

FORMATION OF POLYETHYLENE GLYCOL ON MONTMORILLONITE BY STERILIZATION WITH ETHYLENE OXIDE

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Abstract—The effect of ethylene oxide-sterilization on homoionic (Na⁺, K⁺, Ca²⁺, Cu²⁺, Al³⁺, and Fe³⁺) montmorillonite samples was examined. The results indicate that ethylene oxide polymerized to polyethylene glycol in the interlayer of Cu²⁺-, Al³⁺-, and Fe³⁺-saturated clays, as substantiated by the increase in the d(001) values, as well as by the decrease in the cation-exchange capacity after reaction. On the contrary, ethylene oxide failed to react in the presence of the Na⁺-, K⁺-, and Ca²⁺-clays, likely due to the lower acidity of the exchange cations.

Key Words—Adsorption, Infrared spectroscopy, Ethylene oxide, Interlayer cations, Montmorillonite, Polymerization, Sterilization, X-ray powder diffraction.

INTRODUCTION

Tests for the biodegradability of pesticides are usually made by comparing dissipation curves for sterile and non-sterile soils. Sterilization, however, commonly alters some soil properties, e.g., the specific surface (Eno and Popenoe, 1964), as well as the amount of soluble salts or organic matter (Salonius *et al.*, 1967; Skipper and Westermann, 1973).

Among the sterilization methods commonly used, gamma irradiation requires a highly specialized and expensive equipment. Epoxides, however, are considered to be appropriate sterilizants in studies of the chemical transformation of pesticides in soils, because they induce the least chemical alterations (Skipper and Westermann, 1973). From their examination of the degradation and persistence of 3-chloroaniline, Fletcher and Kaufman (1980) concluded that the amount and the distribution of ¹⁴C residual material in ethylene oxide-treated soil were comparable with those in non-sterile conditions. They also found that, unlike potassium azide and autoclaving, ethylene and propylene oxides caused only a slight inhibition of the peroxidase enzyme. Ethylene and propylene oxides, on the other hand, increased soil pH and extractable Mn, Cu, Fe, and organic matter (e.g., Lopes and Wollum, 1976; Gennari *et al.*, 1987). According to Allison (1951), the increase of organic matter was primarily due to the adsorption of ethylene oxide by organic and inorganic soil colloids. In the same paper, Allison also reported that adsorbed ethylene oxide was converted into ethylene glycol.

In the present study the interactions between ethylene oxide and montmorillonite were examined to investigate whether sterilizant by this material affects the adsorptive capacity of the soil clay. Therefore, ion-exchanged (Na⁺, K⁺, Ca²⁺, Cu²⁺, Al³⁺, and Fe³⁺) mont-

morillonite samples were tested under the standard conditions used with this sterilizant.

EXPERIMENTAL

Materials

The clay used in this study was montmorillonite 25 (bentonite) from Upton, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York. The <2- μ m size fraction was obtained by sedimentation. The Na⁺-, K⁺-, Ca²⁺-, Fe³⁺-, Al³⁺-, and Cu²⁺-exchanged samples were prepared by treating the clay with 1 N solutions of the corresponding metal chlorides. The samples were then centrifuged, washed repeatedly with deionized water until a test of the supernatant solution for chloride was negative, and, finally, dried at room temperature.

Ethylene oxide adsorption

Self-supporting clay films were inserted into polyethylene bags of "BARD" Steril Peel (7.6 cm) Packaging System type. Applications of 12% ethylene oxide in a Freon 12 atmosphere (4×10^5 Pa pressure, 65% RH, 40°C) were carried out for 8 hr, followed by a 3-day desorption.

Cation-exchange capacity

The cation-exchange capacity (CEC) of the homoionic clays, before and after the ethylene oxide treatment, was determined by saturating the clay with 1 N BaCl₂ and then determining desorbed Ba²⁺ after exchange with 0.1 N MgCl₂ (Hendershot and Duquette, 1986).

Physical measurements

Infrared (IR) spectra were recorded with a Perkin-Elmer 683 spectrophotometer. The samples were sub-

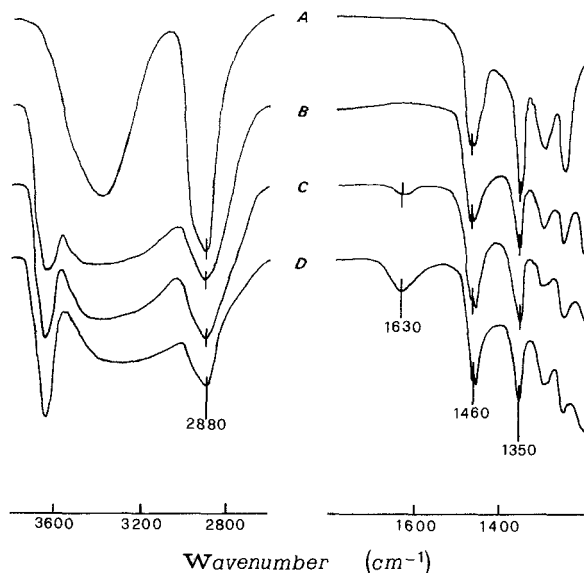


Figure 1. Infrared spectra of (A) polyethylene glycol (neat), (B) Fe-, (C) Al-, and (D) Cu-montmorillonite after reaction with ethylene oxide.

mitted to IR analysis as self-supporting films. X-ray powder diffraction (XRD) data were obtained on a Philips PW 1730 instrument equipped with an Olivetti M-20 computer, using $\text{CoK}\alpha$ radiation. Determination of desorbed Ba^{2+} , for CEC measurements, was made by plasma emission spectrometry using a Beckman Spectraspan IV instrument.

RESULTS

Infrared spectra

With the exception of the Na-, K-, and Ca-montmorillonite samples, the treated samples exhibited IR spectra (Figure 1) different from those of the untreated clays. In particular, the distinguishing features of the Cu-, Al-, and Fe-treated clays were (1) the occurrence of absorption bands centered at 2880 cm^{-1} , attributable to the asymmetric and symmetric stretching vibrations of a methylene group; (2) a double band at 1460 cm^{-1} characteristic of the CH_2 -scissoring mode; and (3) three bands at 1350 , 1300 , and 1240 cm^{-1} , attributable to the CH_2 -twisting and -wagging vibrations (Brown *et al.*, 1950). The intensity of these bands increased in the order $\text{Cu} < \text{Al} < \text{Fe}$, whereas the water-bending vibration at 1630 cm^{-1} became parallelly weaker. The 2880 -, 1460 -, 1350 -, 1300 -, and 1240-cm^{-1} absorptions were strongly weakened by washing the sample with water and were identified as the distinctive IR features of the oily, colorless, liquid residue remaining after evaporation of the aqueous solution. Examination of the absorption bands of the water-extractable product showed that they were characteristic of polyethylene glycol, $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{CH}_2-\text{OH}$

Table 1. $d(001)$ values (\AA) for homoionic montmorillonite samples, untreated and treated with ethylene oxide.¹

Cation	Untreated		Treated	
	25°C	90°C	25°C	90°C
Na^+	12.4	10.5	11.9	10.8
K^+	11.8	10.5	11.3	10.5
Ca^{2+}	14.9	12.4	14.8	12.2
Cu^{2+}	12.4	11.7	13.5	13.3
Al^{3+}	15.1	12.2	18.2	14.3
Fe^{3+}	15.1	11.5	19.0	16.5

¹ Values measured on samples treated as reported in text and examined by X-ray powder diffraction after equilibration at 25°C or dehydration at 90°C .

(Craver, 1980). The same bands were observed by Parfitt and Greenland (1970b) for polyethylene glycol adsorbed on montmorillonite.

The IR spectra of the Na-, K-, and Ca-clays were almost unchanged after treatment, indicating the failure of ethylene oxide to react in the presence of these ions.

For all samples, the formation of ethylene glycol, which was expected to have formed by the reaction of ethylene oxide and water, was excluded also by a comparison with the IR spectra of clays after the adsorption of the pure compound. In addition, no IR evidence was apparent for the formation of 1,4-dioxan and 2-methyl-1,3-dioxolane, reported by Ballantine *et al.* (1983) for experiments carried out under more drastic conditions.

X-ray powder diffraction data

XRD data of the several homoionic montmorillonite samples are listed in Table 1. Note the increase of the basal spacing of the Cu-, Al-, and Fe-treated samples, even after partial dehydration at 90°C , despite the water loss taking place during the reaction. On the other hand, treated Na-, K-, and Ca-montmorillonite samples showed no significant variations of the $d(001)$ values neither before nor after heating at 90°C , confirming that polymerization did not take place in these clays.

Cation-exchange capacity

The CECs of the homoionic montmorillonite samples before and after the treatment with ethylene oxide are listed in Table 2. Note that the CEC values of the Na-, K-, and Ca-clays were practically unchanged on exposure of the clay to ethylene oxide. Instead, a remarkable decrease of CEC, in the order $\text{Cu} < \text{Al} < \text{Fe}$, was observed for the Cu-, Al-, and Fe-montmorillonite samples. This result, which was unexpected because of the high solubility of polyethylene glycol in water, suggests that the polymer, at least in part, remained in the clay and behaved as a hydrophobic screen towards the hydrated cations, part of which were resistant toward the exchange. The partial immobilization of polyethylene glycol (molecular weights between

Table 2. Cation-exchange capacity (meq/100 g) of homoionic montmorillonite samples untreated and treated with ethylene oxide.

Cation	Untreated	Treated
Na ⁺	92.66	91.71
K ⁺	93.80	93.61
Ca ²⁺	92.12	92.18
Cu ²⁺	92.20	75.57
Al ³⁺	91.43	63.46
Fe ³⁺	90.67	58.62

300 and 20,000) and macrocyclic (CH₂-CH₂-O)_n polyethers adsorbed on the montmorillonite materials has already been observed (Parfitt and Greenland, 1970a; Ruiz-Hitzky and Casal, 1978; Casal and Ruiz-Hitzky, 1986).

DISCUSSION

The results indicate that polymerization of ethylene oxide, yielding polyethylene glycol, occurred in Cu²⁺-, Al³⁺-, and Fe³⁺-clays. The reaction took place in the intermellar space of the clay, as substantiated by the increase in the d(001) values following the reaction and the absence of collapse after partial dehydration at 90°C. A polymerization process outside the clay, followed by the adsorption of the formed polyethylene glycol in the interlayer, may be excluded on the basis of the evidence provided by Parfitt and Greenland (1970a). These authors observed that the extent of the polymer adsorption on clays increased in the order Al < Ca < Na < Cs, just opposite to the trend observed here.

The polymerization of ethylene oxide to polyethylene glycol is known to be catalyzed by Lewis or Brønsted acidity and involves the opening of the highly strained three-membered ring. In clay systems, the catalytic reaction likely occurs as an effect of the high degree of dissociation of water molecules. Because the acidity of water in montmorillonite is related to the polarizing effect of the exchanged ion (Mortland, 1968), the Al³⁺ and Fe³⁺ samples should have been more acid than those exchanged with divalent or monovalent ions. On this basis, the different activity of the exchange cations in catalyzing the reaction can be explained.

Effects due to the change of the CEC of clays, e.g., by comparing the adsorption of the pesticide Fluzifop by Cu²⁺-, Al³⁺-, and Fe³⁺-montmorillonite before and after treatment with ethylene oxide, were also checked. As reported by Micera *et al.* (1988), all the untreated clays adsorbed the pesticide from chloroformic solution through complexation and protonation. Instead, for the treated clays, the adsorption was practically absent on Fe-montmorillonite and limited on Al- and Cu-clays, despite the high solubility of polyethylene glycol in chloroform.

In conclusion, in the interlayer of clays, ethylene oxide was found to polymerize to polyethylene glycol,

which diminished the cation-exchange capacity. Only some hydrolyzable ions, however, catalyzed this reaction. Therefore, the practical effects of ethylene oxide sterilization on phyllosilicates may be considered of minor relevance.

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