

INFRARED SPECTRA OF THIOLANE AND TETRAMETHYLENE SULFOXIDE ADSORBED ON MONTMORILLONITE¹

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Abstract—Infrared spectra ($4000\text{--}1200\text{ cm}^{-1}$) were obtained for several homoionic montmorillonite films on which tetramethylene sulfoxide (TMSO) or thiolane were adsorbed at various temperatures and for different periods of exposure. The spectra indicate that the Na-, H-, and natural montmorillonite complexes contain a physically adsorbed species, whereas transition metal-montmorillonite complexes contain both physically adsorbed and metal-complexed species in their interlamellar spaces. Apparently, thiolane adsorbed on most montmorillonites undergoes oxidation to TMSO in an air atmosphere. Consistent with the mechanism proposed earlier for aqueous solutions, the rate of sulfoxide formation increases by increasing the pH of the suspensions from which the clay films were deposited or by increasing the concentration of the water molecules in the interlamellar spaces. The infrared spectra of γ -thiolactone adsorbed on Co-montmorillonites suggest that sulfoxide-type molecules are formed which chelate to the Co ions in the interlamellar spaces.

Key Words—Adsorption, Infrared spectroscopy, Montmorillonite, Tetramethylene sulfoxide, Thiolane.

INTRODUCTION

Thiophanes which possess saturated heterocyclic rings containing sulfur atoms occur as impurities in various sources of petroleum (Rall *et al.*, 1972; Hubbard *et al.*, 1952). These types of sulfur-containing compounds can be absorbed by soils or sediments during oil spillages or seepages. Also, clays, such as cation-substituted montmorillonites, can be used as cheap, energy-nonintensive adsorbers for removing these impurities from crude oil. Knowledge about the structures of the adsorbed species for such compounds on clays can lead to a better understanding of the nature of interaction of such sulfur-containing compounds either with soils and sediments or with clays that can be used to adsorb such impurities from petroleum.

Hidalgo *et al.* (1969) and Cloos *et al.* (1973) obtained structural information for a related compound, thiophene, adsorbed on montmorillonites using infrared spectroscopy. They noted that thiophene is physically adsorbed on nontransition metal-montmorillonites and forms π -bonded complexes with Cu ions on Cu-montmorillonite. Recently, Lorprayoon and Condrate (1981) found from infrared spectra that the nature of sulfolane ($\text{C}_4\text{H}_8\text{SO}_2$) adsorbed on various cation-substituted montmorillonites strongly depends upon the type of exchangeable cation in the interlamellar spaces along with the period of exposure and the temperature of treatment. Whereas metal complexes and physically adsorbed sulfolane were both observed for transition

metal-montmorillonites, only physically adsorbed sulfolane was noted for natural and H-montmorillonites.

The present paper presents the results of an infrared spectroscopic investigation of thiolane ($\text{C}_4\text{H}_8\text{S}$) adsorbed on various cation-substituted montmorillonites in an air atmosphere in an attempt to obtain structural information about its adsorbed species. This simplest thiophane generates adsorbed species which serve as structural models for the adsorbed species present for thiophanes in general. Its infrared properties are compared to those of two other thiophanes, tetramethylene sulfoxide ($\text{C}_4\text{H}_8\text{SO}$) and γ -thiolactone ($\text{C}_4\text{H}_6\text{SO}$), adsorbed on montmorillonites. These two compounds generate adsorbed species which directly relate to the final adsorbed species present for thiolane.

EXPERIMENTAL

Materials

The montmorillonite used in this study originated from a Wyoming deposit and was obtained from O. Hommel Company, Pittsburgh, Pennsylvania. Jang (1971) reported the following chemical analysis and cation-exchange capacity (CEC): $\text{SiO}_2 = 64.80$, $\text{TiO}_2 = 0.16$, $\text{Al}_2\text{O}_3 = 20.50$, $\text{Fe}_2\text{O}_3 = 3.60$, $\text{MgO} = 2.46$, $\text{CaO} = 1.03$, $\text{K}_2\text{O} = 0.47$, $\text{Na}_2\text{O} = 2.12$, L.O.I. (loss on ignition) = 5.7, CEC = 100 meq/100 g. Clay films were prepared by sedimenting clay particles whose equivalent diameters were less than $2\ \mu\text{m}$. Transition metal-montmorillonite was prepared by twice saturating the natural clay with a 1 N aqueous solution of the appropriate metal chloride. The clay was washed several times with distilled water to eliminate excess metal

¹ Based on a Ph.D. thesis submitted by V. Lorprayoon to Alfred University.

and chloride ions. H-montmorillonite was prepared immediately prior to use from a 1% suspension of the natural clay by passing it through a column of Amberlite I.R.-120 (H-form). The concentrations of the resulting 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 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. Because some of the exchangeable cations can react with the aluminum foil, the foil was lined with a thin film of collodion to protect the clay from chemical reactions. The resulting air-dried samples were stripped from the foil by drawing the foil over a sharp edge. Each type of clay film was then put in a sealed bottle and kept under vacuum in a desiccator over P_2O_5 until further use.

Thin films of the Cu-, Ni-, Co-, Zn-, Cd-, Cr-, Na-, H-, and natural montmorillonites were sealed in bottles containing liquid thiolane or tetramethylene sulfoxide for the appropriate exposure period at room temperature. For γ -thiolactone, only films of Co-montmorillonite were treated and analyzed. Clay films treated with tetramethylene sulfoxide and γ -thiolactone were exposed to the liquid for one day; clay films treated with thiolane were exposed for periods of 10 min, 1 hr, 1 day, 1 week, and 1 month. After the exposure, the treated clay films were removed from their bottles and dried for one day in a partially evacuated desiccator at ambient temperature. Some of the clay films treated with one of the three sulfur-containing compounds were then heated for one day at 150°C in air. Also, some clay films treated with thiolane or tetramethylene sulfoxide were heated at 120°C in air rather than at 150°C. Wet chemical, trace emission spectrographic, scanning electron microscopic, and X-ray powder diffraction analyses were used to characterize the films.

Spectral measurements

Infrared (IR) absorption spectra (4000–1200 cm^{-1}) were obtained by placing the clay film in the sample beam of 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 wavenumber accuracy of $\pm 2 \text{ cm}^{-1}$ was obtained.

RESULTS AND DISCUSSION

Figure 1 illustrates the IR spectra of Cu-, Ni-, and H-montmorillonites treated with tetramethylene sulfoxide (TMSO) in an air atmosphere for one day at room temperature and the spectra of these materials after being heated in air at 150°C for one day. The very strong band at $\sim 3625 \text{ cm}^{-1}$ has been assigned to the OH-stretching mode of the hydroxyl ions in the octahedral

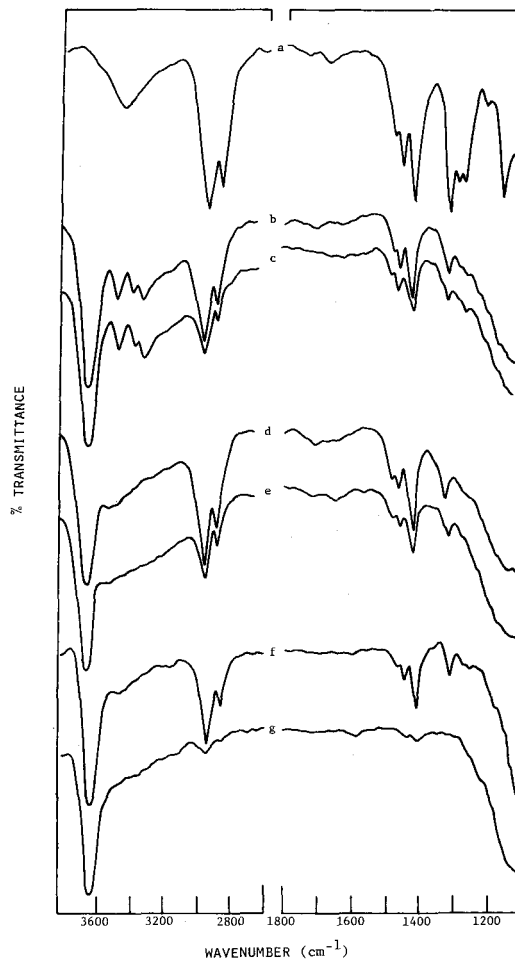


Figure 1. Infrared spectra of (a) liquid tetramethylene sulfoxide (TMSO), (b) and (c) treated Cu-montmorillonite, (d) and (e) treated Ni-montmorillonite, and (f) and (g) treated H-montmorillonite. (b), (d), and (f) = montmorillonites immersed in liquid TMSO for one day at ambient temperature. (c), (e), and (g) = films further heat-treated at 150°C for one day.

sheet of the clay lamellae, which remains unaffected by the various treatments. The 2600–1800 cm^{-1} region is omitted because this region contains no significant spectral features for any of the investigated clay-adsorbate systems. Band maxima locations and assignments are listed in Table 1 for the Cu-montmorillonite-TMSO complex along with those for liquid TMSO. The assignments are consistent with those made previously for liquid TMSO (Klaeboe, 1968). The IR band at $\sim 1625 \text{ cm}^{-1}$, due to physically adsorbed or coordinated water, decreases in intensity after adsorption for all clay systems indicating the replacement of water molecules in the clay by the more polar TMSO molecules (the dipole moment of TMSO is 4.17 debyes). The replacement of water molecules is greater in the TMSO-clay systems than in the sulfolane (TMSO_2)-clay systems after the same period of exposure to the liquid organic phase.

Table 1. Wavenumbers (cm^{-1}) of band maxima and band assignments for Ni-montmorillonite films treated with TMSO and TMS.

Liquid ¹ TMSO	Liquid ² TMS	TMSO-treated film	TMS-treated film	Assignments
		3625 (vvs)	3625 (vs)	OH-stretch
2950	2948	2945 (vs)	2950 (vs)	
2875	2860	2877 (s)	2867 (2)	CH-stretch
		1628 (w)	1628 (w)	
1465	1462	1463 (sh)	1460 (sh)	HOH-bend
1450	1442	1447	1443 (s)	
1414		1410 (vs)	1410 (s)	CH ₂ -scissor
1307	1306	1300 (m)	1300 (m)	
1275	1272	1260 (vw)		CH ₂ -wag
1264	1256	1243 (w, sh)	1250 (m)	

¹ Klaeboe, 1968.

² Giorgini *et al.*, 1977. s = strong; sh = shoulder; vs = very strong; m = medium; w = weak; vvs = very very strong; vw = very weak.

The type of exchangeable cation in the montmorillonite film significantly affects the desorption rates of TMSO, similar to TMSO₂ (Lorprayoon and Condrate, 1981). After heat treatment at 150°C for one day, the IR spectra of the TMSO-treated samples of Na-, H-, and natural montmorillonites indicate lower sulfur contents and lower intensities of the TMSO bands than those of transition metal-montmorillonites (see Figure 1). This notable difference in desorption rate suggests that the adsorption process for TMSO in Na-, H-, and natural montmorillonites mainly involves physical adsorption, whereas for the transition metal cation-exchanged clays, stronger metal-oxygen bonding develops between the TMSO molecules and the exchangeable cations in the interlamellar spaces. Garwood and Condrate (1978) noted that metal complexes are formed in transition metal-montmorillonites that adsorb dimethyl sulfoxide (DMSO) which involve bond formation between the transition metal ions and the oxygen atoms of DMSO molecules. The color changes for the transition metal-clays after adsorption of TMSO also indicate such complex formation in these treated clays. The color changes can be explained by ligand field theory as being due to the replacement of the ligands which coordinate to the exchangeable cations (i.e., water molecules being replaced by TMSO molecules). For Co-clays, the color changes from light reddish-orange to light orange-yellow after exposure to TMSO at ambient temperature for one day. Heat treatment of these TMSO-adsorbed, Co-montmorillonites at 150°C causes a further change in color to dark violet. This latter color change can also be produced by placing the treated Co-containing clay film in a desiccator containing P₂O₅ under a vacuum. However, the color reverts back rapidly to light orange-yellow upon reexposure to an open air atmosphere at room temperature. Garwood and Condrate (1978) not-

ed a similar reversible color change for dimethyl sulfoxide-Co-montmorillonite films. Such changes can be explained on the basis of a change in the coordination of the Co²⁺ from octahedral to tetrahedral states upon heating and vice versa upon cooling and exposure to air (see Weyl, 1959). This process can occur by the loss of two ligands by the metal complex upon heating and the readsorption of two water molecules from the atmosphere upon cooling.

No new bands appeared in the IR spectra of the montmorillonite-TMSO complexes under the conditions of treatment in this study that cannot be assigned to vibrational modes of TMSO, indicating that large amounts of new polymerized or further oxidized products did not form under these conditions. Direct evidence of metal complex formation can not be obtained from the IR spectra of transition metal-montmorillonites by observing the expected larger wavenumber shifts of the S-O stretching mode of TMSO upon bonding of the oxygen atom of TMSO with a transition metal ion. Its band maximum occurs at $\sim 1023 \text{ cm}^{-1}$ for liquid TMSO and is hidden by the bands of the clay matrix upon adsorption in the clay. As may be noted in Table 1, all other bands of TMSO shift slightly from those of the liquid state upon adsorption of TMSO into the clay. Their vibration modes involve mainly vibrational motions of the methylene C-H bonds or the heterocyclic rings. It is difficult to determine whether these slight shifts are due to changes in the environment around the methylene C-H bonds and the heterocyclic rings upon adsorption or due to perturbations by the formation of M-O bonds between oxygen atoms of the sulfoxide groups and transition metal ions.

IR spectra were also measured for homoionic montmorillonite films containing thiolane (TMS). For clay films exposed to liquid TMS for short periods of time, the dominant IR bands in the window region of the clay films occurred at the approximate band locations observed for liquid TMS, indicating the presence of either physically adsorbed TMS or metal-complexed TMS in the interlamellar spaces. Slight color changes were noted for transition metal-montmorillonites upon treatment with TMS, indicating metal complex formation between TMS molecules and the transition metal cations in the interlamellar spaces. After longer periods of exposure for most clay systems, new bands were noted that dominated the spectra, whereas the initial bands decreased in intensity and/or slightly shifted their wavenumber locations. These band changes can be attributed to the oxidation of thiolane to TMSO. Only for Cu-montmorillonites, did the TMS bands remain dominant during the exposure times in this study. Acceleration of sulfoxide formation was noted for all the clay films except Cu-montmorillonite by heat-treating the films at 150°C for one day.

Figure 2 illustrates the IR spectra of Ni-montmorillonite films exposed to liquid thiolane for different per-

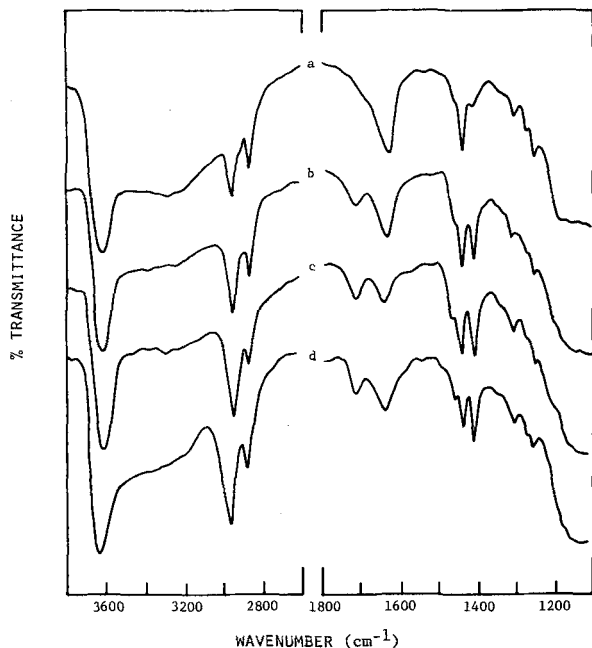


Figure 2. Infrared spectra of Ni-montmorillonite exposed to thiolane (TMS) at room temperature for different periods of time (a) 10 min, (b) 1 hr, (c) 1 day, and (d) 1 month.

roids of time (10 min to 1 month). The spectra of this clay are typical of those for all other investigated clays except Cu-montmorillonite. The replacement of water molecules in the clay after adsorption is clearly indicated by the decrease in intensity of the band at $\sim 1625\text{ cm}^{-1}$. Initially, bands were noted at $\sim 2960, 2870, 1720, 1442, 1300,$ and 1250 cm^{-1} which correlate with those observed for liquid TMS. The wavenumber positions of bands that either increased in intensity or shifted upon longer exposure to TMS are listed in Table 1 for a Cu-montmorillonite that had been exposed to liquid TMS for one month at room temperature. The band features and band locations in the IR spectra of adsorbed species in clay films exposed to TMS for long periods of time in an air atmosphere or heat-treated at 150°C for one day resemble those observed for clay films treated with TMSO. Apparently, TMS is oxidized to TMSO on these clay films in an air atmosphere. However, no other oxidized products formed during the treatment of the clay complexes under the conditions defined in this study. For example, a very strong band at $\sim 1292\text{ cm}^{-1}$ due to the antisymmetric O=S=O stretching mode of sulfolane (TMSO₂) did not increase in intensity during the treatment. Lorprayoon and Condrate (1981) noted this strong band when montmorillonites were treated with TMSO₂. The intensities of the bands for TMS-treated H-, Na-, and natural montmorillonites associated with TMS or TMSO decreased more rapidly than those of treated transition metal-montmorillonites when the

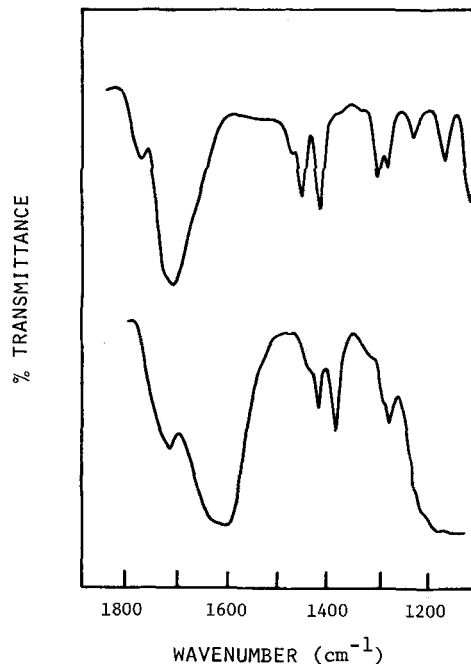


Figure 3. Infrared spectra of (a) liquid γ -thiolactone and (b) Co-montmorillonite exposed to γ -thiolactone for one day at ambient temperature and heat-treated at 150°C for one day.

samples were heated for one day at 150°C , indicating that TMS and TMSO molecules were only physically adsorbed in the former clay films.

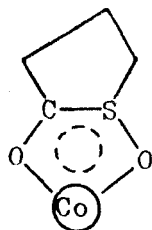
Thiolane can undergo oxidation in aqueous solutions without the presence of clay. Mockel *et al.* (1975) studied the oxidation of thiolane in aqueous solution using a pulse radiolytic technique. They proposed a mechanism in which the rate of sulfoxide formation increased with increased amounts of the hydroxyl ions and radicals, and of the water molecules in the solutions. IR spectra were measured for natural montmorillonite films that were prepared from clay suspensions at different pHs (2.5, 3.5, 4.6, 5.4, 6.7, 7.2, 8.5, and 9.4) and that were exposed to TMS for one day at ambient temperature. The major difference in the spectra after treatment was between the relative intensities of the bands at 1410 and 1442 cm^{-1} which related to the ratio of the concentrations of thiolane to TMSO on the clay. The band at 1442 cm^{-1} increased its intensity with respect to the band at 1410 cm^{-1} as the pH of the clay suspension, from which the film was prepared, increased. The intensity of the former band was much stronger than that of the latter band when the pH was above 3.5. This trend in the relative intensities of the two bands with pH change is consistent with Mockel's mechanism.

The effect of water in the interlamellar space upon oxidation was also investigated. Prior to treatment several montmorillonite films (Zn, Co, and Ni) were heated at 150°C for one day to drive off water from the inter-

lamellar spaces. The films, along with those of samples not preheated, were then exposed to liquid TMS in an air atmosphere for one day at ambient temperatures. Consistent with Mockel's mechanism, the ratios of the intensity of the band at 1410 cm^{-1} to the intensity of the band at 1442 cm^{-1} are larger for the clay films that were not preheated and that contain more water in their interlamellar spaces, indicating that more of the oxidized species was formed. Heating the clays to 150°C could irreversibly collapse some interlayers making these interlayers unavailable for adsorption and reaction. One would expect this change in the number of available interlayers in the clay films to cause a change in the absolute intensities of the IR bands but not in their relative intensities.

The reversible change of the TMS-treated, Co-clay films to a purple color after heating and back to light orange-yellow after cooling in an air atmosphere is similar to that observed for the TMSO-Co-montmorillonite films. This result further supports the formation of similar cobalt-ligand complexes in which the cobalt ions can undergo octahedral-tetrahedral coordination changes.

The IR spectra noted for the adsorbed species present when γ -thiolactone was adsorbed on Co-montmorillonites are consistent with that expected when thiophane oxidizes to sulfoxide. Figure 3 illustrates the IR spectra for liquid γ -thiolactone and Co-montmorillonite exposed to γ -thiolactone for one day at ambient temperature and heated at 150°C for one day. The band at $\sim 1700\text{ cm}^{-1}$ for liquid γ -thiolactone decreased in intensity with respect to the other bands upon treatment of the Co-montmorillonite with γ -thiolactone, and a new band appeared at $\sim 1615\text{ cm}^{-1}$. The intensity decrease of the former band and the appearance of the latter band can be explained by sulfoxide formation, assuming that the generated adsorbed species in the clays involve the following type of chelated complex:



Both metal-oxygen bond formation between the cobalt

ion and the oxygen atom of C=O bond, and the delocalization of the C=O bond by conjugation with the formed S=O bond should lower the bond order and also the force constant of the C=O bond. Therefore, the band maxima of the C=O stretching mode should shift to a lower wavenumber. However, the effects of delocalization and metal-oxygen bond formation were not observed for S=O because the S=O stretching mode at $1200\text{--}1100\text{ cm}^{-1}$ is overlapped by the intense bands of the montmorillonite matrix. Similar shifts have been noted for many metal chelate complexes that involve delocalization and metal-ligand bond formation (Nakamoto, 1978). A reversible color change was noted upon hydration or dehydration with these γ -thiolactone-treated, Co-clay films similarly to Co-montmorillonite films treated with TMSO or DMSO, indicating coordination changes also for the Co-ions in the former films.

REFERENCES

- Cloos, P., Vande poel, D., and Camerlynck, J. P. (1973) Thiophene complexes on montmorillonite saturated with different cations: *Nature* **243**, 54–55.
- Garwood, G. A. and Condrate, R. A. (1978) The IR spectra of dimethyl sulfoxide adsorbed on several cation-substituted montmorillonites: *Clays & Clay Minerals* **26**, 273–278.
- Giorgini, M. G., Paliani, G., and Cataliotti, R. (1977) Vibrational spectra and assignments for tetrahydrothiophane, tetrahydroselenophene and tetrahydrotellurophene: *Spectrochim. Acta, Ser. A* **33**, 1083–1089.
- Hidalgo, A., Rodriguez-Pascual, C., and Serratos, J. M. (1969) Molecules adsorbed on laminar silicates: *C. R. Acad. Sci. Ser. B* **269**, 1169–1172.
- Hubbard, W. N., Finke, H. L., Scott, D. W., McCullough, J. P., Katz, C., Gross, M. E., Messerly, J. F., Pennington, R. E., and Waddington, G. (1952) Thiacyclopentane: heat capacity, heats of fusion and vaporization, vapor pressure, entropy, heat of formation and thermodynamic functions: *J. Amer. Chem. Soc.* **74**, 6025–6030.
- Jang, Sung Do (1971) Infrared spectra of some amino acids adsorbed on montmorillonites: Ph.D. thesis, Alfred University, Alfred, New York, 157 pp.
- Klaeboe, P. (1968) The vibrational spectra of tetramethylene sulfoxide: *Acta Chem. Scand.* **22**, 369–371.
- Lorprayoon, V. and Condrate, R. A. (1981) Infrared spectra of sulfolane adsorbed on cation-substituted montmorillonites: *Clays & Clay Minerals* **29**, 71–72.
- Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*: 3rd ed., Wiley, New York, 448 pp.
- Rall, H. T., Thompson, C. J., Coleman, H. J., and Hopkins, R. L. (1972) Sulfur compounds in crude oil: *U.S. Bur. Mines Bull.* **659**, 187 pp.
- Weyl, W. A. (1959) *Coloured Glasses*: Society of Glass Technology, Sheffield, 168–196.

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Резюме—Были получены инфракрасные спектры ($4000\text{--}1200\text{ cm}^{-1}$) для нескольких гомоионных фильмов монтмориллонита, на которых адсорбировались четыре метиленовая сероокись (TMSO) или тиолан при различных температурах и временах экспозиции. Спектры указывают на то, что Na-, H-, и нейтральные монтмориллонитовые комплексы содержат физически адсорбированные вещества, в то время как переходные комплексы металл-монтмориллонит содержат оба: физически адсорбированные и металло-составные вещества в межслойных пространствах. По видимому, тиолан, адсорбированный на большинстве монтмориллонитов, окисляется до TMSO в атмосфере воздуха. Согласно с ранее предложенным механизмом для водных растворов скорость формирования сероокиси увеличивается при увеличении pH суспензии, из которых осаждались глинистые фильмы или при увеличении концентрации молекул воды в межслойных пространствах. Инфракрасные спектры γ -тиолактона, адсорбированного на Co-монтмориллонитах, указывают на образование молекул типа сероокиси, которые присоединяются к иону Co в межслойных пространствах. [E.C.]

Resümee—Es wurden Infrarotspektren ($4000\text{--}1200\text{ cm}^{-1}$) von verschiedenen gleichionigen Montmorillonitfilmen aufgenommen, an die Tetramethylsulfoxid (TMSO) oder Thiolan bei verschiedenen Temperaturen und während unterschiedlicher Zeitspannen adsorbiert wurden. Die Spektren deuten darauf hin, daß Na-, H-, und natürliche Montmorillonitkomplexe eine physikalisch adsorbierte Spezies enthalten, während Montmorillonitkomplexe mit Übergangsmetallen sowohl physikalisch adsorbierte als auch durch die Metallionen komplexierte Spezies zwischen den Schichten enthalten. Offensichtlich wird meistens das an die Montmorillonite adsorbierte Thiolan an der Luft zu TMSO oxidiert. In Übereinstimmung mit dem Mechanismus, der früher für wässrige Lösungen vorgeschlagen wurde, steigt die Geschwindigkeit der Sulfoxidbildung mit zunehmendem pH der Suspensionen, aus denen die Tonfilme ausgefällt wurden, oder mit zunehmender Konzentration an Wassermolekülen zwischen den Schichten. Die Infrarotspektren von γ -Thiolacton adsorbiert an Co-Montmorillonite weisen darauf hin, daß Sulfoxid-artige Moleküle gebildet werden, die durch Chelatbildung mit den Co-Ionen in den Zwischenschichten gebunden sind. [U.W.]

Résumé—Des spectres infra-rouges ($4000\text{--}1200\text{ cm}^{-1}$) ont été obtenus pour plusieurs films de montmorillonite homoionique sur lesquels la sulphoxide tétraméthylène (TMSO) ou la thiolane ont été adsorbées à des températures variées et pour des périodes d'exposition différentes. Les spectres indiquent que les complexes montmorillonite-Na, -H, et naturelle contiennent une espèce adsorbée physiquement, tandis que des complexes de montmorillonite à métal de transition contiennent à la fois des espèces adsorbées physiquement et des espèces complexées au métal dans leurs espaces interlamellaires. Apparemment, la thiolane adsorbée sur la plupart des montmorillonites subit l'oxidation en TMSO dans l'air. Suivant le mécanisme proposé précédemment pour des solutions aqueuses, la vitesse de formation de sulphoxide augmente avec l'accroissement du pH des suspensions à partir desquelles les films d'argile ont été déposés ou en augmentant la concentration des molécules d'eau dans les espaces interlamellaires. Les spectres infra-rouges de thiolactone- γ adsorbée sur des montmorillonites-Co suggère que des molécules du type sulphoxide sont formées, qui chélatent aux ions Co dans les espaces interlamellaires. [D.J.]