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

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Abstract—The i.r. spectra (4000–1200 cm⁻¹) are obtained for several cation-substituted-montmorillonite–lysine complexes that were prepared at their natural pH's. Analyses of the spectra of copper-, cobalt-, nickel- and zinc–montmorillonite films indicate that bidentate chelate complexes which contain protonated ϵ-amino-groups are present in the interlamellar spaces. Investigation of the spectra of the hydrogen-, calcium- and natural-*montmorillonite* films indicates that the dominant adsorbed species for these complexes is a lysine cation in which both the α- and the ϵ-amino-groups are protonated while the carboxyl group is ionized.

INTRODUCTION

I.R. SPECTROSCOPY can be used to obtain structural information concerning both inorganic and organic compounds adsorbed on clays. Cloos *et al.* (1966) have investigated the i.r. spectra of several simple amino acids adsorbed on sodium-, calcium- and hydrogen–montmorillonite, and determined that protonated cations containing an NH_3^+-group and a COOH-group were the dominant adsorbed species. Recently, Jang and Condrate (1972) have investigated the spectra of α-amino acids adsorbed on transition metal-substituted montmorillonites, and determined that both bidentate chelate and monodentate complexes can be present in the interlamellar spaces. In this study, lysine which contains two amino-groups has been adsorbed on various cation-substituted montmorillonites, and the spectra of the resulting films were used to determine the types of complexes present in their interlamellar spaces. The spectra of related complexes in crystals and solutions have been used to identify the adsorbed species, and to make band assignments.

EXPERIMENTAL

The clay films containing adsorbed lysine were prepared in a manner described earlier by Jang

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and Condrate (1972). The exchangeable cation content for each montmorillonite complex is approximately 100 meq cation/100g clay. The amounts of lysine adsorbed on the transition metal ion-substituted and the hydrogen ion-substituted clays are very close to their cation exchange capacities. Approximately 20 meq lysine/100g clay adsorbed on natural- and Ca–montmorillonite. H–montmorillonite complexes were prepared immediately prior to use, so that the effects of degradation of H–montmorillonite to the Al^{3+}-clay could not be observed in the spectra. X-ray diffraction analysis indicated that lysine formed single-layer complexes in these clays before and after placing the samples in a vacuum. Each self-supporting thin film possesses a diameter of approximately 1 in. and contains approximately 3 mg clay/cm². The i.r. adsorption spectra (4000–1200 cm⁻¹) were obtained for each clay specimen by placing their corresponding self-supporting thin films in the sample beam of a Perkin-Elmer Model 621 double beam grating spectrophotometer. The clay films were mounted in an evacuated cell (cell pressure ~10⁻⁴ torr) with KCl windows. An air purging unit was employed to eliminate adsorption bands due to atmospheric water and carbon dioxide. Calibration of the spectrophotometer was carried out using polystyrene bands and a wave-number accuracy of ±3 cm⁻¹ was obtained.

RESULTS AND DISSCUSION

The i.r. spectra of several cation-substituted montmorillonite complexes containing intercalated

l-lysine prepared at their natural pH's are shown in Figs. 1 and 2. Band assignments for pertinent lysine-montmorillonite complexes are listed in Table 1. A strong band at *ca.* 3630 cm⁻¹ in all spectra is due to the lattice hydroxyl stretching mode for montmorillonite. Also, a weak broad band at *ca.* 3400 cm⁻¹ may be assigned to a water band. All other bands observed above 3000 cm⁻¹ in our spectra are assigned to NH stretching modes. The absence of bands above 3300 cm⁻¹, and the presence of a strong band and a shoulder at 3276 at 3040 cm⁻¹ for the H-montmorillonite complex indicate that the NH stretching modes of this particular complex are due to NH_3^+-groups rather than NH_2-groups. These two wavenumbers are very close to those observed previously for protonated α-amino acid cations adsorbed on H–montmorillonite (Condrate and Jang, 1972). Similar structural interpretations and band assignments are made for Ca- and natural–montmorillonite complexes. Several bands are observed at 3355, 3268, 3150, and 3080 cm⁻¹ for the Cu–clay complex. An earlier investigation involving α-amino-acid-clay complexes showed that bands near 3350 cm⁻¹ can be attributed to NH_2-groups whose
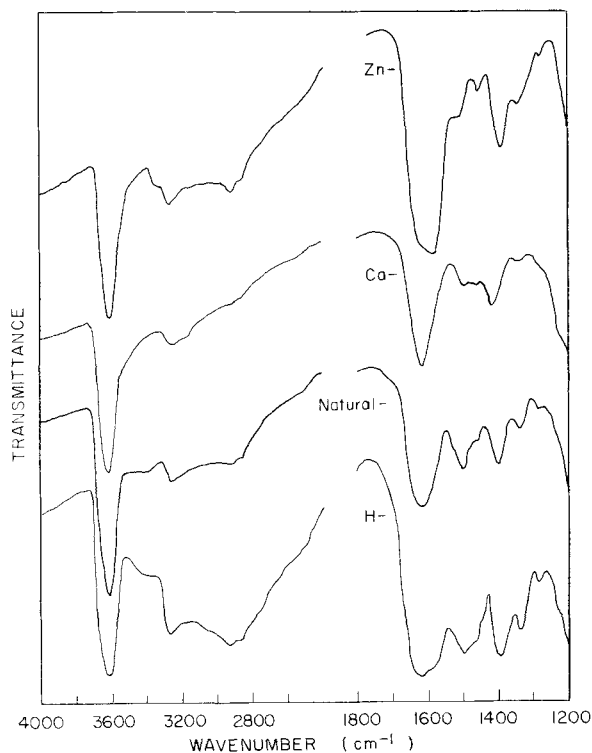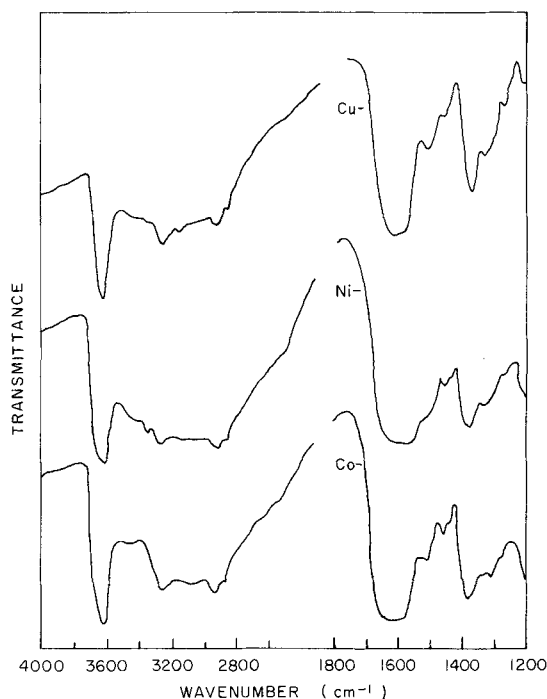

Fig. 2. The i.r. spectra of lysine adsorbed on Co-, Ni-, and Cu–montmorillonite (cell pressure ~ 10⁻⁴ torr).

N-atoms are coordinated to divalent metal cations (Condrate and Jang, 1972). In this study, one of the observed wavenumbers can be assigned to the NH asymmetric stretching mode of an NH_2-group coordinated to a Cu^{2+}-ion. Similar modes are also noted in the same wavenumber range for Co-, Ni- and Zn–montmorillonite complexes, indicating similar types of bonding. One of the other bands in this wavenumber region may be attributed to the NH symmetric stretching mode of the coordinated NH_2-group. The remaining bands observed for these complexes are very close in wavenumber to those of the H– and Ca–clay complexes. Therefore, these bands are assigned to the NH stretching modes of an NH_3^+-group. The observed bands immediately below 3000 cm⁻¹ are empirically assigned to the CH stretching modes of the methylene groups.

In the lower wavenumber region, no bands are observed near 1700 cm⁻¹ for any clay-lysine complex. This observation strongly indicates that no lysine species containing a COOH-group is adsorbed on montmorillonite in major amounts. However, strong peaks occur near 1600 cm⁻¹ for the H-clay complex which can be assigned to NH_3^+ deformation and COO^--asymmetric stretching modes. The broadness of these peaks may be


Fig. 1. The i.r. spectra of lysine adsorbed on H-, natural-, Ca-, and Zn–montmorillonite (cell pressure ~ 10⁻⁴ torr).

Table 1. Band assignments of lysine–montmorillonite complexes prepared at their natural pH-values

H–clay complex	Co–clay complex	Ni–clay complex	Cu–clay complex	Zn–clay complex	Assignments
	3310 (w, sh)	3350 (w)	3355 (w)	3345 (w)	NH_2 str.
	3260 (s, b)	3270 (s, b)	3268 (s)		
3276 (s, b)	ca. 3100 (b)	ca. 3100 (b)	3150 (w)	3137 (sh)	NH_3^+ str.
3040 (b)			3080 (w)		
2937	2930	2960	2944	2930	CH str.
2867	2860	2870	2870	2862	
1625 (vs, b)	1630 (vs, b)	1640 (vs, b)	1630 (vs, b)	1640 (vs, b)	COO^- asym. str.
1605 (sh)	1590 (sh)	1590 (sh)	1590 (sh)	1580 (sh)	and NH_3^+ def.
1497 (s, b)	1515 (m, b)	1510 (m, sh)	1515 (m)	1512 (m, sh)	NH_3^+ sym. str.
1475 (w, sh)	1470 (vw, sh)	1470 (w, sh)	1475 (vw, sh)	1470 (w, sh)	
1460 (m)	1459	1465 (m)	1460 (w)	1458 (w)	CH_2 def.
	1440 (sh)	1445 (sh)	1450 (w, sh)	1445 (sh)	
1395 (s)	1382 (s)	1380 (s)	1378 (s)	1389 (v)	COO^- sym. str.
1340	1340	1340	1340		
1305	1311	1310	1305		CH def.
1275	1280	1275	1275	1280	
		1220	1220		

due to the slightly different wavenumbers for the two NH_3^+-groups. In the spectra of both Ca– and natural–montmorillonite complexes, this broad band is observed at 1615 cm⁻¹, but with less intensity. The observed bands for the Cu–, Co–, Ni–, and Zn–montmorillonite complexes in this wavenumber region are much broader. This observation suggests that the carboxyl stretching mode has shifted to a higher wavenumber due to co-ordination of an oxygen atom of the carboxyl group by the divalent cation, and that one of the NH deformation modes has shifted to a lower wavenumber due to coordination of an NH_2-group.

The bands observed at 1497 cm⁻¹ in each spectrum for the H–, Ca–, and natural–montmorillonite complexes can be readily assigned to the NH_3^+ symmetric deformation mode. This mode occurs at ca. 1515 cm⁻¹ for the rest of the complexes. The peaks at ca. 1470, 1460, and 1440 cm⁻¹ in each spectrum may be attributed to deformation modes of the CH_2-groups since these modes occur in the same wavenumber range as those for β-alanine complexes.
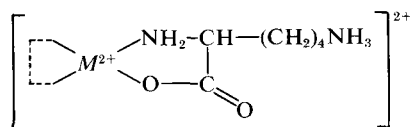
The strong broad bands at ca. 1395 cm⁻¹ for the H– and natural–montmorillonite complexes, and 1416 cm⁻¹ for the Ca–montmorillonite complexes are assigned to the symmetric stretching mode of the COO^--group of the intercalated lysine. This mode, however, is noted at lower wavenumbers for the complexes formed with the transition metal ion-saturated montmorillonites. The change in wavenumber of this mode occurs in the following order:

$$Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}.$$
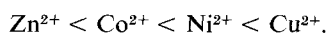
The trend in wavenumber is similar to that observed by Nakamoto et al. (1961) for various α-amino-acid-metal chelated complexes. It is related to the covalent character of the M—O bond attached to the carboxyl group. As the covalent character of M—O bond increases, the wavenumber for symmetric COO^- stretching mode decreases. This trend and the location of the symmetric carboxyl stretching mode present further evidence for the coordination of the carboxyl group with the divalent cation in the transition metal saturated montmorillonites. The wavenumbers below these peaks are less important for our structural analyses. However, they may be attributed to the vibrational modes of the CH_2-groups.

The results of the chemical analyses for the clay–lysine complexes indicated that transition metal ion-substituted montmorillonites adsorbed significantly greater amounts of lysine than those of α-amino acids. The amounts of lysine adsorbed by the transition metal ion-saturated montmorillonites are very close to the cation exchange capacities of the clays. This stoichiometric ratio indicates that each transition metal ion is associated with two lysine molecules. Our i.r. study indicates that each of the lysines chelate to the transition metal. Small amounts of other types of lysine species may be adsorbed on these montmorillonite complexes, but they were undetectable by our method. Chelation would be expected because the lysine zwitterion having the configuration, $NH_3^+(CH_2)_4CH(NH_2)COO-$, predominates in aqueous solutions, and a chelated complex can be readily formed by bonding one of the carboxyl oxygen atoms and the

N-atom of the α-amino-group with the Cu^{2+}-ion of the clay. It is improbable that a chelated complex is formed involving the ϵ-amino-group, because either an 8-membered or 9-membered chelate ring would be formed which are known to be less stable than 5-membered chelate rings. From the above results, we conclude that the best model for the adsorbed species on transition metal-ion substituted montmorillonites may be given by the following configuration:

$$\left[M^{2+} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} NH_2-CH-(CH_2)_4NH_3 \\ | \\ O-C \\ \quad \backslash\!\!\backslash O \end{array} \right]^{2+}$$

Sufficient spectra data are not available to determine whether this complex is in the *cis*- or the *trans*-form. Raman spectra are necessary to make this prediction.

Interpretation of the i.r. spectra for lysine adsorbed on H–, Ca– and natural–montmorillonites indicates that lysine cations are present in the interlamellar spaces with the following configuration:

$$\left[NH_3{}^+-CH_2-CH_2-CH_2-CH_2-CH-COO^- \atop \qquad\qquad\qquad\qquad\qquad\qquad\quad | \atop \qquad\qquad\qquad\qquad\qquad\qquad\quad NH_3{}^+ \right]$$
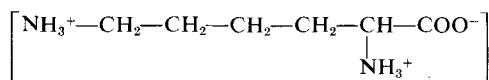
This adsorbed species is quite different from α-amino acid cations that can be adsorbed on H–montmorillonite (Jang and Condrate, 1972).

The lysine cation possesses an ionized COO$^-$-group instead of a COOH-group. The cationic charge is maintained for this species by the protonation of both amino groups.

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Résumé—Les spectres infrarouges (4000–1200 cm^{-1}) ont été obtenus pour plusieurs complexes montmorillonite à cation échangé—lysine, préparés à leurs pH naturels. L'analyse des spectres de films de montmorillonite saturée par le cuivre, le cobalt, le nickel et le zinc, indique que des complexes chélates bidentates contenant des groupes ϵ amino protonés sont présents dans les espaces interlamellaires. L'étude des spectres de films de montmorillonite naturelle ou saturée par l'hydrogène et le calcium, indique que l'espèce adsorbée dominante dans ces complexes est un cation lysine dans lequel les groupes α et ϵ aminés sont protonés à la fois, tandis que le groupe carboxyle est ionisé.

Kurzreferat—Für mehrere kationisch substituierte Montmorillonit-Lysin Komplexe, die bei ihren natürlichen pH-Werten bereitet wurden, werden die Ultrarotspektren (4000–1200 cm^{-1}) erhalten. Analysen der Spektren von Kupfer–, Kobalt–, Nickel– und Zink–Montmorillonit Filmen zeigen an, dass in den interlamellaren Zwischenräumen zweifach gezackte Chelatkomplexe gegenwärtig sind, die protonierte ϵ-Aminogruppen enthalten. Die Untersuchung der Spektren der Wasserstoff–, Calcium– und natürlichen–Montmorillonit Filme deutet darauf hin, dass die überwiegend adsorbierte Sorte dieser Komplexe ein Lysinkation ist, in welchem die α- und die ϵ-Aminogruppen protonisiert sind, während die Carboxylgruppe ionisiert ist.

Резюме — Для ряда катион-замещенных комплексов монтмориллонит-лизина, приготовленных при естественных значениях pH, получены инфракрасные спектры в области 4000–1200 см$^{-1}$. Анализ спектров пленок Cu–, Co–, Ni– и Zn–монтмориллонита показывает, что в межслоевом пространстве изученных образцов присутствуют бидентатные хелатные комплексы, содержащие протонированные ϵ-аминогруппы. Исследование спектров пленок H–, Ca– и природ–ных монтмориллонитов показывает, что преобладающей адсорбированной компонентой в этих комплексах являются катионы лизина, в которых как α-, так и ϵ–аминогруппы являются протонированными, тогда как карбоксильная группа ионизирована.