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THE I.R. SPECTRA OF DIMETHYL SULFOXIDE ADSORBED ON SEVERAL CATION-SUBSTITUTED MONTMORILLONITES*

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Abstract—The i.r. spectra (4000–1200 cm^{-1}) are obtained for several homoionic montmorillonite films on which various amounts of dimethyl sulfoxide (DMSO) were adsorbed. Analyses of these spectra indicate that H- and natural-montmorillonite-DMSO complexes contain an intercalated layer of physisorbed DMSO while transition metal cation substituted-montmorillonite-DMSO complexes possess both physi- and chemisorbed DMSO in their interlamellar spaces. The latter species involve coordination of DMSO molecules with the exchangeable cations by their oxygen atoms. Most of the interlamellar water is replaced by DMSO as the latter molecules penetrate the interlamellar spaces. Heat-treating transition metal cation substituted-montmorillonite-DMSO complexes at 120°C for 48 hr results in both the desorption of physisorbed DMSO and the retention of intercalated monolayers involving DMSO-transition metal cation coordination. A water-sensitive, reversible color change (tan to light purple) is produced by either desiccating over P_2O_5 or heat-treating at 120°C the cobalt-montmorillonite-DMSO complex. Interpretation of the visible spectra suggests that Co^{2+}-cations undergo changes from octahedral to tetrahedral coordination during desiccation or heating. Band assignments are made for the clay complexes using the assignments for related gases, liquids, and crystals.

Key Words—Chemisorption, Dimethylsulfoxide, Montmorillonite, Physisorption.

INTRODUCTION

Very little work has been reported in the literature regarding the adsorption of dimethyl sulfoxide (DMSO) on clays and clay minerals. Gonzalez Garcia and Sanchez Camazano (1968a,b) applied DMSO in the identification of clay minerals present in mixtures. For instance, kaolinite could be differentiated from chlorite by X-ray analysis because the monolayer complex formed between DMSO and kaolinite possessed a characteristic distinguishable basal spacing of 11.18 Å. Horton (1970) has described a kaolinite-DMSO intercalation complex which can be used for the gradual release of sulfoxide in a moist atmosphere for drug therapy. Olejnik et al. (1968) examined the infrared spectra of DMSO complexes with the kaolin minerals and found that DMSO bonds via its oxygen atom to the clay hydroxyl surface. Gonzalez Garcia and Sanchez Camazano (1965, 1966) and Gonzalez Garcia et al. (1967) have reported structural studies of DMSO-montmorillonite complexes using instrumental techniques such as X-ray diffraction, TGA, and DTA analyses. Although infrared spectroscopy was cited in the latter study, no spectra were illustrated for any DMSO-clay complexes. Berkheiser and Mortland (1975) studied the variability in the exchange position in smectite using various montmorillonites swelled by a series of solvents including DMSO. In this study, we will report the infrared spectra of several homoionic montmorillonite-DMSO complexes, and interpret them in terms of the species present in the clay films.

EXPERIMENTAL

The montmorillonite used in this study originated from Wyoming. Clay films were prepared from clay particles whose equivalent diameters were less than 2 microns. 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. H-montmorillonite was prepared immediately prior to use from a 1% suspension of natural clay by passing it through a column of Amberlite I.R.-120 (H-form). 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 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 most exchangeable cations react with aluminum foil, the foil had to be lined with a thin film of collodion to protect the clay from chemical reactions. The resulting air-dried film specimens 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 quickly depositing controlled volumes of DMSO onto their centers, and then placing them in a large empty glass desiccator for 4 hr.

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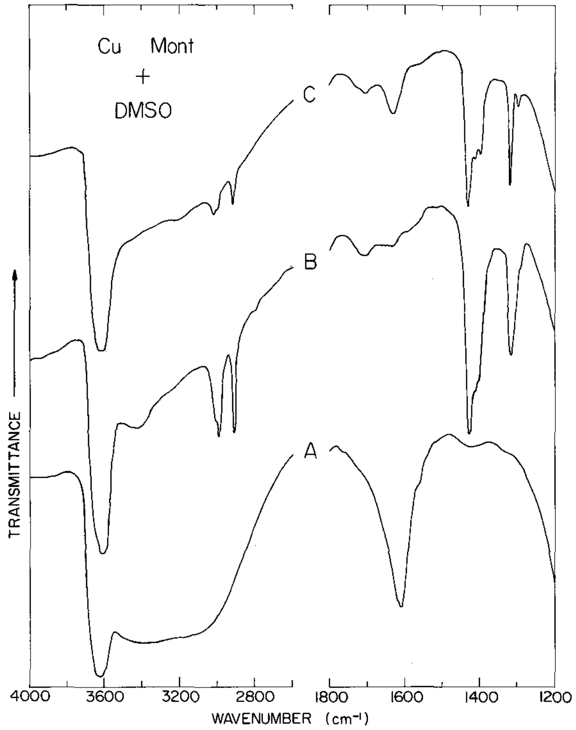

Fig. 1. The infrared spectra of a DMSO-Cu-montmorillonite complex after several different treatments: A) blank clay film with no DMSO adsorbed, B) both 4 hr exposure to DMSO and 20 hr desiccation over P_2O_5, C) 48 hr heat-treatment at 120°C.

Table 1. Wave numbers of band maxima and band assignments for Cu- and Co-montmorillonite-DMSO complexes.

Cu	Co	Assignments
3017 3001	3024 3003	} Asym. C-H str.
2920	2920	Sym. C-H str.
2827	2817	Comb. or overtone
1636	1630	H-O-H bend
1431 1415 1403	1433 1417 1404	} Degenerate C-H def.
1340	1350	comb.
1320 1297	1318 1297	} Sym. C-H def.

DMSO-saturated Co-montmorillonite films were also prepared by immersing the untreated clay films completely in liquid DMSO, or by exposing the untreated films to a vapor atmosphere of DMSO. Some treated film samples were desiccated for 28 to 48 hr over P_2O_5 and/or heat-treated for 48 hr at 120°C in air. Wet chemical, trace emission spectrographic, SEM and X-ray analyses were used to characterize the films.

The i.r. absorption spectra (4000–1200 cm^{-1}) were obtained for the clay specimens by placing their corresponding self-supporting thin films in the sample bean of a Perkin-Elmer Model 621 double beam grating spectrophotometer. An air purging unit was employed 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 ±2 cm^{-1} was obtained.

RESULTS AND DISCUSSION

I.R. spectra were measured for various homoionic montmorillonite films containing DMSO. Figure 1 illustrates the i.r. spectra obtained for a Cu-montmorillonite-DMSO complex after various treatments. The very strong band at 3625 cm^{-1} is assigned to the OH-stretching mode of the hydroxyl ions in the alumina sheet of the clay lamellae. This band remains unaffected by the various treatments. The 2600–1800 cm^{-1} region is omitted from the i.r. spectra because this region contains no significant spectral features for any of the investigated clay-adsorbate systems. Band assignments are listed in Table 1 for Cu- and Co-montmorillonite-DMSO complexes. As may be noted, these assignments are consistent with those made for DMSO in related phases (Forel and Tranquille, 1970; Cotton et al., 1960). The observed band locations for one of the symmetric C–H deformation modes of Co- and Cu-clay-DMSO complexes are 1318 and 1320 cm^{-1}, respectively. These bands are shifted 8 to 17 cm^{-1} higher than those observed for DMSO either in the gas (1310 cm^{-1}) and liquid (1310 cm^{-1}) states or in various solutions (1303 cm^{-1}). A similar shift in band location was noted for the related band of crystals containing a Co-DMSO complex (1314 cm^{-1}). In the latter complex, DMSO molecules are coordinated to cobalt cations via their oxygen atoms. The observed spectral data seem to suggest that the transition metal-montmorillonite-DMSO complexes contain chemisorbed species involving the direct coordination of DMSO molecules to metal cations. This species is present along with physisorbed DMSO. Spectral changes due to the heat treatment of the transition metal-clay-DMSO films are consistent with the presence of both chemisorbed and physisorbed species in the interlamellar spaces. Bands related to the normal vibrations of DMSO sharpen and are more clearly resolved after the heat treatment. Each band is the resultant of the bands for the related modes of both the physisorbed and the chemisorbed DMSO (Figure 1B). Heat treatment drives off physisorbed DMSO, increasing the relative concentration of chemisorbed DMSO in the clay film. This change in relative concentrations causes the observed bands to sharpen (Figure 1C). Similar results are also observed for DMSO-treated montmorillonites containing Zn, Ni, and Cd. The related bands for the DMSO complexes with natural and H-montmorillonites decrease in intensity without sharpening after heating, indicating the presence of only physisorbed DMSO.

Direct DMSO-metal ion coordination in the clay in-

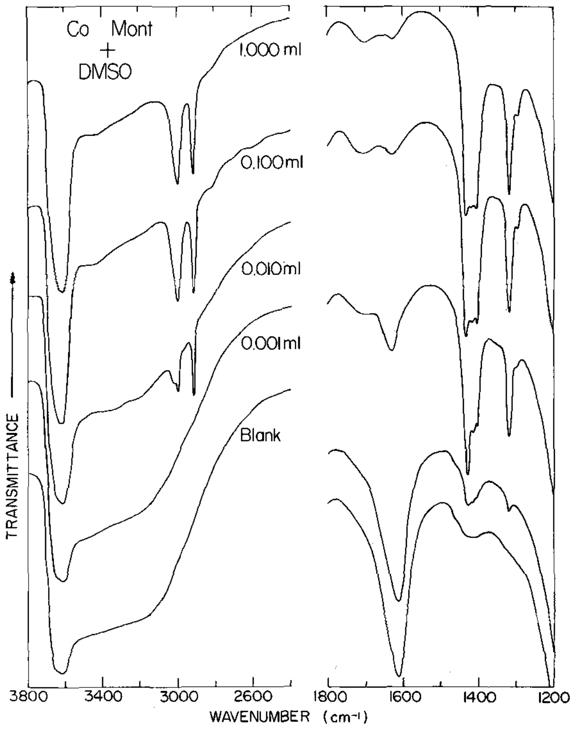

Fig. 2. The infrared spectra of complexes formed after depositing various amounts of DMSO on thin clay films of Co-montmorillonite.

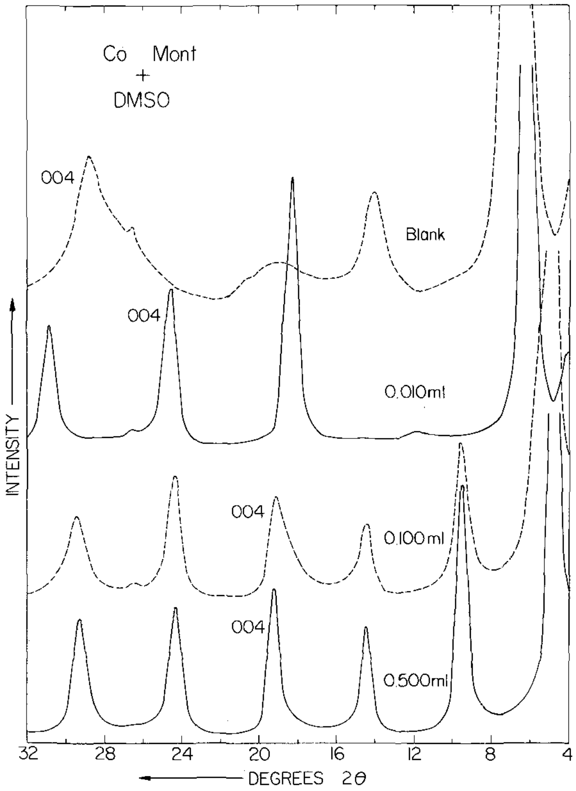

Fig. 3. The X-ray powder diffraction patterns of complexes formed after depositing various amounts of DMSO on thin clay films of Co-montmorillonite.

terlayers requires the concomitant removal of some water of hydration from the coordination spheres of the exchangeable cations. One may reasonably expect that a strongly polar solvent such as DMSO (4.3 Debye) should compete with adsorbed water molecules (1.85 Debye) for binding sites in the interlayer spaces of a clay. Olejnik et al. (1968) determined by infrared spectroscopy that intercalation of DMSO into hydrated halloysite displaces the interlamellar water. In the present case, a band is observed at 1612 cm^{-1} for untreated Cu-montmorillonite (Figure 1A). This band results from an overlap of bands at 1598 and 1632 cm^{-1}. Dowdy and Mortland (1967) have assigned the former band to the bending mode of water coordinated to Cu-cations, while they have assigned the latter band to the bending mode of water loosely adsorbed on the clay. The observed band shifts to ca. 1630 cm^{-1} and dramatically decreases in intensity after the film is treated with DMSO. Similar trends in spectral changes are noted for Co-, Ni-, Zn-, and Cd-montmorillonite films. The shift can be explained by assuming that the majority of water molecules coordinated to the metal cations are replaced by DMSO molecules. This interpretation is consistent with the results obtained by Berkheiser and Mortland (1975) for Cu-montmorillonite treated with DMSO. Their ESR studies indicated that the Cu^{2+}-ions are solvated by the DMSO molecules and are located away from the clay surface. Interestingly, their X-ray basal spacings were 18.4 Å whereas the spacings in this study were only 14.1 Å. This difference can be explained by the differences in both the amount of DMSO added to the clay film and the length of time of exposure. Their preparation procedure was to submerge a clay film in a bath of DMSO for 10 days while in this study only 26 μl of DMSO was allowed to interact with the clay film for 4 hr. Two important points may be made with respect to these contrasting procedures and X-ray results. First, solvation of Cu-montmorillonite by DMSO appears to be a stepwise process. A stable monolayer complex (d_{001} = 14.1 Å) forms at low DMSO loadings, and then a double layer complex (d_{001} = 18.4 Å) is formed when the DMSO loading is sufficiently increased. This stepwise solvation of montmorillonite was studied in greater detail for the Co-clay-DMSO system and will be discussed later. Second, the stereochemistry of the Cu^{2+}-ions in the monolayer complex ought to be quite different from that observed by Berkheiser and Mortland (1975). Their results from isotropic ESR spectra together with their large basal spacings indicated that the Cu-DMSO complex ions rapidly tumble in the interlayer. One may reason that the monolayer complex, occupying a less expanded interlayer, would be more restricted and less likely to tumble.

Analysis of the ESR spectra for our Cu-DMSO-clay complex should show an orientation dependence of the g $\perp$ and g $\parallel$ components of the g-tensor.

The effect of the initial concentration of the adsorbate on the adsorption processes was investigated using Co-montmorillonite as a model system. A series of complexes was prepared by varying the amount of DMSO deposited on Co-clay films. The DMSO-treated films were kept in desiccators for 48 hr at ambient temperature. The desiccators were then opened, and the specimens were exposed to air at ambient temperature for approximately 20 hr in order to evaporate excess DMSO from some of the clays. The infrared spectra (Figure 2) show conclusively that each of the complexes contained a chemisorbed species involving DMSO-Co coordination. As expected, the DMSO bands grow and the water band weakens in intensity and shifts as the initial concentration of the adsorbate is increased. However, above an added DMSO volume of 0.100 ml, no increase in DMSO band intensities is observed. This result suggests that the Co-clay film is completely saturated with DMSO when the volume of the aliquot is the above mentioned amount. X-ray diffraction patterns were also obtained for several members in this series and are shown in Figure 3. Analysis of the X-ray data (Table 2) clearly reveals the stepwise solvation process involved as the basal spacings increase from 12.6 Å to 14.5 Å and then to 18.3 Å for the blank Co-clay film, 0.010 ml- and 0.100 ml-DMSO-Co-clay specimens, respectively. X-ray patterns for complexes containing intermediate amounts of DMSO possessed broader bands indicating some degree of interstratification. These results are consistent with the i.r. data and indicate that a double layer is fully developed when the film is saturated. Infrared band features for DMSO-saturated clay films are entirely independent of the technique of saturating the films. The saturated films may be prepared by immersing the film in a bath of the absorbate, exposing it to a vapor of the absorbate or by depositing a controlled amount of absorbate on it allowing the liquid to penetrate the film. In each case, the i.r. spectra are identical.

An interesting reversible color change was observed in the case of the Co-montmorillonite-DMSO complex after it was desiccated for 20 hr over P_2O_5. Initially, before desiccation, the Co-clay-DMSO complex possessed a light tan color similar to that for a Co-clay film that was not treated with DMSO. However, after desiccation, the treated film's color changed to light purple. Upon removal of the complex from the desiccator, the specimen gradually reverted to the original tan color within several minutes. The purple color change could be achieved again either by desiccating the complex or by heating it at 120°C for a few minutes. Weyl (1959) noted similar color changes for various glasses containing cobalt. For instance, most cobalt glasses which are pink at room temperature turn blue on heating. The cobalt cations in these glasses undergo a coordination change from octahedral to tetrahedral upon heating. Apparently, cobalt cations in the DMSO-treated clay films undergo similar coordination changes upon desiccation or heating. This change in coordination can be achieved by the loss of two water molecules from the cobalt complex during desiccation or heating, leaving the Co^{2+}-ion tetrahedrally coordinated to four DMSO molecules. The reverse change can occur by the readsorption of two water molecules per cation during exposure to water vapor, resulting in octahedral coordination of the Co^{2+}-ion to four DMSO and two H_2O molecules. A distant possibility exists that DMSO may form a four-coordinated square-planar complex with Co^{2+}-ions upon desiccation or heat treatment. However, this possibility seems unlikely because most ligands will not normally form such complexes with Co^{2+}-ions (Cotton and Wilkinson, 1966).

Table 2. X-ray basal spacings and interlamellar spaces for complexes formed after depositing various amounts of DMSO on thin Co-montmorillonite films.

DMSO volume (ml)	d_{001} (Å)	Interlamellar space (Å)
0.0 (blank)	12.6	3.0
0.010	14.5	4.9
0.100	18.3	8.7
0.500	18.4	8.8

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Резюме- Инфракрасные спектры /4000-1200см$^{-1}$/ были получены для нескольких гомоионных монтмориллонитовых шлифов с различным количеством адсорбированного диметилового сульфоксида /ДМСО/. Анализы этих спектров указывают,что Н- и натуральные монтмориллонит-ДМСО комплексы содержат интеркалированный слой физически сорбированного ДМСО,в то время как комплексы обменный металлический катион переходной группы-монтмориллонит-ДМСО содержат как физически так и химически сорбированные ДМСО в своих межслойных промежутках. В последних разновидностях наблюдаются координационные связи молекул ДМСО с обменными катионами,образуемые их кислородными атомами. Большая часть межслойной воды замещается ДМСО,когда его молекулы проникают в межслойные промежутки. Обработка теплом при температуре 120°С в течение 48 часов комплексов металлический обменный катион переходной группы-монтмориллонит-ДМСО приводит к десорбции физически сорбированного ДМСО,но удерживает интеркалированные монослои,включающие координационные связи ДМСО-металлический катион переходной группы. Изменение водочувствительного,обратимого цвета /от рыжевато-коричневого до светло-пурпурного/ происходит или при высушивании над P_2O_5 или при обработке теплом при 120°С комплекса кобальт-монтмориллонит-ДМСО. Интерпретация видимого спектра предполагает,что катионы Co^{2+} изменяют свои октаэдрические координационные связи на тетраэдрические в течение высушивания или нагревания. Определение связей для глинистых комплексов было сделано по аналогии с родственными газами,жидкостями и кристаллами.

Kurzreferat- Die Infrarotspektra(4000-1200 cm^{-1}) von verschiedenen homoionischen Montmorilloniten,auf die unterschiedliche Mengen von Dimethylsulfoxyd(DMSO) adsorbiert waren,wurden aufgenommen.Analyse dieser Spektra deuten darauf hin,daß H-und natürliche Montmorillonit-DMSO-Komplexe eine eingebettete Schicht von physikalisch adsorbiertem DMSO enthalten, wohingegen mit Übergangsmetallkationen substituierte Montmorillonit-DMSO-Komplexe sowohl physikalisch wie auch chemisch adsorbiertes DMSO in ihren interlaminaren Räumen besitzen.Die letztere Sorte ist mit Koordination der Sauerstoffatome der DMSO-Moleküle mit den austauschbaren Kationen verbunden. Das meiste interlaminare Wasser wird durch DMSO ersetzt, sobald die DMSO Moleküle die interlaminaren Räume penetrieren.Wärmebehandlung der mit Übergangsmetallkationen substituierten Montmorillonit-DMSO Komplexe,bei 120°C für 48 Std.,resultierte in der Desorption von physikalisch adsorbiertem DMSO wie auch in der Beibehaltung der eingebetteten Einzelschichten, welche mit DMSO - Metallkationkoordination verbunden sind.Ein wasserempfindlicher,reversibler Farbumschlag(von beige zu hellviolet) wird entweder durch Entwässern des Kobalt-Montmorillonit-DMSO-Komplexes über P_2O_5 oder Wärmebehandlung bei 120°C erhalten.Interpretation der sichtbaren Spektren,schlagen vor daß Co(II)Kationen,während des Entwässern oder der Wärmebehandlung,von oktahedrischer zu tetrahedrischer Koordination überwechselt.Die Bestimmung der Bänder für die Tonkomplexe wird durch Vergleich mit ähnlichen Gasen, Flüssigkeiten und Kristallen gemacht.

Résumé-Les spectres infra-rouges (4000-1200 cm^{-1}) ont été obtenus pour plusieurs films de montmorillonite homoionique sur lesquels diverses quantités de sulfoxide diméthyl ont été adsorbées (DMSO).Les analyses de ces spectres indiquent que les complexes H-montmorillonite - DMSO et montmorillonite naturelle - DMSO contiennent un feuillet intercalaire de DMSO physisorbé,tandis que les complexes de montmorillonite substituée par des cations de métal de transition - DMSO ont à la fois du DMSO physisorbé et chemisorbé dans les espaces interlamellaires.Cette dernière espèce implique la coordination de

molécules de DMSO avec les cations échangeables par l'intermédiaire de leurs atomes d'oxygène.La plupart de l'eau interlamellaire est remplacée par du DMSO,puisque les molécules de ce dernier pénètrent les espaces interlamellaires.Le traitement à la chaleur de complexes montmorillonite substituée par des cations de métal de transition - DMSO à 120°C pendant 48 heures donne les résultats suivants:à la fois la désorption de DMSO phisisorbé,et la rétention de mono-feuillets intercalaires impliquant la coordination des molécules de DMSO avec les cations du métal de transition.Un changement de couleur (de brun à mauve pâle),sensible à l'eau,est produit soit par la dessication sur P_2O_5,soit par traitement à la chaleur à 120°C du complexe cobalt-montmorillonite - DMSO.L'interprétation des spectres visibles suggère que les cations CO^{2+} subissent des changements de coordination de mode octaédrale à tétraédrale pendant la dessication ou l'échauffement.Des bandes sont attribuées aux complexes argileux employant les attributions faites pour les gaz, liquides et cristaux apparentés.