 |

¹ Montmorillonite No. 25 from Upton, Wyoming.

and 1.7×10^{-25} M to be calculated for the Ca^{2+} and Cu^{2+} complexes, respectively.

SUMMARY AND CONCLUSIONS

The results demonstrate that acifluorfen effectively complexed metal ions in montmorillonite. These findings are significant for the soil chemistry of acifluorfen, inasmuch as the inactivation following complex formation is responsible for the loss of herbicidal activity. Dissolved sodium acifluorfen may interact with iron and aluminum in clay minerals to give very sparingly soluble complexes. Due to the occurrence of Al and Fe as hydrous metal oxides also, these compounds are likely involved in adsorption of the pesticide and metal complex formation. As a consequence of these interactions, relevant soil processes, e.g., the reversible adsorption of metal ions, may be affected.

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