Interaction of Chlordimeform with a Vermiculite-Decylammonium Complex in Aqueous and Butanol Solutions

ABSTRACT — The interaction of a vermiculite-decylammonium complex with chlordimeform in aqueous or butanol solutions was studied. When the complex is treated with an aqueous solution of chlordimeform, the degradation of chlordimeform occurs in the interface of the interlamellar space through a basic hydrolysis process, to yield a secondary amide which remains as a neutral molecule in the interlamellar space, together with the decylammonium ions. If the complex is treated with butanol solutions of chlordimeform, this organic cation does not interact with the clay mineral and the decylammonium ions decompose to ammonium ions, because of the high acidity of the residual water.

Introduction

The process of inorganic cation exchange in clay minerals is, nowadays, perfectly known. Likewise, clay minerals can strongly adsorb organic cations in their interlamellar spaces through a cation exchange process (MORTLAND, 1970; THENG, 1974). Cationic pesticides are also adsorbed by an ion-exchange process in the interlamellar space of montmorillonite and vermiculite (WEBER et al., 1965; HAYES et al., 1978; PEREZ RODRIGUEZ & HERMOSIN, 1979; HERMOSIN & PEREZ RODRIGUEZ, 1981; MORILLO et al., 1983).

The intercalation of some organic species by alkylammonium clay complexes has been studied (THENG, 1974), but there is not much work devoted to the behaviour of such alkylammonium clay complexes versus other organic cations (specially pesticides) or to the effect of the solvent on such process.

The present paper reports a study of the interaction of chlordimeform, an organic cationic pesticide, in aqueous or butanol solutions with decylammonium-vermiculite, in order to investigate the mechanism of such processes and the influence of the solvents used.

Experimental

The vermiculite used in this study was obtained from the «Santa Olalla» deposit (Huelva, SW Spain), and it was in the Na⁺ form. The vermiculite-decylammonium complex was prepared according to the method proposed by LAGALY & WEISS (1969).

Technical grade chlordimerform (N'-(4-chloro-2-methylphenyl)-N,N-dimethyl methanoimidamide hydrochloride) was used. This pesticide is soluble in water (50% by weight) and ionizes completely giving the chlordimeform cation (CfH⁺) and chloride anion. Chlordimeform is very stable in aqueous solution up to pH 6.5, above which, it begins to hydrolize according to the following steps ((a)→(b)→(c)→(d)):

(a) Cl—⟨ ⟩—N=CH—N(CH₃)₂ · ClH
CH₃
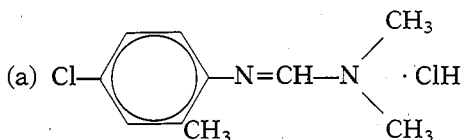
Chlordimeform chlorhydrate
pH > 5

(b) Cl—⟨ ⟩—N=CH—N(CH₃)₂
CH₃
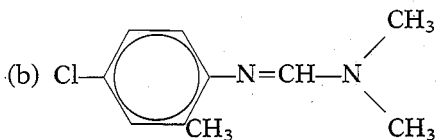
Chlordimeform
pH > 6.5

(c) Cl—⟨ ⟩—NH—C(O)H
CH₃
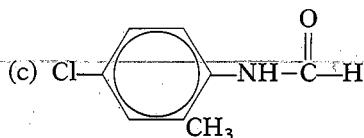
N-Formyl-4-chloro-o-toluidine
pH > 8

(d) Cl—⟨ ⟩—NH₂
CH₃
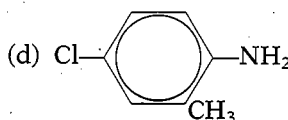
4-chloro-o-toluidine

The vermiculite-decylammonium complex was treated with 25 mmol/l of aqueous (pH = 4.8) or butanol solutions of chlordimeform, at 60 °C, shaking several times. The chlordimeform solutions were changed weekly.

The interplanar spacings were determined by X-ray powder diffraction using several orders of the (001) reflections. The samples were examined as oriented films supported on glass slides.

The infrared absorption spectra were recorded from 4000 cm⁻¹ to 400 cm⁻¹ using a Perkin Elmer double beam spectrophotometer. Samples were examined as KBr discs.

Results and discussion

The information about the interaction of the decylammonium-vermiculite complex with aqueous and butanol solutions was obtained from the study of the changes observed by X-ray diffraction and IR spectroscopy of the decylammonium-

vermiculite complex after several treatments.

Interaction of aqueous solutions of chlordimeform with the vermiculite-decylammonium complex

The X-ray powder diffraction analysis of the vermiculite-decylammonium complex treated with water, and with aqueous solutions of chlordimeform for one and nine weeks are shown in Fig. 1.

The vermiculite-decylammonium complex shows a basal spacing of 21.21 Å which, according to JOHNS & SEN GUPTA (1967), corresponds to the fully collapsed phase. In this complex a monolayer of the alkylammonium ions is in the interlamellar space with its chains inclined with respect to the silicate layer. The 0.3 Å difference between our value for this basal reflection and that reported by JOHNS & SEN GUPTA (1967) may be attributed to the possible different layer charge and/or to some interlamellar water.

The basal spacing of the vermiculite-decylammonium complex increases to 27.98 Å after one week of treatment with aqueous chlordimeform solutions, but the higher orders of this reflection are not clearly defined (Fig. 1b). After two weeks the basal spacing of 27.98 Å and the rest of the basal reflections appear clearly defined, remaining without change until the end of the treatment (Fig. 1c). These results show an expansion of the interlamellar space
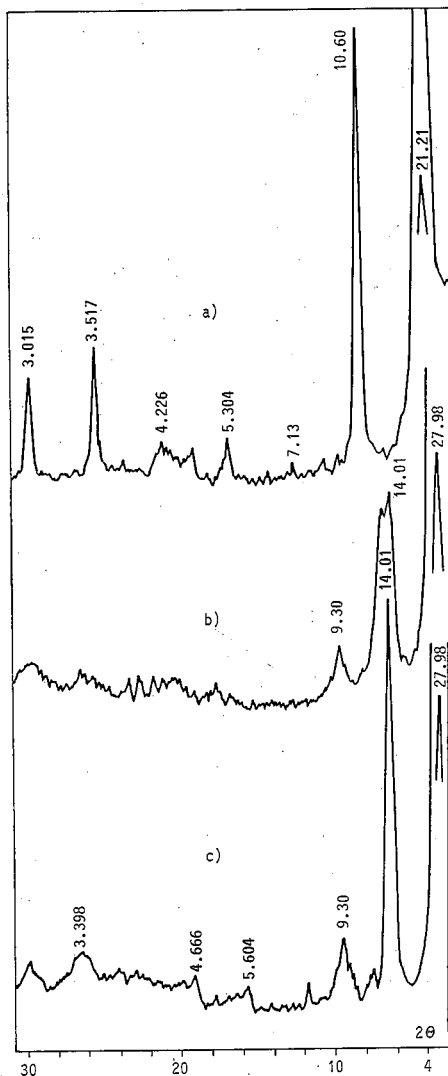

Fig. 1 - X-ray powder diffractograms of the vermiculite-decylammonium complex treated with: a) water for five weeks, b) aqueous solution of chlordimeform for one week, c) aqueous solution of chlordimeform for nine weeks.

of the vermiculite-decylammonium complex. This is not due to a cationic exchange between the chlordimeform and the decylammonium cations to yield a vermiculite-
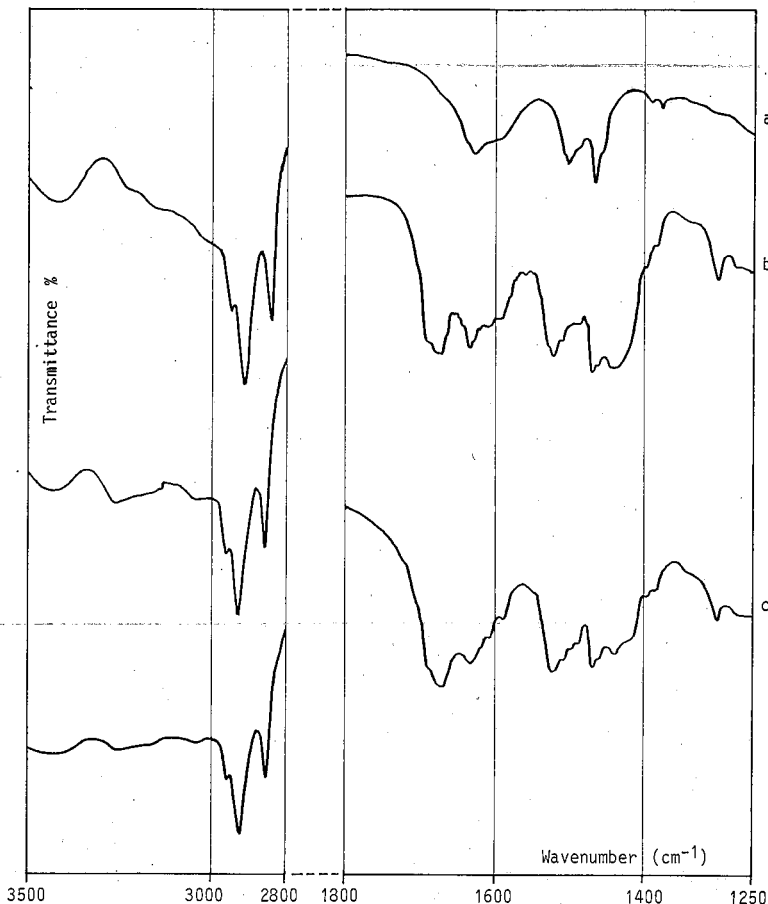
Fig. 2 - IR spectra of the vermiculite-decylammonium complex treated with: a, water for five weeks; b, aqueous solution of chlordimeform for one week; c, aqueous solution of chlordimeform for nine weeks.

chlordimeform complex, because this latter should have a basal spacing of 14.6 Å (MORILLO *et al.*, 1983). The higher values of this basal reflection suggest that decylammonium cations remain in the interlamellar space together with other organic species which produce a change of arrangement or disposition of the alkylammonium ions.

The study by IR spectra of this vermiculite-decylammonium complex without treatment and treated with aqueous chlordimeform solutions permits more direct information of the species in the interlamellar spaces of these complexes to be obtained. These spectra are shown in Fig. 2, for the regions 3500-2800 cm^{-1} and 1800-1250 cm^{-1}, where the more interesting features appear.

The spectrum of the decylammonium vermiculite complex (Fig. 2a) shows the characteristic bands cor-

responding to the -CH$_3$ (2950, 1450 cm^{-1}), -CH$_2$-(2920, 2850, 1460 cm^{-1}) and -NH$_3^+$ (3100, 1625, 1570, 1500 cm^{-1}) groups of the alkylammonium ions. The vibrations at 1625 cm^{-1} and 1500 cm^{-1} correspond to the asymmetrical and symmetrical NH deformation of the -NH$_3^+$ groups. At 1570 cm^{-1} a shoulder appears corresponding to the symmetrical -NH deformation of the -NH$_3^+$ groups bonded to the basal oxygens by a stronger H-bond (SERRATOSA *et al.*, 1970). The 1625 cm^{-1} band also corresponds to the OH deformation of water, since at 3400 cm^{-1} the OH stretching band is observed, indicating the presence of some interlamellar water.

When the vermiculite-decylammonium complex is treated with an aqueous solution of chlordimeform for one to nine weeks, the infrared spectra show the vibrations of the decylammonium ions at slightly frequencies, together with others at 1675, 1523 and 1300 cm^{-1}. These new bands, appearing clearly defined after nine weeks of treatment, do not correspond to chlordimeform cations and can be assigned to the amide I (C = 0 stretching), amide II (NH deformation) and amide III (combination of C-N and N-H vibrations) bands of a secondary amide, besides the 1600-1450 cm^{-1} bands of the aromatic rings. Since a secondary amide is the product of the irreversible hydrolysis of chlordimeform when the pH is higher than 6.5, this process should occur when chlordimeform begins to enter in the interlamellar space of the decylammonium-vermiculite complex from the aqueous solutions. The pH in the interlamellar space should be close to neutrality because of the presence of alkylammonium ions, whose hydrophobic character prevents the entry of the bulk solution.

The 27.98 Å final complex obtained should be similar to the partially collapsed complex described by JOHNS & SEN GUPTA (1967). The alkylammonium ions remain in the interlamellar space with the same or less inclination, in addition to the neutral molecules of N-formyl-4-chloro-o-toluidine. The amide molecules can be associated to the alkylammonium ions by H-bonds between -NH$_3^+$ and -C=0 groups, as suggested by the observed shiftings in the frequency of the amide band from 1700 to 1675 cm^{-1} (BELLAMY, 1975) and the 1620 cm^{-1} band (N-H deformation of -NH$_3^+$) to 1630 cm^{-1} (DONER & MORTLAND, 1969).

Interaction of the butanol solution of chlordimeform with the vermiculite-decylammonium complex

The X-ray powder diffraction analysis of the vermiculite-decylammonium complex treated with butanol and with butanol solutions of chlordimeform for one and nine weeks, are shown in Fig. 3. The vermiculite-decylammonium treated with butanol shows a basal spacing of 21.19 Å which, after one week of treatment with the chlordimeform
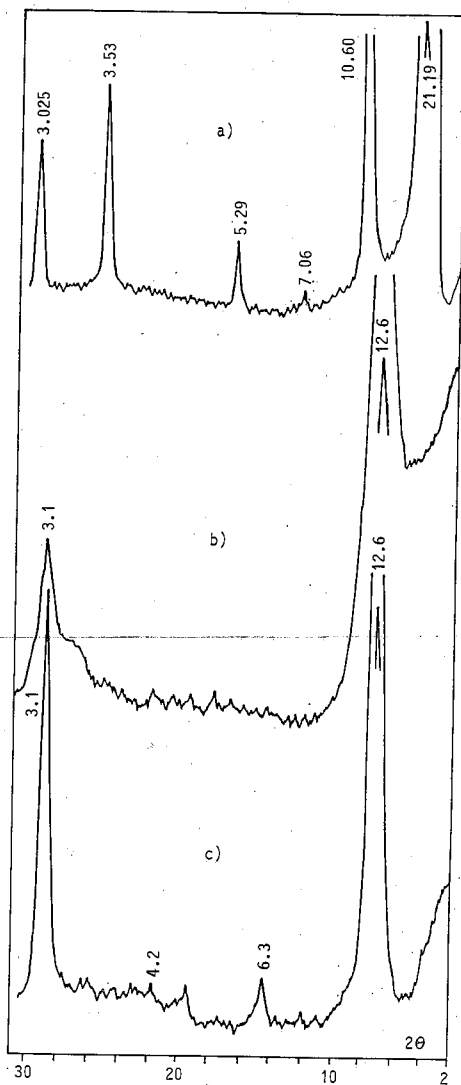
Fig. 3 - X-ray powder diffractograms of the vermiculite-decylammonium complex treated with: a) butanol for one week, b) butanol solution of chlordimeform for one week, c) butanol solution of chlordimeform for nine weeks.

spacing from 21.19 Å to 12.6 Å shows a change which doesn't agree with the formation of the vermiculite-chlordimeform complex, but suggests an important alteration of the interlamellar space.

IR spectra of the vermiculite-decylammonium complex treated with butanol for one week and with the chlordimeform solution in butanol for one and nine weeks are shown in Fig. 4. The spectrum of the sample treated with butanol for one week is equal to that described above for water treatment. Butanol does not affect the vermiculite-decylammonium spectrum.

The spectra of the vermiculite-decylammonium complex treated with the chlordimeform solution in butanol for one and nine weeks show many differences in relation to the last one. The absorptions at 3250, 3040, 2800 and 1430 cm^{-1} are clearly characteristics of the ammonium ion (NH$_4^+$) in the interlamellar space. Also bands at 2900, 2800 and 1470 cm^{-1} of the C-H of CH$_2$ or CH$_3$ groups are present besides the water bands at 3420 and 1625 cm^{-1}.

These data show the presence of ammonium ions in the interlamellar space of vermiculite together with aliphatic chain compounds, since the basal spacing (12.6 Å) is higher than that of the ammonium-vermiculite (10.5 Å for our sample). These features suggest a decomposition of the alkylammonium ions, by a process similar to that described by DURAND et al. (1972) for the alteration of alkylammonium ions in the interlamellar

butanol solution, decreases to 12.6 Å (Fig. 3b) and whose higher basal diffractions appear perfectly defined after nine weeks of treatment (Fig. 3c).

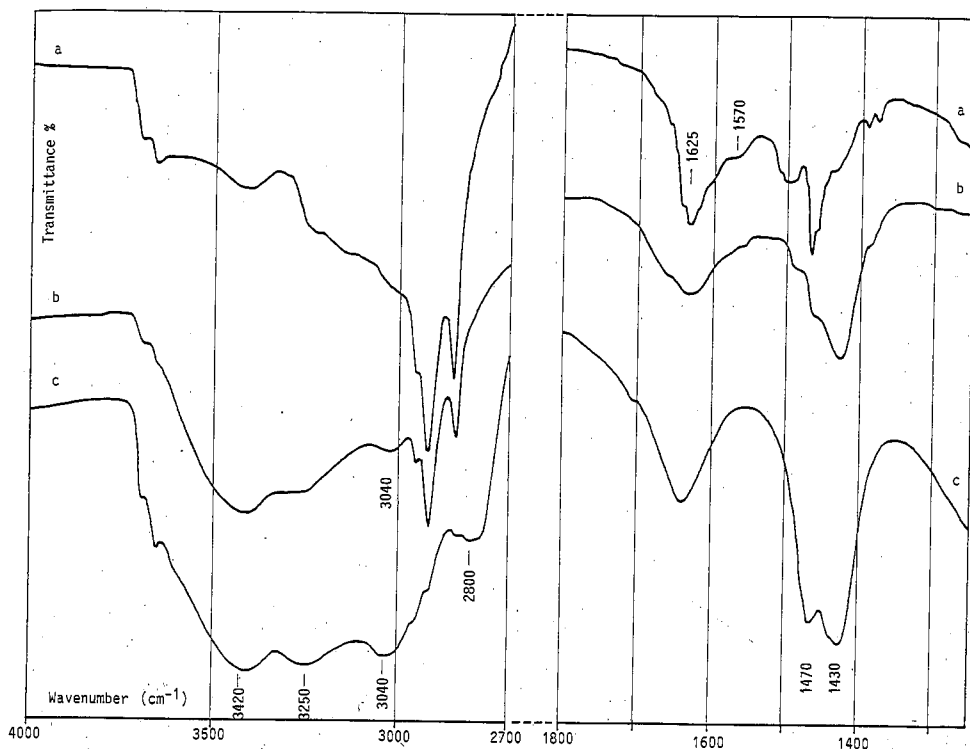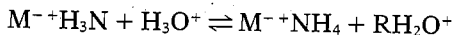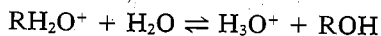The decrease of the complex basal

Fig. 4 - IR spectra of the vermiculite-decylammonium complex treated with: a, butanol for one week; b, butanol solution of chlordimeform for one week; c, butanol solution of chlordimeform for nine weeks.
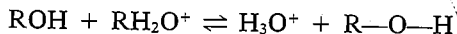
space of clay minerals in an inert atmosphere:

reaction 1
$$M^{-+}H_3N + H_3O^+ \rightleftharpoons M^{-+}NH_4 + RH_2O^+$$

reaction 2
$$RH_2O^+ + H_2O \rightleftharpoons H_3O^+ + ROH$$

reaction 3
$$ROH + RH_2O^+ \rightleftharpoons H_3O^+ + R—O—H$$

The C-N rupture is attributed to the high acidity of the small amount of water present in the system which probably is highly protonated, since the solvent of the chlordimeform is butanol. This rupture could be partially facilitated by the silicate surface in which the -NH$_3^+$ groups of the alkylammonium ions are located in the hexagonal (trigonal) «holes» (JOHNS & SEN GUPTA, 1967). The organic species resulting from the alkylammonium decomposition (*reactions 2 and 3*) are partially released to the solution or to the external surface, and another part remains in the interlamellar space probably in a more or less flat position.

The failure of chlordimeform to enter into the interlamellar space is

due to the solvent effect in which the chlordimeform should be deprotonated by the residual water of the clay, since the H_3O^+ is the real interacting species.

Conclusions

The interaction of chlordimeform in aqueous or butanol solutions with decylammonium-vermiculite occurs by different mechanisms as an effect of the solvent:

— in *aqueous medium*, the chlordimeform is hydrolyzed yielding a secondary amide which remains in the interlamellar space together with the alkylammonium ions;

— in *butanol medium*, the alkylammonium ions are decomposed to yield interlamellar ammonium ions, as well as the aliphatic products of such decomposition.

REFERENCES

BELLAMY L.J., 1975. *The Infrared Spectra of Complex Molecules*. Vol. I, J. Wiley & Sons, New York.

DONER M.E., MORTLAND M.M., 1969. *Intermolecular interaction in montmorillonite: NH-CO systems*. Clays Clay Miner. **15**, 259-271.

DURAND D., PELET R., FRIPIAT J.L., 1972. *Alkylammonium decomposition on montmorillonite surfaces in an inert atmosphere*. Clays Clay Miner. **20**, 21-35.

HAYES M.H.B., PICK M.E., TOMS B.A., 1978. *The influence of organocation structure on the adsorption of mono and of bipyridilium cations by expanding lattice clay minerals. I and II*. J. Colloid & Interface Sci. **65**, 254-275.

HERMOSIN M.C., PEREZ RODRIGUEZ J.L., 1981. *Interaction of chlordimeform with clay minerals*. Clays Clay Miner. **29**, 143-152.

JOHNS W.D., SEN GUPTA P.K., 1967. *Vermiculite-alkylammonium complexes*. Am. Miner. **52**, 1706-1724.

LAGALY G., WEISS A., 1969. *Determination of the layer charge in mica-type layer silicates*. Pp. 234-277, in: Proc. Int. Clay Conf. 1969, Tokyo, Vol. I, Israel Universities Press, Jerusalem.

MORILLO E., PEREZ RODRIGUEZ J.L., HERMOSIN M.C., 1983. *Estudio del complejo interlaminar vermiculita-clordimeform*. Bol. Soc. esp. Min. **7**, 25-30.

MORTLAND M.M., 1970. *Clay organic complexes and interactions*. Adv. Agron. **22**, 75-117.

PEREZ RODRIGUEZ J.L., HERMOSIN M.C., 1979. *Adsorption of chlordimeform by montmorillonite*. Pp. 227-234, in: Proc. Int. Clay Conf. 1978, Oxford (M.M. Mortland and V.C. Farmer, editors), Developments in Sedimentology 27.

SERRATOSA J.M., JOHNS W.D., SHIMOYAMA A., 1970. *IR study of alkylammonium vermiculite complexes*. Clays Clay Miner. **18**, 107-113.

THENG B.K.G., 1974. *Interactions with positively charged organic species*. Pp. 211-238, in: The Chemistry of Clay-organic Reactions, Adam Hilger, London.

WEBER J.B., PERRY P.W., UPCHURCH R.P., 1965. *The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D, and prometone by clays, charcoal, and an anion-exchange resin*. Soil Sci. Soc. Amer. Proc. **29**, 678-687.