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An Infrared Examination of Ion-Exchanged Montmorillonite Treated With Polyethylene Oxide

By Steve W. Webb, D. A. Stanley, and B. J. Scheiner



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 9036

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

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Robert C. Horton, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	μL	microliter
cm ⁻¹	wavenumber	mm	millimeter
h	hour	pct	percent
min	minute	s	second
mL	milliliter		

AN INFRARED EXAMINATION OF ION-EXCHANGED MONTMORILLONITE TREATED WITH POLYETHYLENE OXIDE

By Steve W. Webb,¹ D. A. Stanley,² and B. J. Scheiner³

ABSTRACT

The Bureau of Mines is researching a new technology for dewatering clay suspensions that consists of flocculation by high-molecular-weight polyethylene oxide (PEO) polymer and subsequent removal of water from the flocs via a trommel. The minimum amount of PEO required to dewater the clays depends on the ions adsorbed on the surface of the clay particles. Infrared studies were performed on clays with Li^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , or Sr^{2+} adsorbed, with and without adsorbed PEO, to develop data to aid in understanding the dewatering mechanism.

Hydroxyl stretching modes between $3,400$ and $3,250\text{ cm}^{-1}$, associated with water adsorbed on the clay, showed changes in intensity proportional to the ionic charge-to-radius ratio; that is, the ionic potential. In addition, a water-bending vibration of adsorbed water at $1,630\text{ cm}^{-1}$ showed variations associated with water desorption. The data are consistent with changes in adsorption of PEO resulting from variation of the acidity of water coordinated with the exchange ions, induced by the variation in field strength of the ions with the ionic potential.

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INTRODUCTION

The Bureau of Mines is developing technology to dewater a variety of clay-containing mine wastes. This technology involves flocculation by a high-weight polyethylene oxide (PEO) polymer and subsequent removal of water from the flocs by mechanical deformation in a trommel.

Field studies and previous laboratory studies proved that the ion-exchange form of the clay affected the amount of PEO needed for successful dewatering. This report presents detailed infrared studies of PEO treated ion-exchanged montmorillonite clays conducted to obtain a basic understanding of how the exchange ion of the clay affects the dewaterability of these waste materials. Such an understanding could provide an

improvement in the Bureau-developed dewatering technique.

The study of clay-organic complexes can be greatly facilitated with the use of infrared spectroscopy. Characteristic functional groups of both the clay and the organic can be readily detected in the infrared region of the spectra between 4,000 to 200 cm^{-1} . The infrared spectra of control and PEO-treated, ion-exchanged (new ions adsorbed in place of those originally present) montmorillonite were closely scrutinized for any changes due to adsorption of the polymer. In this manner, the nature of the interaction between the clay and the organic polymer, PEO, may be better understood.

PREVIOUS WORK

Infrared (IR) methods have been widely utilized in the study of clay minerals for 40 yr. Mineral characterization studies by Adler (1),⁴ Farmer (2), and Ferraro (3), to name a few, have resulted in the compilation of infrared data on a wide variety of minerals and clays.

During this time, a number of infrared studies were performed on clays of the smectite group, which is referred to as the montmorillonite group in the older literature. Serratosa (4) and Jorgenson (5) examined the dehydration behavior of montmorillonite. The effects of isomorphic lattice substitution in the octahedral layer of montmorillonite were investigated by Stubican and Roy (6), Tettenhorst (7), and Calvet and Prost (8). Prost (9) described the hydration mechanism for hectorite in a number of different ion-exchange states. The phenomenon of swelling in montmorillonite was investigated using infrared spectroscopy by Lerot and Low (10). These and a number of other related works (11-15) have added significant contributions to

the current knowledge of the structure and properties of the smectites.

One of the most useful applications of infrared spectroscopy is the characterization of adsorption bonds formed in clay-organic complexes. Excellent review articles on the subject have been prepared by Mortland (16) and Theng (17-18). Basically, when an organic molecule is adsorbed onto the surface of a clay mineral, bonds are formed that cause characteristic shifts in the IR frequency of various spectral bands. The interpretation of the shift of IR bands following adsorption frequently yields valuable insight into the mode of attachment of the adsorbing molecule (16).

MacEwan studied the adsorption of a number of organic substances on montmorillonite and concluded that the polar groups of the organic molecules were held to the surface of the clay by a C-H....O-type bond (19). Hydrogen bonds formed between hydrogen of the organic molecule and the oxygen atoms of the clay surface have long been held by many researchers to play an important role in the adsorption process. Evidence was later given that the surface oxygen atoms of the clay (montmorillonite) are weak

⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.

electron donors and therefore capable of forming only weak hydrogen bonds (20).

Initial studies describing the interaction of clay minerals and nonionic organic molecules reported that the bonding forces were nonelectrostatic in nature (21). Serratosa demonstrated that the adsorption of nonionic organics by montmorillonite was controlled by the exchangeable cations (22). Farmer (20) extended this idea by describing three major modes of adsorption of polar organic molecules by montmorillonite:

1. Direct coordination of the organic molecule to the exchange ion.
2. Conversion of adsorbed bases to the protonated cationic form.
3. Indirect coordination of the organic molecule through a water bridge (20). The mode of adsorption of low-molecular weight (MW = 200 to 20,000) polyethylene glycol on montmorillonite was described by Parfitt and Greenland as a dipole linkage between the ether groups of the polymer and the hydration shell of the exchange ion (23).

EXPERIMENTAL METHODS AND MATERIALS

As mentioned earlier, infrared spectroscopy is well suited to detecting spectral frequency shifts induced by the adsorption of organic materials upon the surface of the clay. For this reason, ion-exchanged montmorillonite samples were treated with a high-molecular-weight PEO polymer (MW = 5 million) and analyzed with IR in the range of 4,000 to 300 cm^{-1} utilizing the following procedure.

Ion-exchanged clays were prepared from a Wyoming bentonite using a method described by Stanley and Scheiner (24). One percent suspensions (weight of solids to volume of water or w/v) of each ion-exchanged montmorillonite (Li^+ , Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , and Ba^{2+}) were prepared and allowed to stir for a period of 24 h, to insure adequate dispersal of the clay particles. In a like fashion, a 0.1-pct polymer solution of a 5 million MW PEO obtained from a commercial source was prepared using ultrapure water as the solvent.

To a 100-mL portion of each 1 pct w/v ion-exchanged clay suspension was slowly added 100 mL of the appropriate 0.1-pct polymer solution, with stirring. Each such mixture was stirred for 10 min, a duration adequate for complete flocculation. Control samples were prepared similarly, using ultrapure water instead of polymer solution.

Upon addition of the polymer and subsequent flocculation of the divalent-exchange clays treated with the 5 million MW PEO, large flocs were formed that were

inappropriate for thin-film IR analysis. These samples were therefore homogenized in a blender for a period of 30 s to reduce the flocs size to an acceptable level.

Thin films of each of the control and polymer-clay suspensions were prepared by withdrawing 100 μL of the treated or control sample and placing it upon an AgBr disc (20 mm diam by 2 mm). The AgBr discs were placed in a desiccator under atmospheric pressure and room temperature until the water was evaporated from the sample.

Each of the thin-film mounts was scanned from 4,000 to 300 cm^{-1} using a Perkin-Elmer 684 Infrared Spectrophotometer.⁵ Each of the IR scans was performed using a medium slit width, a 5-min scan time, and with the instrument in percent transmission mode.

The infrared instrument was controlled by an "obey" routine generated on a Perkin-Elmer 3600 Data Station. This software routine provided the instrument operator automated control of the infrared equipment to insure that the IR data were accumulated under uniform conditions. The AgBr discs were automatically scanned from 4,000 to 300 cm^{-1} , and the resulting spectra were flattened and smoothed to reduce noise and other sources of interference.

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

RESULTS AND DISCUSSION

INFRARED ANALYSES OF THE UNTREATED
ION-EXCHANGED MONTMORILLONITE SAMPLES

Spectral interpretations of the infrared adsorption patterns of montmorillonite are numerous and extremely detailed (4, 6, 12-13, 22, 25-29). Figure 1 shows a typical infrared scan (4,000 to 500 cm^{-1}) obtained from a thin-film mount of a calcium-exchanged montmorillonite. The major spectral band assignments for figure 1 are described in table 1. Note that the references for the band assignments given are included in table 1. The spectra of all the

ion-exchanged clay samples analyzed in this investigation, with the exception of ammonium-exchanged montmorillonite, conform quite closely to the spectral bands given in table 1.

The infrared spectra of ammonium-exchanged montmorillonite differ from the other ion-exchanged forms in that N-H stretching vibrations at 3,040 cm^{-1} and 2,870 cm^{-1} and N-H bending vibration at 1,430 cm^{-1} occur as a result of the presence of the ammonium (NH_4^+) ion in the interlayer. The presence of these peaks can be verified in figure 2.

TABLE 1. - Spectral interpretation of major montmorillonite infrared absorption peaks

Peak ¹	Position, cm^{-1}	Attribute	Reference
A.....	3,620	Structural hydroxyl stretch (AlMgOH or AlAlOH).	6, 8, 26-27, 29, 39
B.....	3,395	Adsorbed water stretch (OH)....	6, 8, 22, 27, 39
C.....	3,250	...do.....	6, 8, 22, 39
D.....	1,630	Adsorbed water bend H-O-H.....	6, 39
E.....	1,000-1,200	Si-O stretching.....	28
F.....	920	Al-Al-OH bend.....	7, 15, 27, 39
G.....	880	Fe(III)-Al-OH bend.....	15, 27
H.....	840	Mg-Al-OH bend.....	15, 27
I.....	800	Fe(II)-Fe(III)-OH bend or Mg-Mg-OH bend.	8, 15
J.....	520	Si-O-Al bend or Si-O bend.....	6-7, 25

¹The letters designate the individual peaks shown in figure 1.

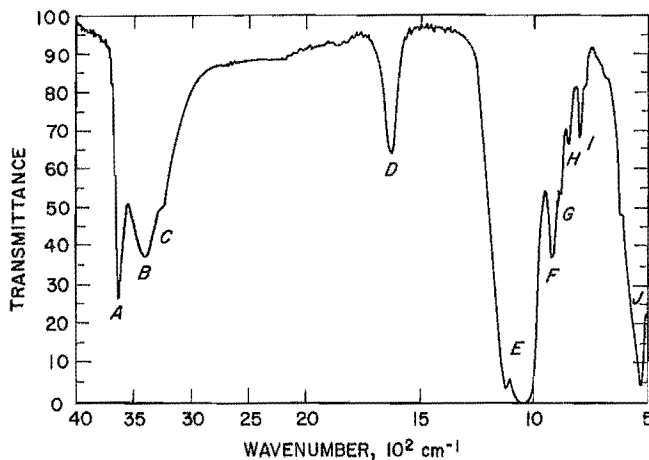


FIGURE 1.—Infrared adsorption spectrum of calcium montmorillonite (4,000 to 500 cm^{-1}). The letter designations in this figure are explained in table 1.

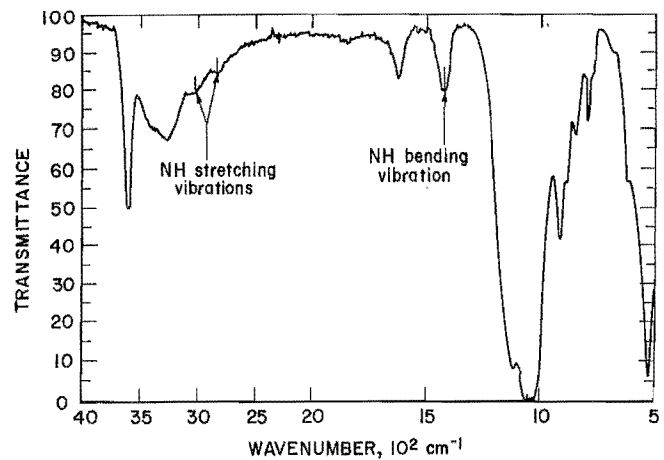


FIGURE 2.—Infrared adsorption spectrum of ammonium montmorillonite (4,000 to 500 cm^{-1}).

In order to develop baseline conditions for the untreated clays, spectral interpretation was conducted upon the eight ion-exchanged control samples. In this manner, the influence of the exchangeable cations upon the clay lattice could be better evaluated. Close examination of the IR bands of the untreated clays revealed that the adsorbed interlayer region was influenced to a large extent by the presence of the exchange ion.

The broad peak at approximately $3,400\text{ cm}^{-1}$ and the more sharply defined peak at $1,630\text{ cm}^{-1}$ correspond to the hydroxyl stretching and water bending vibrations, respectively, of adsorbed interlayer water (4-5). Figure 3A is a composite of the eight control samples as they appear from $3,800\text{ cm}^{-1}$. Note the consistency in the peak intensity for the structural hydroxyl peaks of $3,620\text{ cm}^{-1}$ in relation to the broad adsorbed water peaks of $3,400\text{ cm}^{-1}$. Just as the constancy of the $3,620\text{-cm}^{-1}$ peak is an indication of the unchanging character of the structural hydroxyl groups, the variability of the $3,400\text{-cm}^{-1}$ peak is an indicator of the influence exerted on the interlayer water by the exchange ion. Similarly, the adsorbed water bending vibration of $1,630\text{ cm}^{-1}$ also varies as a function of the exchanged ion present, as seen in figure 3B.

A similar conclusion was reached by Theng and Scharpenseel (31), who demonstrated that humic acid adsorption on ion-exchanged montmorillonite was controlled largely by the ionic potential. Ionic potential is defined as the ratio of the exchange ion valence (Z) to its ionic radius (r). In a later work (17), the ionic potential (Z/r) was described as a measure of the influence the interlayer cation exerted over neighboring molecules (i.e., hydration water molecules).

The peak area of the $1,630\text{-cm}^{-1}$ water bending vibration can be related to the amount of water present in the interlayer region (30). Because the $1,630\text{-cm}^{-1}$ peak is relatively isolated and free from

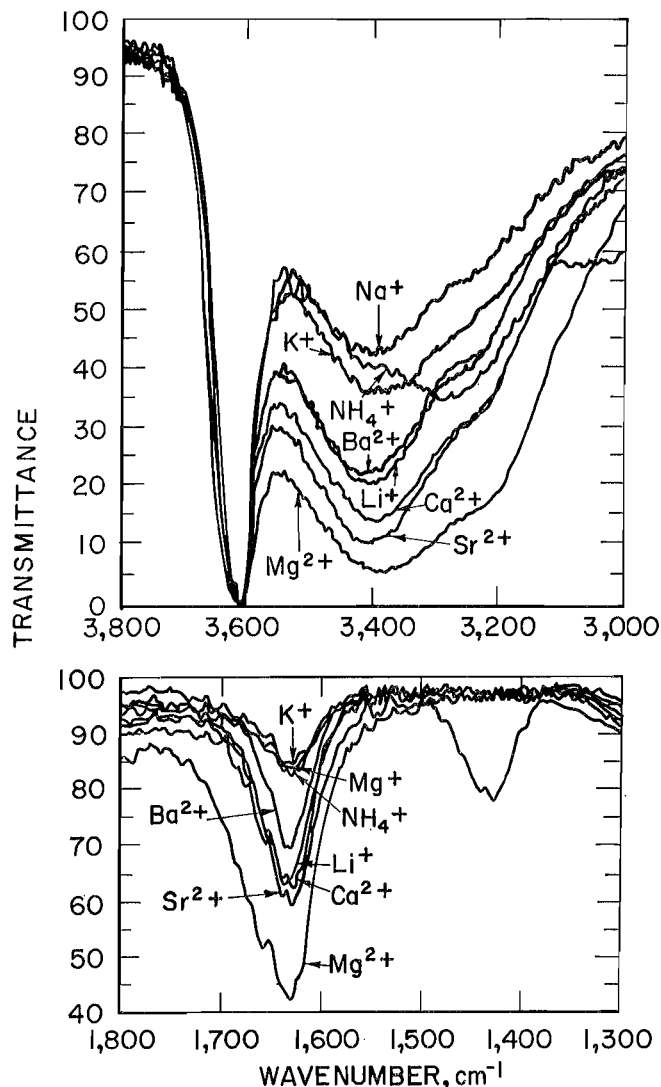


FIGURE 3.—Composite spectra of eight ion-exchanged montmorillonite samples. A, $3,800$ to $3,000\text{ cm}^{-1}$; B, $1,800$ to $1,300\text{ cm}^{-1}$.

interference, quantitative determinations can be easily made. With the use of the Perkin-Elmer-supplied quantitative analysis routine, SINGLE, the relative peak height and area for each of the control samples at $1,630\text{ cm}^{-1}$ can be routinely determined. The values obtained from the SINGLE analysis are given in table 2.

The values of ionic radii, listed in table 2, were taken from the work of Nightingale (32). These data were, in turn, used to calculate the values of ionic potential (Z/r) for the exchange ions also listed in table 2.

Table 2. - Atomic radii for selected cations compared to the peak area of the $1,630\text{-cm}^{-1}$ peak for the ion-exchanged montmorillonites

Exchange ion	Valence (Z)	Ionic radius (r), ¹ Å	Ionic potential (Z/r)	Relative peak area
Li ⁺	1	0.60	1.67	7.223
Na ⁺	1	.95	1.05	2.692
NH ₄ ⁺	1	1.33	.75	3.637
K ⁺	1	1.48	.68	3.266
Mg ²⁺	2	.65	3.08	17.390
Ca ²⁺	2	.99	2.02	9.646
Ba ²⁺	2	1.13	1.48	7.135
Sr ²⁺	2	1.35	1.77	9.142

¹Radius values taken from Nightingale (30).

A plot of the peak areas versus ionic potential, as seen in figure 4, indicates that these two parameters are indeed linearly related. This is a further indication that the amount of hydration water present in the interlayer is strongly influenced by the polarizing effect of the exchange ion.

INFRARED ANALYSIS OF PEO

In order to better characterize the effect of polymer adsorption upon the ion-exchanged clays, an infrared scan was performed on a 0.1-pct PEO solution. A

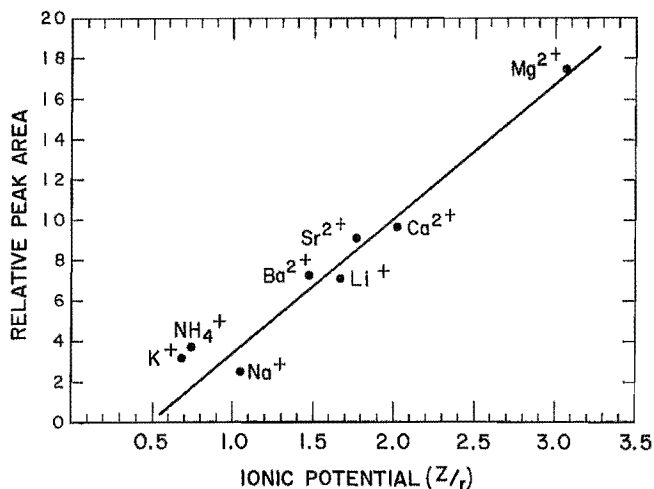


FIGURE 4.—Graph of relative peak area of $1,630\text{-cm}^{-1}$ hydroxyl bending vibration versus the ionic potential of the exchange cation.

thin-film mount was again prepared from 100 μL of the 0.1-pct polymer solution evaporated upon an AgBr disc. The results of this IR scan have been summarized in figure 5, and the appropriate band assignments are summarized in table 3. The interpretation of the infrared absorption pattern of PEO has been described in great detail by Bailey and

TABLE 3. - Spectral interpretation of major PEO peaks (33)

Peak frequency, ¹ cm^{-1}	Attribute
2,940 (m).....	CH ₂ antisymmetric stretch.
2,880 (s).....	CH ₂ symmetric stretch.
1,460 (m).....	CH ₂ scissor.
1,340 (s).....	CH ₂ wag.
1,280 (m).....	CH ₂ twist.
1,235 (m).....	CH ₂ twist.
1,140 (s).....	CO stretch, CH ₂ rock.
1,100 (vs).....	CO stretch.
1,055 (m).....	CO, CC stretch, CH ₂ rock.
960 (s).....	CH ₂ rock, CH ₂ twist.
840 (s).....	CO stretch, CC stretch, CH ₂ rock.

¹(m), medium; (s), strong; (vs), very strong.

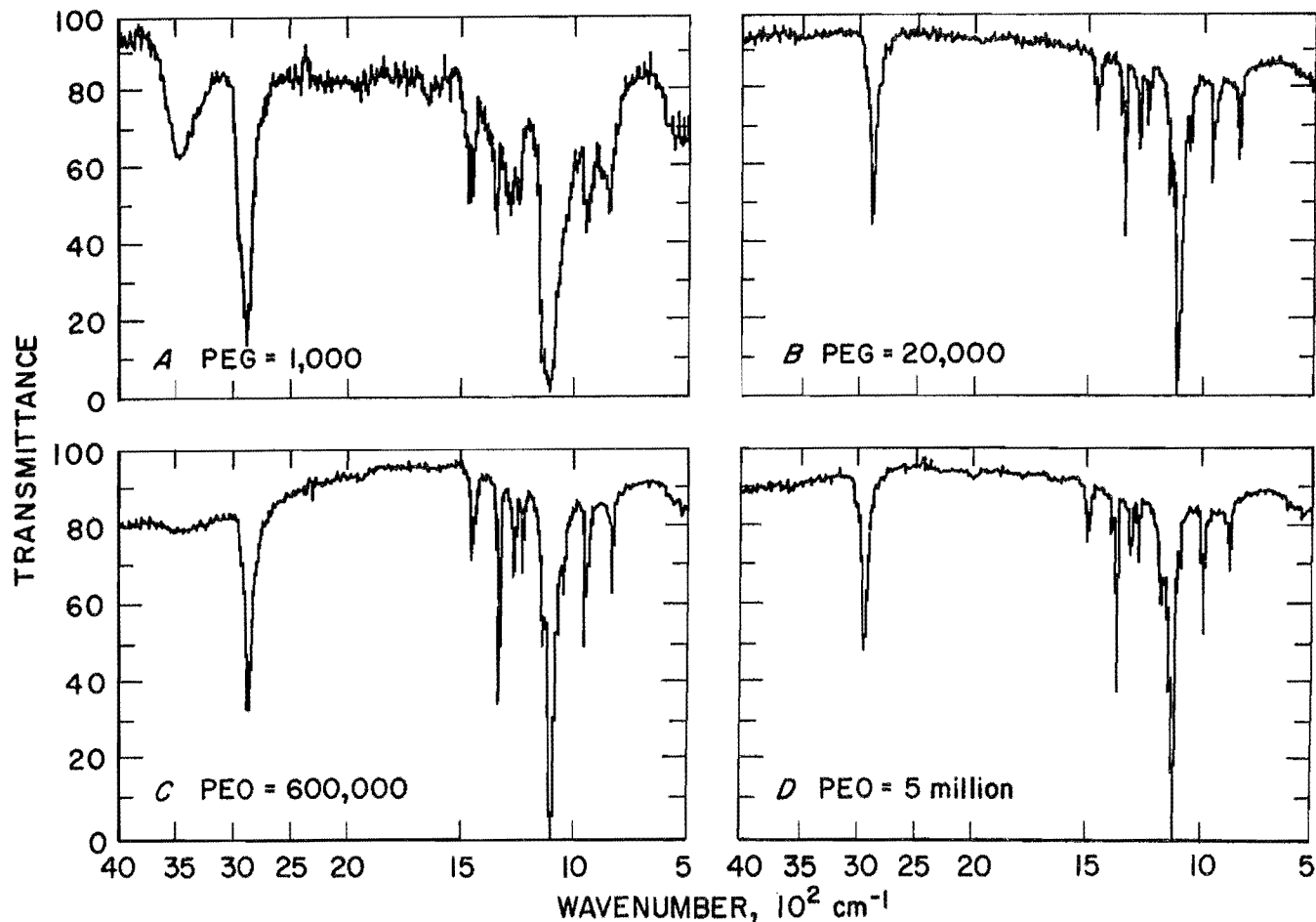


FIGURE 5.—Reference spectra of PEG and PEO polymers of different molecular weights.

Koleske (33). The description of these spectral bands in table 3 has been prepared from this work.

INFRARED ANALYSES OF THE POLYMER-TREATED MONTMORILLONITE SAMPLES

The ion-exchanged clays treated with the PEO polymer solution were scanned in the IR region from 4,000 to 300 cm^{-1} using methods discussed. The spectra of control samples were compared with those of polymer-treated samples in an effort to discern changes in the IR spectra resulting from interaction between montmorillonite and polymer.

Observed Changes in Hydroxyl and C-H Stretching Vibrations

The IR spectral region of 4,000 to 2,000 cm^{-1} has been previously described

(see tables 1 and 3) as the region in which the structural hydroxyl and interlayer-stretching vibrations of the montmorillonite and the C-H stretching vibrations of the polymer occur. In addition, it has been demonstrated that the presence of interlayer water is controlled largely by the ionic potential of the exchange ion, which is manifested in this region of the spectra. In figures 6 and 7, the 3,800- to 2,400- cm^{-1} region is depicted for both the control and PEO-treated samples of the monovalent and divalent exchanged montmorillonites, respectively.

From figures 6 and 7, as might be expected, it can be seen that the addition of PEO has absolutely no effect on the structural hydroxyl peak at 3,620 cm^{-1} . However, the intensity of the interlayer-water OH stretching vibrations at 3,400 and 3,250 cm^{-1} was reduced for those

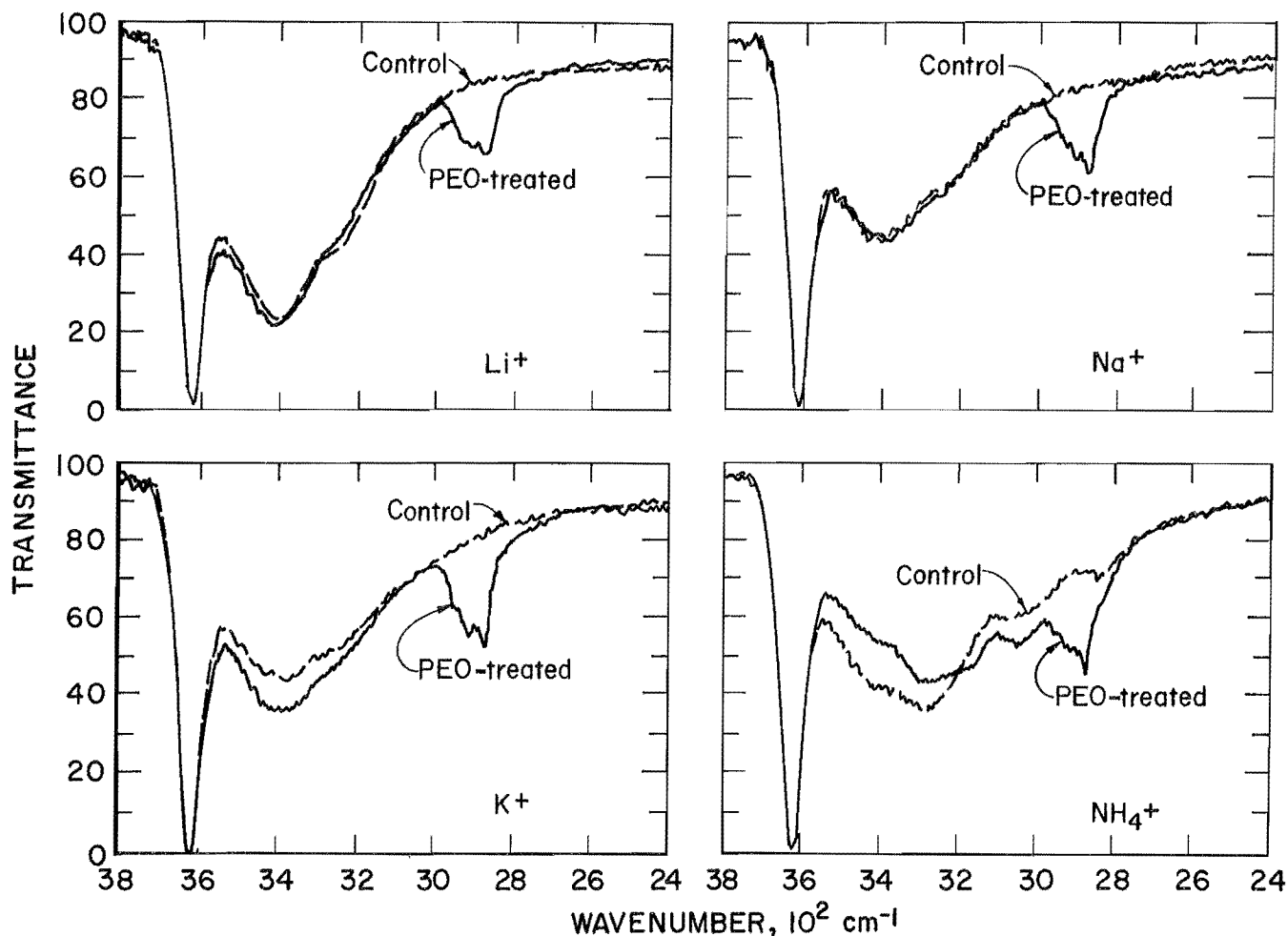


FIGURE 6.—Infrared spectra of monovalent-exchanged montmorillonite treated with PEO compared with control samples (3,800 to 2,400 cm^{-1}).

clays exchanged with the following cations: K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , and Sr^{2+} . This phenomenon is consistent with the desorption of interlayer-water due to polymer adsorption, previously described in the literature by Parfitt and Greenland (23) and Theng (17). That the Na^+ and Li^+ exchanged clays did not readily give up their interlayer hydration water upon adsorption of PEO is totally consistent with the poor dewaterability and strong gel-forming characteristics of these clays observed by Bureau of Mines researchers (24, 34).

Other manifestations of clay-polymer interactions can be identified in the 4,000- to 2,000- cm^{-1} region. For example, the C-H stretching vibration of PEO found at 2,880- cm^{-1} shifts to 2,870 cm^{-1} upon interaction with the surface of the clay. Rubio and Kitchener (35)

suggested that the $-\text{CH}_2\text{CH}_2-$ links of the PEO chain are sufficiently "hydrophobic" to lead to physical adsorption. Presumably, this interaction is responsible for the apparent shift of the 2,880- cm^{-1} peak. In addition, the 2,940- cm^{-1} peak denoting the antisymmetric stretch of CH_2 , which occurs as a weak- to medium-intensity shoulder in figure 7, becomes a much more well-defined peak at 2,910 cm^{-1} .

Farmer and Russell (36) reported that interlayer water coordinated to strongly polarizing cations such as Mg^{2+} and Cu^{2+} was more acidic and as a result formed stronger hydrogen bonds in water than might ordinarily be expected. They cited the broad intense peaks found in the region below 3,300 cm^{-1} as evidence of this behavior. The exchanged clays examined in the current investigation have

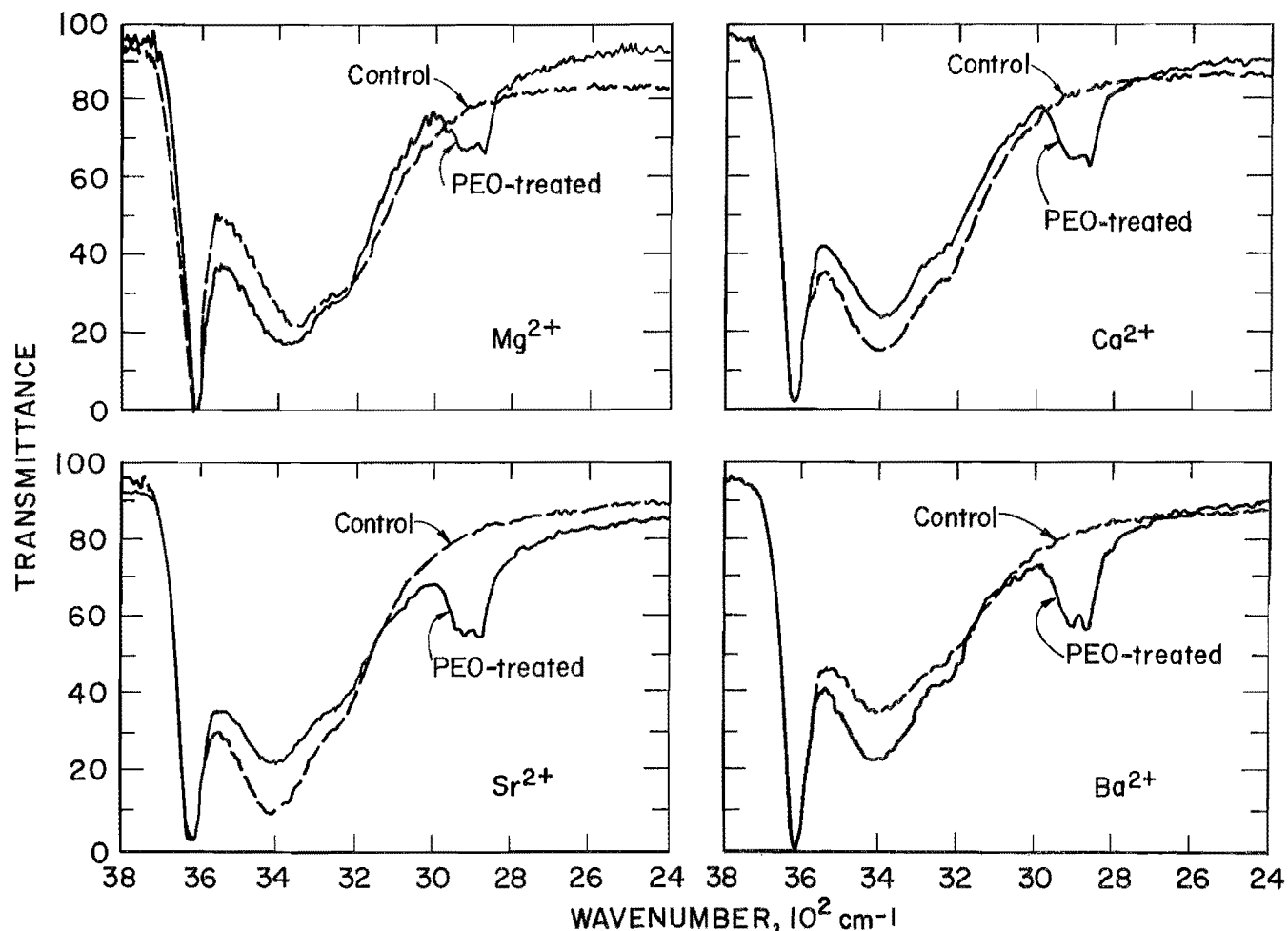


FIGURE 7.—Infrared spectra of divalent-exchanged montmorillonite treated with PEO compared with control samples (3,800 to 2,400 cm^{-1}).

broader, more intense bands in the 3,300- cm^{-1} region for those exchange ions having the higher values of ionic potential. (Refer to figures 6 and 7.) Later studies by Mortland and Raman (37) and Frenkel (38) have confirmed that the surface acidity of ion-exchanged montmorillonite follows the sequence $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} = \text{Li}^{+} > \text{Na}^{+} = \text{K}^{+}$, which is also consistent with the ionic potential for each of these cations.

Frenkel concluded that the surface Lewis acidity of the water coordinated to the clay exchange ion was controlled largely by the polarizing strength of the exchange ion (38). This is important because the ether group of PEO can be regarded as a weak Lewis base. The water bridge is a result of a bond between the

weakly acidic water coordinated to the exchange ion and the basic polymer. This conclusion has an extremely important impact upon the current investigation because it indicates that those clays having exchange ions of increasing ionic potential are much more likely to participate in water bridging.

Desorption of Interlayer Water Upon Treatment of Clay With PEO

For the montmorillonite-PEO complex, the major IR peaks for the 2,000- to 1,100- cm^{-1} region (see table 1 and 3) are the water bending vibration (1,630 cm^{-1}) and the CH_2 deformational bands (1,460 cm^{-1} , 1,340 cm^{-1} , and 1,280 cm^{-1}). This region of the spectrum is illustrated in

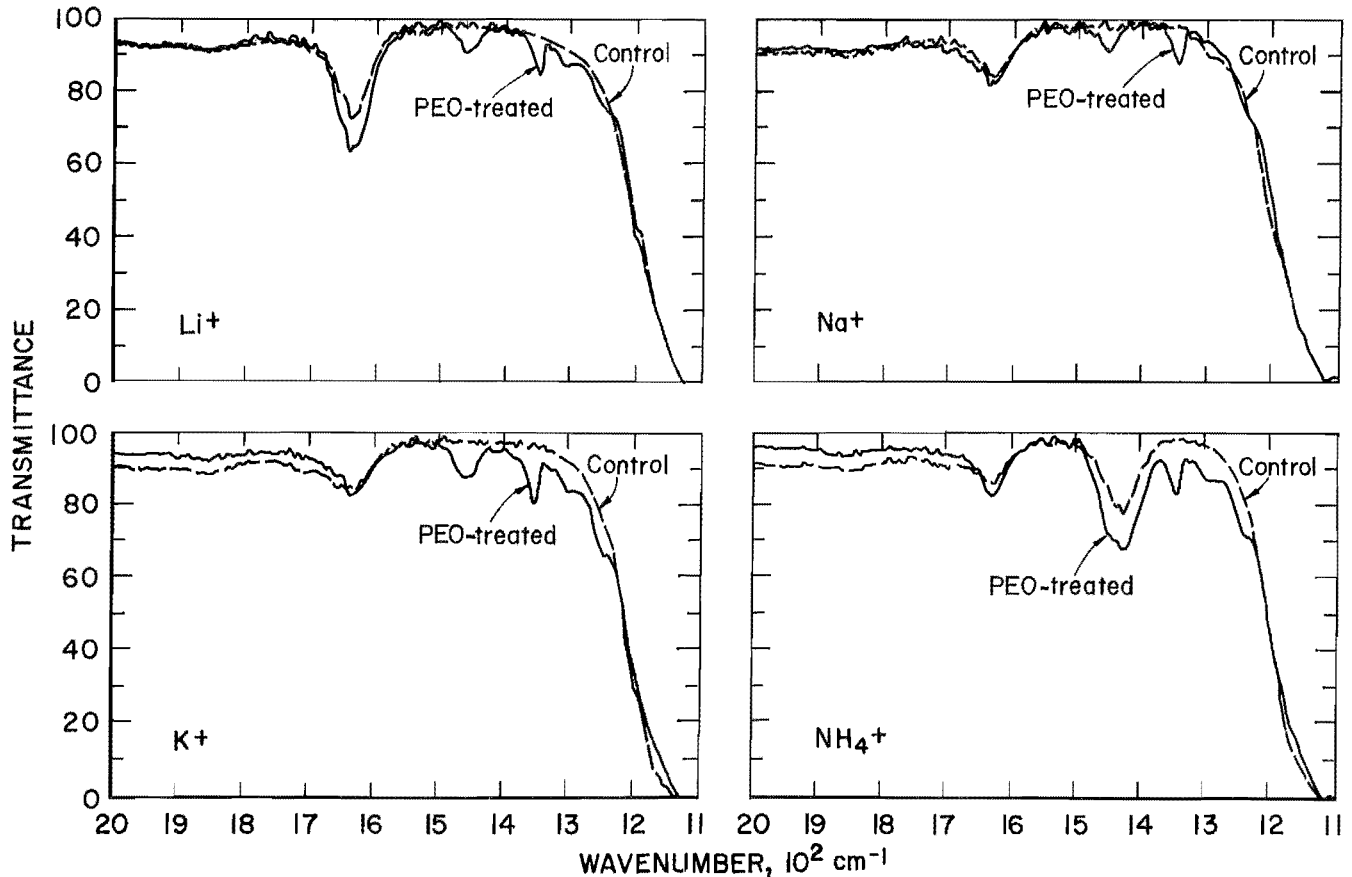


FIGURE 8.—Infrared spectra of monovalent-exchanged montmorillonite treated with PEO compared with control samples (2,000 to $1,100\text{ cm}^{-1}$).

figures 8 and 9 for the monovalent- and divalent-exchanged clays, respectively.

As shown in the discussion concerning figure 3B, the $1,630\text{-cm}^{-1}$ water bending vibration was related to the amount of hydration water present in the interlayer region of the clay. Little (39) has described this deformation band in great detail. Little demonstrated that upon heating, this band decreased rapidly as interlayer water was driven off. As in the case of the intense stretching vibrations of the $3,300\text{- to }3,600\text{-cm}^{-1}$ region, the adsorption of PEO led to the desorption of interlayer water as evidenced by the decrease in intensity of the $1,630\text{-cm}^{-1}$ peak. (See figures 8 and 9.)

Because the $1,630\text{-cm}^{-1}$ water band is relatively isolated from sources of spectral interference and background

noise, the quantitative analysis routine, SINGLE, can be utilized to verify the desorption of interlayer water as a result of PEO adsorption. The relative peak areas of the $1,630\text{-cm}^{-1}$ band were determined for the polymer-treated clays in the same manner as that used in table 2. The experimental values for the control and polymer treated samples have been tabulated in table 4.

Generally, the data of table 4 confirm the observation of polymer desorbed water. It must therefore be concluded that the adsorption of PEO onto montmorillonite involves the displacement of interlayer water by PEO. The variation in measured values for Na^+ and K^+ in table 4 represents experimental error inherent in the data if it is assumed that these exchanged clays experience little or no water loss as a result of

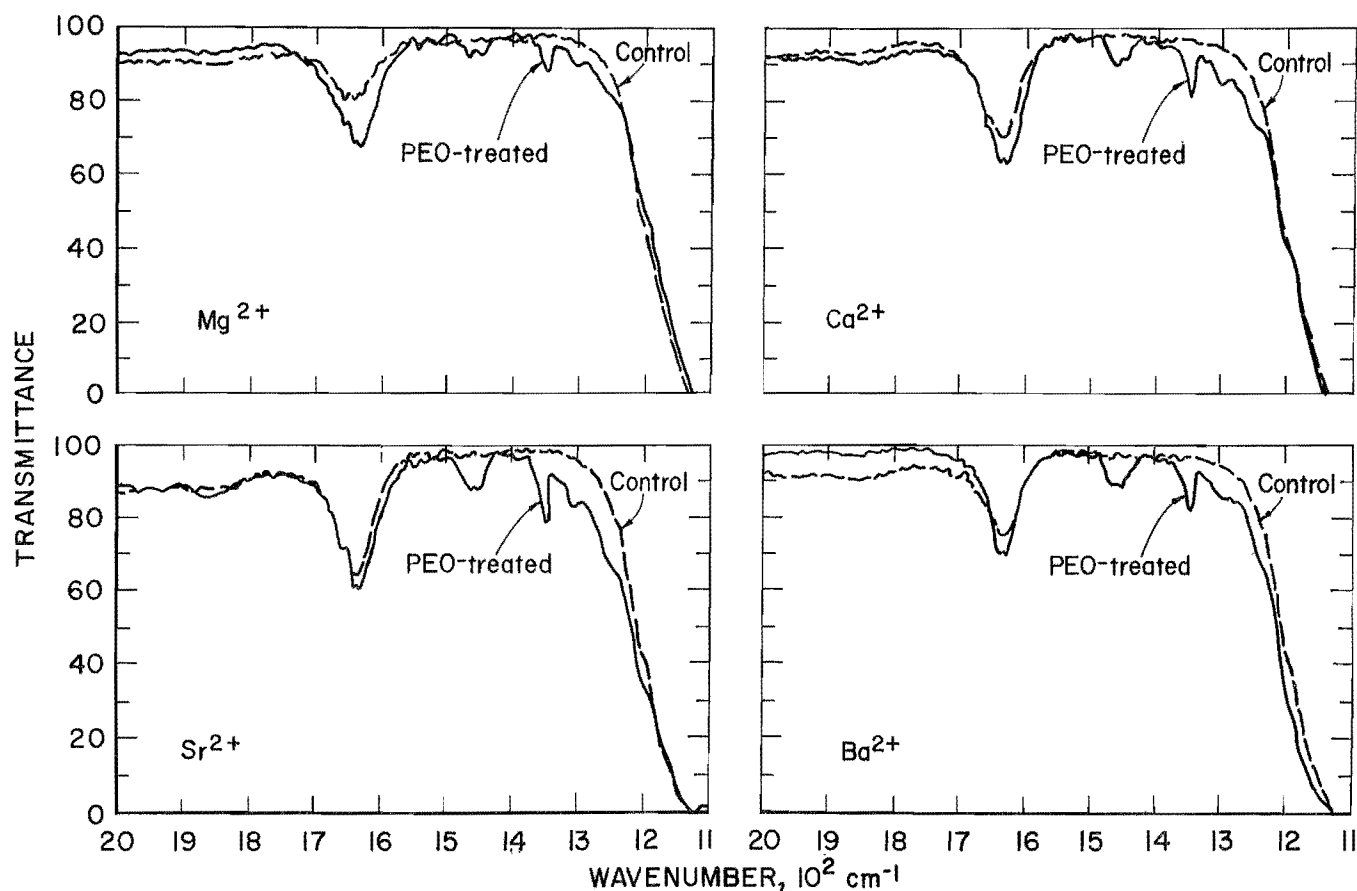


FIGURE 9.—Infrared spectra of divalent-exchanged montmorillonite treated with PEO compared with control samples (2,000 to 1,100 cm^{-1}).

TABLE 4. - SINGLE analyses of 1,630- cm^{-1} peak for eight ion-exchanged montmorillonite samples treated with PEO

Exchange Ion	Relative peak height		Relative peak area	
	Control	Treated	Control	Treated
Li ⁺	0.112	0.088	7.223	5.543
Na ⁺044	.047	2.692	3.417
NH ₄ ⁺055	.033	3.637	2.391
K ⁺043	.048	3.266	4.021
Mg ²⁺225	.056	17.390	4.426
Ca ²⁺143	.101	9.646	7.003
Ba ²⁺121	.073	7.135	5.166
Sr ²⁺137	.129	9.142	9.137

polymer treatment (as seems to be the case).

Evidence of Hydration-Shell Bridging

Another very interesting feature of the $1,630\text{-cm}^{-1}$ band was observed only for the magnesium-exchanged clay. Upon treatment of the clay with PEO, the $1,630\text{-cm}^{-1}$ vibration shifted to $1,641\text{ cm}^{-1}$ as a sharper, more well defined doublet (fig. 10). Serratosa described a similar phenomenon encountered during benzonitrile adsorption analyses upon magnesium-exchanged montmorillonite (22). In this work, the water bending vibration was observed to have shifted from $1,637$ to $1,648\text{ cm}^{-1}$. Serratosa felt that this indicated that the water molecules of the hydration layers were more involved in hydrogen bonding in the benzonitrile-treated sample than in the untreated control (21). This was taken to be evidence of hydration shell bridging, previously discussed.

In view of the high ionic potential of the magnesium ion, the explanation given by Serratosa seems very applicable to the current data. It is curious that the other ion-exchanged clays did not exhibit similar frequency shifts of the

$1,630\text{-cm}^{-1}$ peak. A possible explanation for this is that the polarizability of the magnesium ion is sufficiently strong to induce an observable peak shift, whereas for the other exchanged clays the exchange ion's influence is significantly reduced so as to make the shift unobservable. In any event, the perturbation of the $1,630\text{-cm}^{-1}$ peak is an indication of a disturbing influence acting through the hydration water of the ion. Presumably, this is a manifestation of the adsorbed polymer interacting with the exchange ion through a water bridge.

Surface Effects of Clay-Polymer Interaction

In the earlier discussions of the $2,880\text{-cm}^{-1}$ C-H stretching vibration, mention was made of the apparent shift of this peak to $2,870\text{ cm}^{-1}$ upon adsorption of the polymer to the surface of the clay. Similarly, the CH_2 deformational bending vibrations ($1,500$ to $1,200\text{ cm}^{-1}$) were found to have also shifted as a result of adsorption upon the clay surface. Figure 11 has been prepared from the spectrum of 5 million MW PEO given in figure 5 and the spectrum of

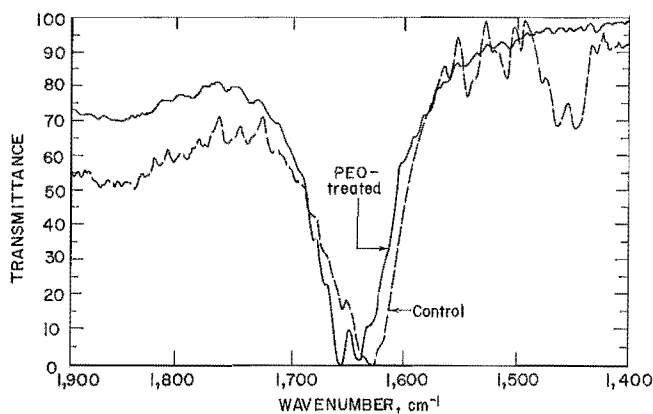


FIGURE 10.—Apparent shift in the $1,630\text{-cm}^{-1}$ hydroxyl bending vibration of magnesium-exchanged montmorillonite upon treatment with PEO ($1,900$ to $1,400\text{ cm}^{-1}$).

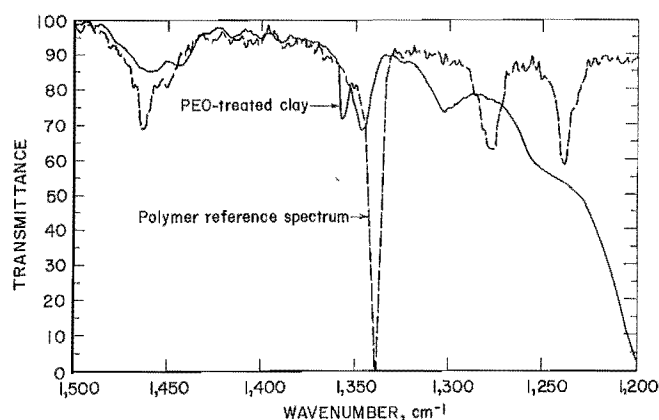


FIGURE 11.—Perturbation of PEO CH_2 bending vibrations upon adsorption of polymer onto calcium-exchanged clay ($1,500$ to $1,200\text{ cm}^{-1}$).

calcium montmorillonite treated with 5 million MW PEO shown in figure 9 for the 1,500- to 1,200- cm^{-1} region. Clearly, the adsorption of the polymer onto the clay has resulted in displacement of the CH_2 bending vibrations described in table 3. The shifting of the CH_2 bending vibrations was observed for all the exchanged clay samples and is presumably indicative of surface effects between the clay and polymer. These types of interactions have been described by Rubio and Kitchener (35).

Examination of 1,400- to 500- cm^{-1} Region

The final region of the infrared spectrum examined for the clay-polymer

system is 1,400 to 500 cm^{-1} . As shown in table 1, this region of the clay spectrum includes the bending vibrations of the octahedral and tetrahedral layers which compose the crystal lattice of the clay. This region is dominated by the intense Si-O stretching vibrational bands at 1,200 to 1,000 cm^{-1} and the Si-O-Al bending vibration at 520 cm^{-1} . Figures 12 and 13 are IR scans of this region for the control and polymer-treated samples of the monovalent and divalent clays, respectively. Generally, this region of the clay spectrum does not show any variability as a result of polymer adsorption. This is probably due to overlap of the clay Si-O bands at 1,200 to 1,000 cm^{-1} and the polymer C-O

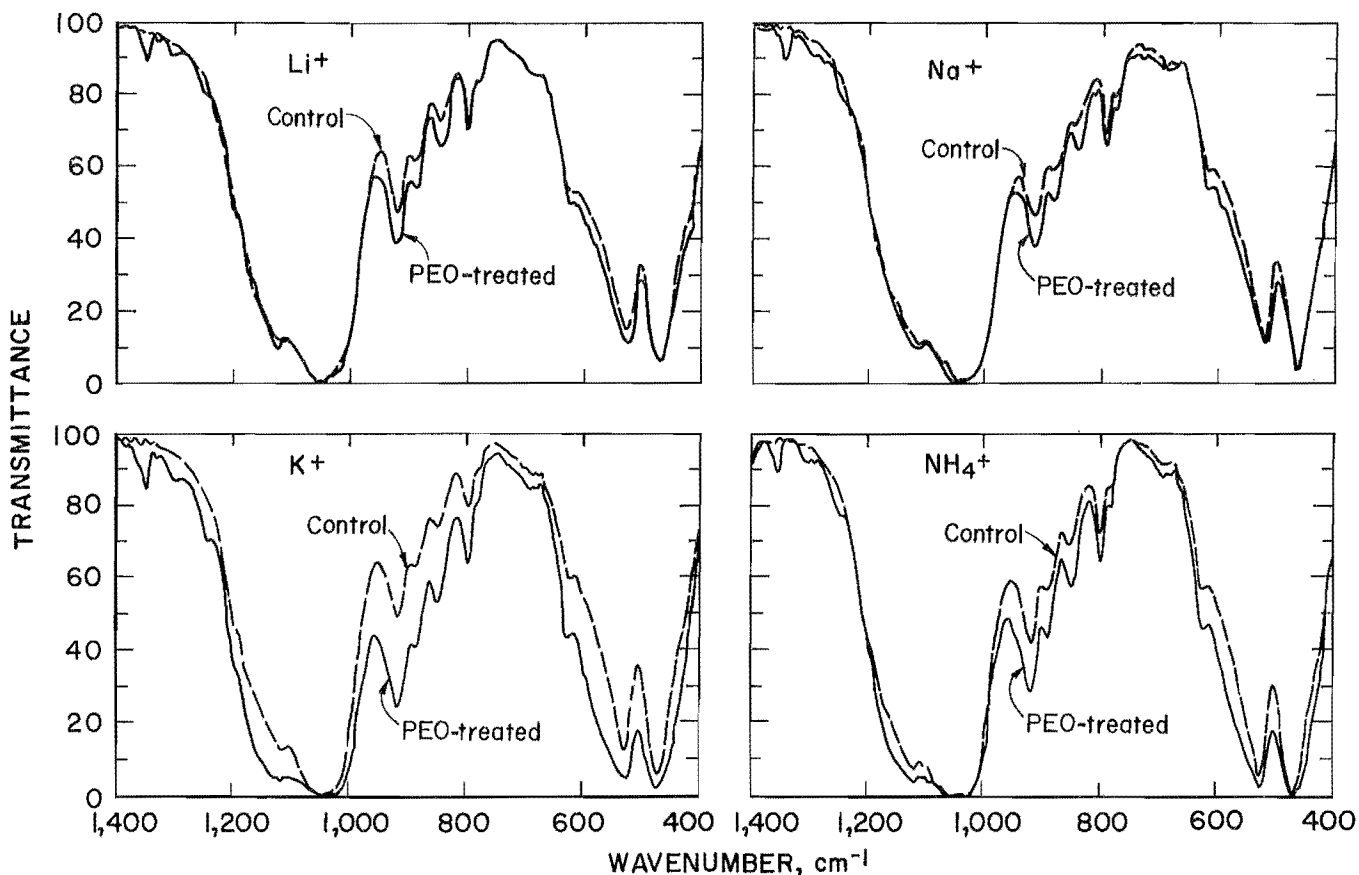


FIGURE 12.—Infrared spectra of monovalent-exchanged montmorillonite treated with PEO compared with control samples (1,400 to 400 cm^{-1}).

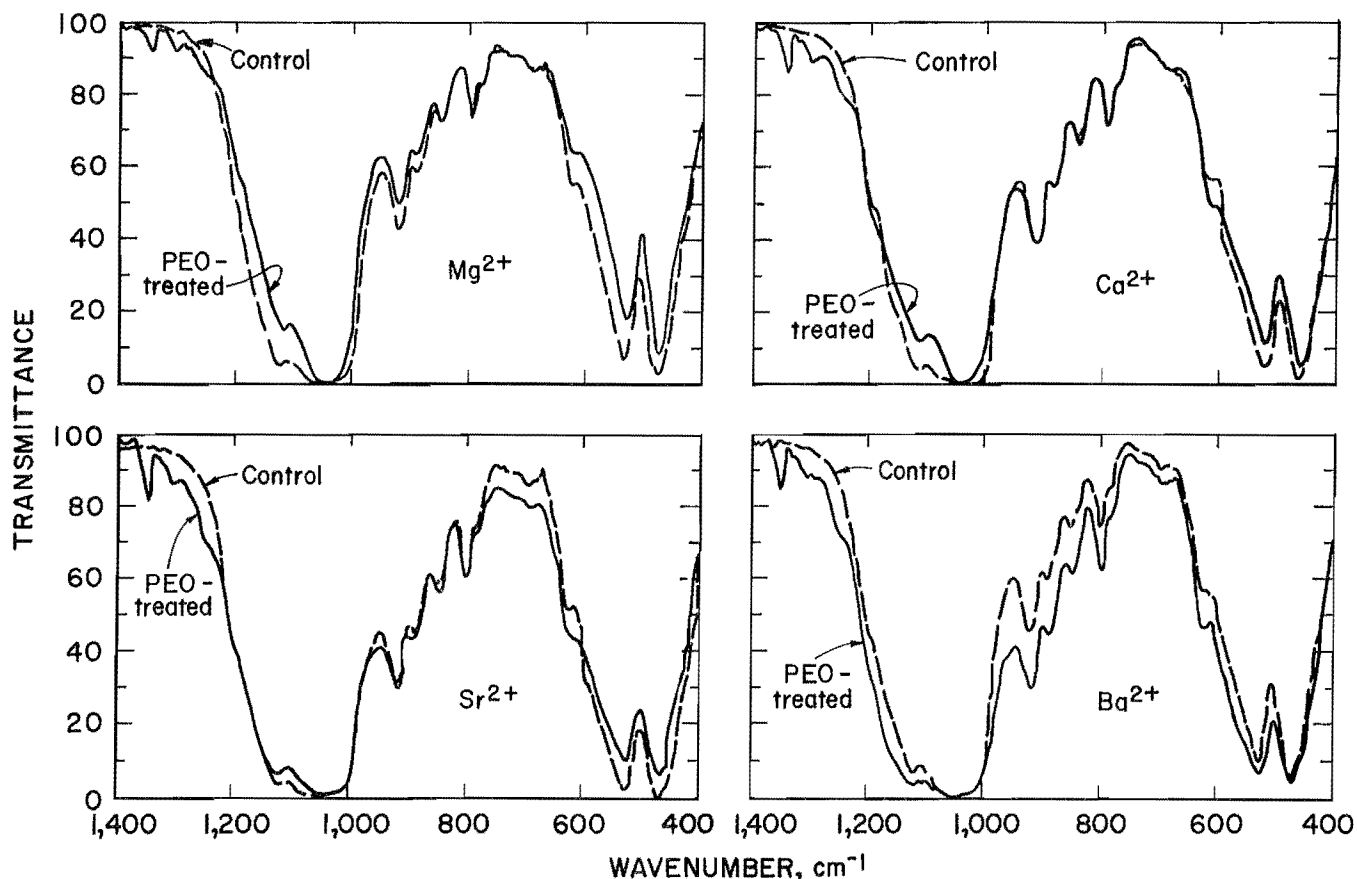


FIGURE 13.—Infrared spectra of divalent-exchanged montmorillonite treated with PEO compared with control samples (1,400 to 400 cm^{-1}).

stretching vibration at $1,100 \text{ cm}^{-1}$. The C-O stretching band corresponds to the ether linkage of the polymer and could not be observed because it was completely masked by the intense Si-O band. This is unfortunate in the sense that the ether

linkage is presumed to be the point of attachment between the clay and polymer in a water bridge. Any perturbation of this band upon adsorption of polymer, therefore, could not be observed.

CONCLUSIONS

Infrared spectroscopy indicates that the hydration water of the montmorillonite interlayer is controlled largely by the ionic potential of the exchange ion. The peak area and intensity of the $1,630\text{-cm}^{-1}$ water bending vibration are directly proportional to the ionic potential, which is evidence of the influence exerted upon the hydration water by the exchangeable cation.

Upon adsorption of polymer, hydration water is displaced as the polymer interacts with the clay through a water bridge consisting of the interlayer cation, the

hydration sheath, and the ether linkage of the polymer chain. A shift in the $1,630\text{-cm}^{-1}$ peak of the magnesium-exchanged montmorillonite water bending vibration is taken to be evidence of this type of clay-polymer interaction. Subsequent shifts in the C-H stretching and CH_2 bending vibrations of the polymer occur as a result of surface interactions between the clay and polymer. The C-O stretching vibration of the polymer chain could not be observed at $1,100 \text{ cm}^{-1}$ because of the masking effect of the intense Si-O band at 1,200 to $1,000 \text{ cm}^{-1}$.

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