

## INFRARED SPECTRA OF SULFOLANE ADSORBED ON CATION-SUBSTITUTED MONTMORILLONITES<sup>1</sup>

**Key Words**—Adsorption, Infrared spectroscopy, Montmorillonite, Sulfolane, Tetramethylene sulfone.

Various sulfur-containing organic compounds are found as impurities in petroleum sources (Rall *et al.*, 1972). Knowledge of the structures of such materials when they are adsorbed in the interlamellar space of clays generates useful information concerning either the nature of interaction of sulfur pollutants with soil or the optimum make-up of clays that could be used to adsorb such impurities from petroleum. Garwood and Condrate (1978) investigated dimethyl sulfoxide adsorbed on various montmorillonites using infrared spectroscopy (IR). Both Hidalgo *et al.* (1969) and Cloos *et al.* (1973) investigated thiophene adsorbed on montmorillonite. This paper presents the results of investigation of an oxidized product of thiophane, sulfolane (C<sub>4</sub>H<sub>8</sub>SO<sub>2</sub>), adsorbed on different cation-substituted montmorillonites.

<sup>1</sup> Based on the doctoral dissertation of V. Lorprayoon, Alfred University, Alfred, New York.

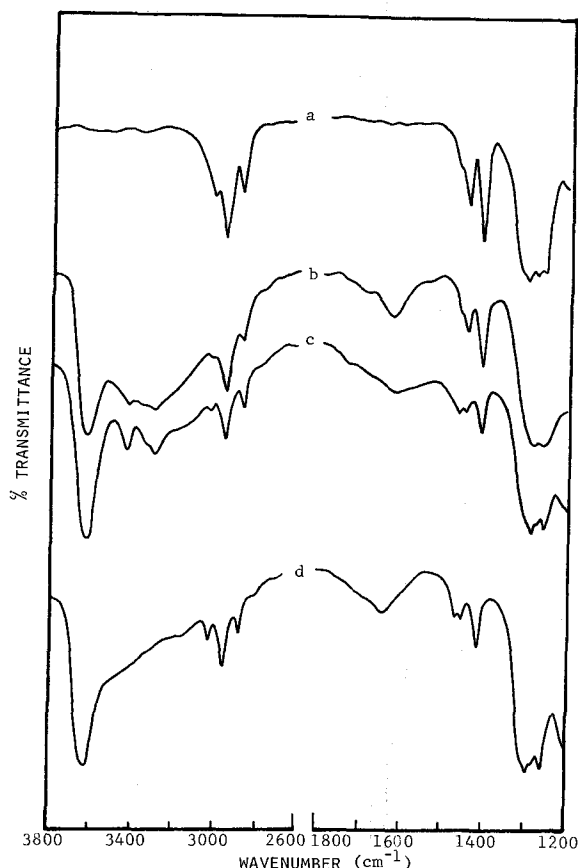


Figure 1. Infrared spectra of (a) liquid sulfolane, (b) Cu-montmorillonite immersed in liquid sulfolane for one day and dried in desiccator for one day, (c) Cu-montmorillonite further heat-treated in air at 150°C for one day, and (d) sulfolane-treated Ni-montmorillonite heated in air at 150°C for one day.

### EXPERIMENTAL

#### Materials

The montmorillonite used in this study was obtained from O. Hommel Company, Pittsburgh, Pennsylvania, from a Wyoming deposit. Jang (1971) reported the following chemical analysis and cation-exchange capacity (CEC): SiO<sub>2</sub> = 64.80, TiO<sub>2</sub> = 0.16, Al<sub>2</sub>O<sub>3</sub> = 20.50, Fe<sub>2</sub>O<sub>3</sub> = 3.60, MgO = 2.46, CaO = 1.03, K<sub>2</sub>O = 0.47, Na<sub>2</sub>O = 2.12, L.O.I. = 5.7, CEC = 100 meq/100 g. Clay films were prepared from particles whose equivalent diameters were less than 2 μm. The fraction containing these clay particles was collected by sedimentation from a 5% clay suspension in distilled water. Transition metal substituted montmorillonite was prepared by saturating natural clay with a 1 N aqueous solution of the appropriate metal chloride. The clay had to be washed several times with distilled water to eliminate free metal ions. The concentrations of the resulting clay suspensions were adjusted so that the clay made up approximately 2.4% of the weight of the aqueous suspensions. Self-supporting thin films (approximately 3.2 cm in diameter, 20 μm thick) were prepared by evaporating 2-ml aliquots of the clay suspensions on an aluminum foil supported by a flat glass plate. Since many exchangeable cations react with aluminum foil, the foil was first lined with a thin film of collodion to protect the clay from chemical reactions. The resulting air-dried films were easily stripped from the foil by drawing the foil over a sharp edge.

The films of the various cation-substituted montmorillonites were treated by immersing them in liquid sulfolane for 24 hr at room temperature and then drying them in a desiccator for another 24 hr. Some of the treated clay films were heated in air at 150°C for 24 hr. Wet chemical, trace emission spectrographic, scanning electron microscopic, and X-ray powder diffraction analyses were used to characterize the films.

Table 1. Wave numbers (cm<sup>-1</sup>) of band maxima and band assignments for Cu- and Ni-montmorillonite-sulfolane complexes.

Liquid sulfolane <sup>1</sup>	Cu	Ni	Assignments
~3004 s,sh	3020	3020	
~2975 s,sh			
2952 vs	2953	2954	C-H stretching
~2920 s,sh			
2880 s	2880	2880	
1461 m	1466	1465	
1448 s	1448	1449	CH <sub>2</sub> scissor
~1418 m,sh			
1412 vs	1413	1413	
~1313 vs,sh			CH <sub>2</sub> wag
1301 vvs	1290	1292	antisym OSO stretching
1275 vs	1275	1275	CH <sub>2</sub> wag
1259 s	1250	1250	CH <sub>2</sub> twist

Katon and Fearheller (1965).

<sup>1</sup> s = strong; sh = shoulder; vs = very strong; m = medium; vvs = very very strong.

### Spectral measurements

IR absorption spectra ( $4000\text{--}1200\text{ cm}^{-1}$ ) were obtained using a Perkin-Elmer Model 621 double beam, grating spectrophotometer. An air purging unit was used to eliminate absorption bands due to atmospheric water and carbon dioxide. Calibration of the spectrophotometer was carried out using polystyrene bands, and a wave number accuracy of  $\pm 2\text{ cm}^{-1}$  was obtained.

### RESULTS AND DISCUSSION

The desorption rates of sulfolane from transition metal ion-exchanged montmorillonites were much slower than those observed from hydrogen-exchanged, sodium-exchanged, or natural montmorillonites, suggesting that adsorbed species involving stronger metal-sulfolane ligand bonds are present in the former clay films. Consistent with this interpretation, color changes were noted for the transition metal ion-exchanged montmorillonite films upon treatment with sulfolane, indicating the replacement of transition metal ion-water bonds with transition metal ion-sulfolane bonds. Figure 1 illustrates the IR spectra of copper montmorillonite treated with sulfolane at room temperature, and also heat treated in air at  $150^\circ\text{C}$ . The IR spectra of sulfolane-treated nickel montmorillonite heated at  $150^\circ\text{C}$  and liquid sulfolane are also included. The band assignments for liquid sulfolane and for the related bands of the sulfolane-treated transition metal ion-substituted montmorillonites are listed in Table 1. The vibrational modes involving either the methylene C-H bonds or the heterocyclic ring appear for the clay complexes in the same general regions of the spectra as for liquid sulfolane. Larger shifts in the band location of antisymmetric OSO stretching mode from that of liquid sulfolane were observed for treated transition metal-substituted montmorillonites than for sodium-substituted or natural montmorillonite. For example, this mode occurs at  $1301\text{ cm}^{-1}$  for liquid sulfolane, and at  $1290$  and  $1292\text{ cm}^{-1}$  for the treated Cu- and Ni-substituted clay films, respectively. Similar shifts were observed with Co-, Zn-, and Cr-substituted clay films. Reedijk *et al.* (1969) noted similar small shifts for this mode when transition metal ions bonded to sulfolane in crystals via the lone-pair orbitals of the oxygen atoms. The magnitude of the shift of this  $\text{SO}_2$  stretching vibration was

much smaller than observed for sulfoxides because the metal-ligand bonds are much weaker for sulfolane complexes. In treated H-montmorillonite, this mode was observed at  $1294\text{ cm}^{-1}$ . The shift in bond location for this clay complex was probably due to ion-dipole interaction between the  $\text{SO}_2$ -group of sulfolane with the hydrogen or hydronium ions in the clay. The bands for the symmetric OSO stretching mode ( $\sim 1150\text{ cm}^{-1}$ ) were not observed in this study because they were hidden behind bands associated with the clays. In contrast to adsorption studies with thiophene and thiophane on substituted montmorillonites, no new oxidized or polymerized products were detected under the conditions of treatment in this study.

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(Received 28 July 1980; accepted 16 August 1980)