

INFRARED SPECTROSCOPIC STUDY OF ADSORBED WATER ON REDUCED-CHARGE Na/Li-MONTMORILLONITES

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Abstract—Infrared (IR) spectra in the fundamental and near-IR regions were obtained for Na-saturated Wyoming montmorillonite and reduced-charge Na/Li-saturated Wyoming montmorillonites hydrated under water vapor at 50% RH and dehydrated under vacuum. For the Na-montmorillonite, changes in the intensities of the structural OH-bending modes, particularly that of the MgAlOH group, were observed as the clay was dehydrated. This result was interpreted as evidence that exchangeable Na ions lose solvation water and settle into the ditrigonal cavities on the clay surface as it becomes desiccated. For the Na/Li-montmorillonites, the structural OH-bending modes also decreased in IR intensity because of Li⁺ migration into the octahedral sheet. The fundamental IR spectra of D₂O adsorbed by the montmorillonites showed characteristic absorptions at 2685, 2510, 2400, and 1205 cm⁻¹ that decreased in intensity proportionally to the cation-exchange capacity. This result, along with corroborating data from X-ray powder diffractograms and from near-IR diffuse reflectance spectra of H₂O adsorbed by the clays, suggest that the exchangeable cations on Na-montmorillonite dissociated from the clay surface as it hydrated and played a significant role in organizing the structure of adsorbed water at low water contents.

Key Words—Cation-exchange capacity, Infrared spectroscopy, Montmorillonite, Reduced charge, Water adsorption.

INTRODUCTION

In a recent study of the swelling of montmorillonite, Low (1981) advanced the hypothesis that the exchangeable cations in aqueous suspensions of Na-montmorillonite are not dissociated significantly from the clay mineral surface. According to this hypothesis, the reduction in the chemical potential of water in the interlayers of Na-montmorillonite and the subsequent free swelling of the clay are not primarily the result of osmotic forces produced by swarms of dissociated, exchangeable Na cations. Instead, they are caused by an epitaxial structure induced in the interlayer water by the oxygen atoms of the clay surface. The induced water structure is assumed to have a lower potential energy than bulk liquid water, resulting in a lower chemical potential of the interlayer water and the initiation of free swelling. This view is contrary to the long-standing description of clay swelling in terms of diffuse double layer theory, which assumes that essentially all of the exchangeable cations dissociate from a Na-montmorillonite surface (van Olphen, 1977, Ch. 10).

One method by which the Low hypothesis can be evaluated experimentally is through the investigation of any changes that occur in the properties of Na-montmorillonite-water mixtures as the cation-exchange capacity (CEC) of the clay is varied systematically. The CEC of a montmorillonite can, in fact, be reduced in a

controlled manner through the Hofmann-Klemen technique (Hofmann and Klemen, 1950; Brindley and Ertem, 1971 and the references cited therein), in which a smectite mineral that initially contains some proportion of exchangeable Li ions is heated in air for 24 hr at 220°C. This treatment causes the Li ions to migrate into the octahedral sheet to satisfy deficits of positive charge resulting from ionic substitutions and thereby to lower the CEC of the clay mineral (Calvet and Prost, 1971; Brindley and Ertem, 1971).

Maes and Cremers (1978) studied Na⁺-Cs⁺ exchange in montmorillonite suspensions after the CEC of the clay was reduced through the Hofmann-Klemen technique. The principal result of their study, which included data obtained for a variety of different montmorillonites, was that the selectivity of the clay for Cs⁺ over Na⁺ decreased as the CEC decreased. The explanation of these data given by Maes and Cremers (1978, 1979) was that decreasing the surface charge density of the clay increased the tendency for the exchangeable cations to behave with respect to the clay surface as a diffuse ion swarm (i.e., as dissociated ions). Therefore, exchange selectivity differences decreased for cations of the same valence.

In the language of coordination chemistry (Sposito, 1981a), the results of Maes and Cremers (1978) would be attributed to a decreased tendency of the exchangeable cations to form inner-sphere complexes with the

clay surface as the CEC decreased. Because Cs^+ is not as hard a Lewis acid as Na^+ (Sposito, 1981b, Ch. 3), the principle of Hard and Soft Acids and Bases (HSAB) indicates that the clay surface acts as a relatively softer Lewis base than water in selecting Cs^+ over Na^+ (Sullivan, 1977). When the CEC is decreased, the anionic field strength of the clay surface decreases and the clay becomes an even softer Lewis base. This increase in softness, according to the HSAB principle, will decrease the extent of surface complex formation with Na^+ and Cs^+ , which are hard Lewis acids. Therefore, exchange selectivity differences will diminish.

On the other hand, if it is assumed, following Low (1981), that essentially all of the Na ions on montmorillonite are bound firmly all of the time in inner-sphere surface complexes, then decreasing the CEC should have no significant effect on Na^+ - Cs^+ exchange selectivity. At any CEC value, a negligible fraction of the exchangeable cations would be dissociated from the clay surface. Exchange selectivity would remain the same and would be determined by the difference in stability constants for the surface complexes containing Na^+ or Cs^+ . That this prediction was not substantiated experimentally for reduced-charge montmorillonites (Maes and Cremers, 1978) is evidence against Low's hypothesis.

Brindley and Ertem (1971) and Clementz *et al.* (1974) examined the hydration of Na-montmorillonite as the CEC of the clay was reduced by the Hofmann-Klemen technique. They found that free swelling of the clay in water was inhibited completely after the CEC had been reduced to about 68% of its initial value and that water vapor adsorption was diminished significantly. This behavior of the clay is consistent with the view that swelling is associated with the solvation properties of the exchangeable cations, but is contrary to Low's hypothesis.

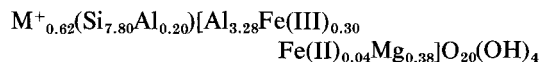
In the present paper, additional data are presented concerning the hydration of Na-montmorillonite as affected by a reduction in CEC. The infrared (IR) spectra of Na-montmorillonite and reduced-charge Na/Li-montmorillonite in both the fundamental and near-IR regions are used as a probe of the effects of exchangeable cations on the arrangement of water molecules on the clay surface at low water contents. Spectra of this kind, which have not been published before, are compared with the results of available IR studies of adsorbed H_2O and D_2O on Na-saturated smectites (Farmer and Russell, 1971; Prost, 1975) to help determine whether the oxygen surface plays the dominant role in organizing the structure of adsorbed water on Na-montmorillonite hypothesized by Low (1981).

EXPERIMENTAL

Preparation of clay films

Montmorillonite SWy-1, obtained from the Source Clays Repository of The Clay Minerals Society, was

used in this study. Chemical data for this montmorillonite, from Crook County, Wyoming, were reported independently by Weaver and Pollard (1973, p. 65) and by van Olphen and Fripiat (1979, p. 19). The data given by Weaver and Pollard (1973) lead to the unit-cell formula:



which is characteristic of Wyoming montmorillonites in showing ionic substitutions in both the tetrahedral and octahedral sheets. The data given by van Olphen and Fripiat (1979) pertain to an unpurified sample and, therefore, could not be used to calculate a structural formula.

The montmorillonite sample was purified and saturated with Na^+ according to the procedure described in detail by Sposito *et al.* (1981), except that HCl and NaCl were employed as reagents instead of HClO_4 and NaClO_4 . This difference has no effect on the results in the present study. A 1-g portion of the Na-saturated clay was converted to a Li-clay by mixing it with 25 ml of 1 M LiCl and centrifuging the slurry for 10 min at about 25,000 g. This procedure was repeated three times, after which the clay sample was divided, placed in two glass bottles containing 100 ml each of 1 M LiCl, and shaken on a rotary shaker for about 60 hr. Both the Na- and Li-montmorillonite samples were centrifuged, washed once with distilled water, and finally washed with isopropyl alcohol until a test with AgNO_3 showed no remaining chloride in the supernatant solution. (A preliminary check established that AgNO_3 was soluble in isopropyl alcohol.)

The salt-free, homoionic clays were mixed in isopropyl alcohol to produce Na/Li-montmorillonite with varying proportions of the two exchangeable cations. The sample masses were selected to result in a suspension containing about 5 kg clay/m³. The suspensions were shaken for 48 hr, then centrifuged and resuspended in distilled water to make a mixture again containing about 5 kg clay/m³. After being shaken vigorously for a few minutes, the suspension was placed dropwise onto three separate spots on a sheet of mylar film and left to dry under ambient conditions. Some properties of the dried clay films, determined after the IR experiments were completed, are listed in Table 1. The measured CEC of the Na-saturated film, 0.91 mole charge/kg clay, is in agreement with the CEC inferred from the structural formula based on the chemical composition data for Crook County, Wyoming, montmorillonite (Weaver and Pollard, 1973).

Infrared spectroscopy

Each clay film was mounted between two mica frames held together by machine screws. The film supported in this fashion then was introduced into a specially designed sample cell that was described in detail by Prost

Table 1. Selected properties of the montmorillonite films.

Clay film sample no.	Film density (kg/m ²)	Exchangeable cations (meq/100 g) ¹		
		Na	Li	CEC
1	0.0161	91	0	91
2	0.0138	63	10	73
3	0.0165	42	12	54

¹ Determined by flame emission spectrophotometry after cation displacement with 1 M CH₃COONH₄.

(1975). With this device, IR spectra (absorbance mode) in the wavenumber range 200 to 4000 cm⁻¹ were recorded on a Perkin-Elmer model 580 spectrophotometer, with the clay film either under a vacuum of about 0.01 torr or under a D₂O RH of about 50%. Several spectra of the clay films were taken under these conditions. The films were placed in a muffle furnace while still between the mica frames and were heated at 250°C for exactly 24 hr to cause a migration of exchangeable Li⁺, when present, into the octahedral sheet of the clay (Calvet and Prost, 1971). After a heated clay film had been cooled to room temperature, it was placed back in the spectrophotometer sample cell, evacuated briefly, and left under D₂O vapor at 50% RH for 24 hr in order to rehydrate fully. Preliminary experiments showed that longer periods of standing under D₂O did not change the peak positions in subsequent IR spectra of the clay. After the clay film had been rehydrated, it was exposed to alternating vacuum and D₂O vapor until there was no significant IR absorbance at 3400 cm⁻¹, indicating nearly complete replacement of residual adsorbed H₂O by D₂O. The clay film was exposed once again to vacuum and a spectrum was made. Following this, the film was exposed for exactly 10 min to D₂O vapor at 50% RH and another absorption spectrum was taken.

Diffuse reflectance spectra (absorbance mode) of the clay films under H₂O vapor at about 60% RH also were made in the wavelength range 1300 to 2500 nm on a Beckman visible-near-IR spectrophotometer equipped with an integrating sphere coated by BaSO₄. BaSO₄ was used as a reference for these spectra.

X-ray powder diffraction

X-ray powder diffractograms (CuK α radiation) of the clay films, under H₂O vapor at 50% RH and after saturation with ethylene glycol were taken on a Philips recording diffractometer equipped with a cell to control sample relative humidity.

RESULTS AND DISCUSSION

Structural OH-bending vibrations

Calvet and Prost (1971) described the changes in intensity and wavenumber expected for the stretching and bending vibrations of structural OH groups in Li-mont-

morillonite after the migration of Li⁺ into the octahedral sheet has taken place. For the Camp Berteau montmorillonite investigated by these authors, significant decreases in the intensity of the OH-stretching mode and changes in both the intensity and wavenumber of the OH-bending modes in Li-montmorillonite after heating at 220°C were observed. However, for Wyoming montmorillonite, the studies of Clementz *et al.* (1974) and Poinignon (1977) indicate that the OH-bending modes offer a more sensitive probe of Li⁺ migration into the octahedral sheet than does the OH-stretching mode.

The structural OH-bending mode in montmorillonite absorbs between 700 and 950 cm⁻¹ and shows a series of discrete peaks that indicates the cation composition in the octahedral sheet (Farmer, 1974, p. 349). The OH-bending mode of the Al₂OH group absorbs near 920 cm⁻¹; that of Fe(III)AlOH absorbs near 890 cm⁻¹; that of MgAlOH absorbs near 840 cm⁻¹; and that of Fe(II)Fe(II)OH absorbs near 800 cm⁻¹. Because quartz is present in the Crook County, Wyoming, montmorillonite and contributes a strong band at 800 cm⁻¹ (van Olphen and Fripiat, 1979, p. 308), the last-mentioned OH-bending peak could not be investigated in the present study. Calvet and Prost (1971) observed a decrease in intensity of the 920 cm⁻¹ peak and an upward shift in its wavenumber to 935 cm⁻¹ in a Li-montmorillonite heated at 220°C for 24 hr. The peaks at 890 and 845 cm⁻¹ shifted downward in wavenumber to 855 and 810 cm⁻¹, respectively. These same shifts in wavenumber were verified for Li-saturated Wyoming montmorillonite by Clementz *et al.* (1974) and Poinignon (1977).

The reference montmorillonite in the present study is a Na-montmorillonite from Wyoming heated 24 hr at 250°C. The unsmoothed IR spectra (absorbance mode) of the structural OH-bending vibrations for this clay, both under vacuum and in the presence of D₂O vapor at 50% RH (Figure 1A), show that hydration of the clay tends to increase the intensities of the peaks near 918, 885, and 851 cm⁻¹ in the dehydrated clay spectrum. The cause of this intensity change is believed to be the movement of exchangeable Na⁺ out of the ditrigonal cavities in the silicate surface as these cations become solvated by D₂O molecules. When the clay mineral is under vacuum, the interlayer region collapses, indicating that the exchangeable Na⁺ are desolvated and settle partly into the ditrigonal cavities (Mooney *et al.*, 1952). Under this condition, the electric field of Na⁺ exerts a repulsive force on the proton in the structural OH group nearest the bottom of the ditrigonal cavity, and the bending mode of this OH group is expected to show less IR absorbance than it does when Na⁺ is not present in the ditrigonal cavity (cf. Calvet and Prost, 1971, Fig. 3). Accordingly, the hydration of the clay, which solvates an exchangeable Na⁺ and displaces it from the ditrigonal cavity, should produce an increase in the IR absorbance of the bending mode of an OH group formerly

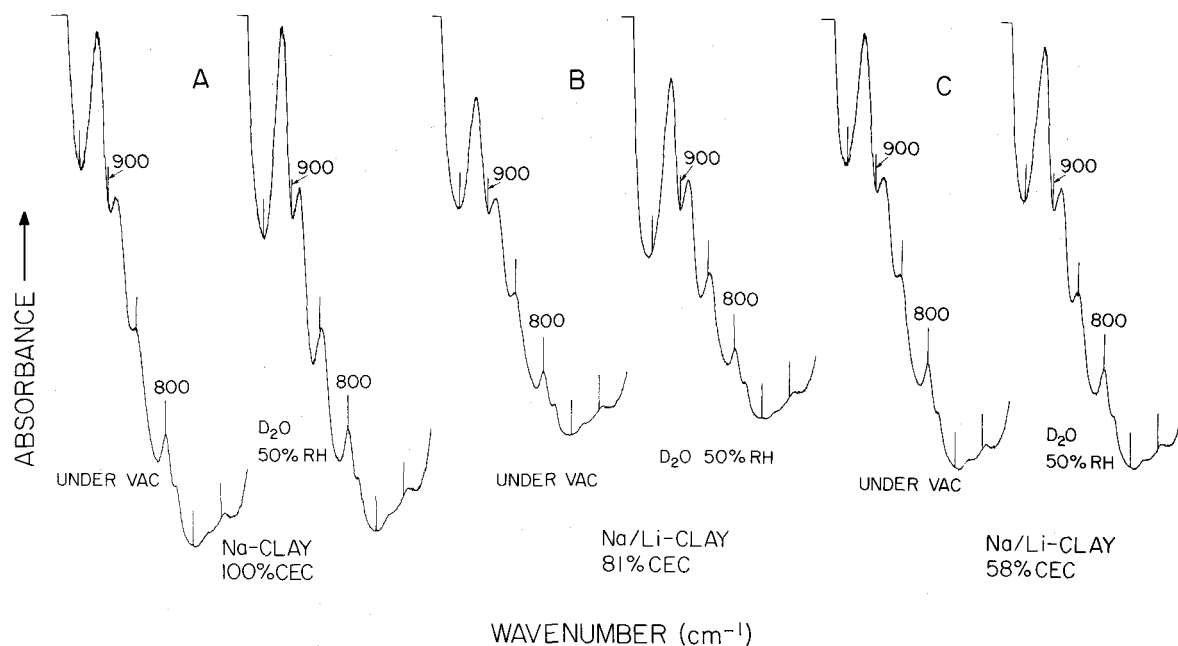


Figure 1. Unsmoothed infrared spectra of structural OH-bending vibrations as influenced by D_2O adsorption: (A) Na-montmorillonite, (B) 81% CEC Na/Li-montmorillonite, (C) 58% CEC Na/Li-montmorillonite. Instrumental settings for the spectra were: absorbance $\times 1$; wavenumber $\times 1$; noise attenuation, 2A; beam at normal incidence.

perturbed by an Na^+ . The fact that the shift in intensity is the most pronounced for the OH-bending mode of $MgAlOH$ suggests that, as the clay is dehydrated, exchangeable Na^+ settle preferentially into ditrigonal cavities over sites of ionic substitution in the octahedral sheet.

Figures 1B and 1C show the IR spectra of the structural OH-bending vibrations for reduced-charge Na/Li-montmorillonites under vacuum and under D_2O vapor at 50% RH. The most important feature seen in these spectra as the CEC decreases is the diminishing intensity of the OH-bending peak for $MgAlOH$ in the hydrated clay. A pronounced decrease in the intensity of this mode, relative to the case of hydrated Na-montmorillonite, is expected when Li^+ has migrated into the clay mineral structure (Calvet and Prost, 1971).

The data in Table 1 show that some of the Li^+ ions that were on the clay surface before heating remain exchangeable after heating (column 4). The fact that these exchangeable Li^+ ions always represented about 12% of the original CEC suggests that they are associated principally with sites of charge deficit in the tetrahedral sheet. The corresponding Al^{3+} substitution required would be about 0.08 ions per unit cell, well within the possible range of 0.00 to 0.20 indicated by the structural formula given above. Lithium ions satisfying negative charge originating in the tetrahedral sheet are thought to remain largely exchangeable after heating at $220^\circ C$ (Hofmann and Klemen, 1950; Brindley and Ertem, 1971; Maes and Cremers, 1978). Some of the remaining ex-

changeable Li^+ indicated in Table 1, of course, may be adsorbed on the broken edges of clay platelets, where migration into the octahedral sheet is less probable (Calvet and Prost, 1971).

Adsorbed D_2O spectra

Figure 2 shows the 1200 to 4000 cm^{-1} spectra of the Na- and Na/Li-montmorillonites hydrated under D_2O vapor at 50% RH. The distinguishing features of these IR spectra are the structural OH peak at 3625 cm^{-1} and the D_2O absorptions at 2685 , 2510 , 2400 , and 1205 cm^{-1} . The wavenumbers of these five absorptions do not change as the CEC of the clay mineral decreases. However, the intensities of the D_2O absorptions do change significantly.

The peaks at 2685 , 2510 , and 1205 cm^{-1} and the shoulder at 2400 cm^{-1} in the IR spectrum of the Na-montmorillonite in Figure 2 correspond very well with the peaks at 2690 and 2525 cm^{-1} and the shoulder at 2410 cm^{-1} reported by Farmer and Russell (1971) for D_2O adsorbed by Na-montmorillonite. They also correspond well with the peaks at 2690 , 2515 , and 1205 cm^{-1} and the shoulder at 2400 cm^{-1} reported by Prost (1975, Figure 33A) for D_2O adsorbed by Na-hectorite. Both clays were hydrated under 50% RH. The peaks at 2690 and 2525 – 2515 cm^{-1} have been assigned, respectively, to the stretching modes of weakly and strongly hydrogen-bonded OD groups in D_2O molecules that solvate the exchangeable cations (Farmer, 1978). The peak at 1205 cm^{-1} can be assigned to the bending mode of ad-

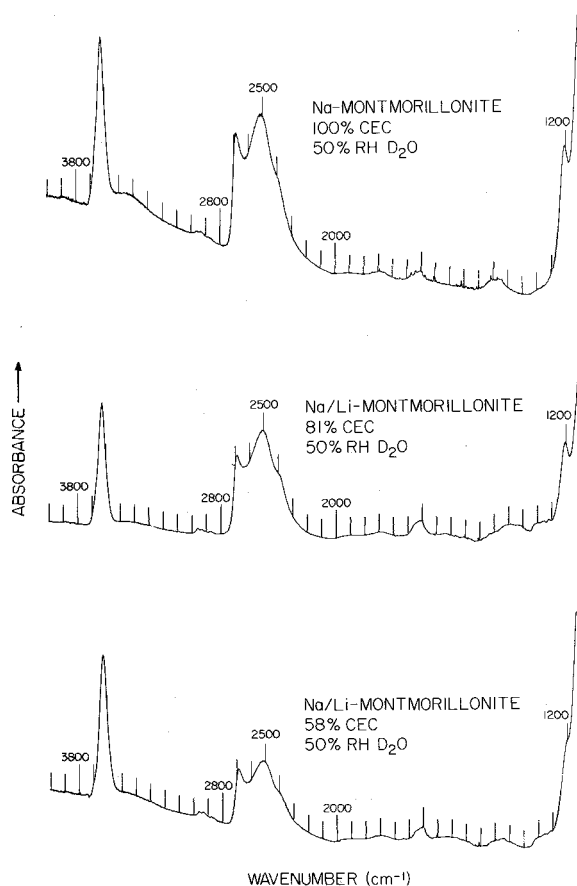


Figure 2. Unsmoothed infrared spectra of hydrated Na- and Na/Li-montmorillonites in the wavenumber range 4000 to 1200 cm^{-1} . Each sample was exposed to D_2O vapor at 50% RH exactly 10 min before the spectrum was made. Instrumental settings the same as in Figure 1.

sorbed D_2O , with the shoulder at 2410–2400 cm^{-1} being its first overtone.

It is evident in Figure 2 that the general line shape of the D_2O absorptions does not change as the CEC decreases. Because D_2O adsorbed on Li-hectorite gives peaks at 2690, 2520, 2400, and 1207 cm^{-1} (Prost, 1975, Figure 36A), no effect of exchangeable Li^+ on the wavenumbers of the peaks in Figure 2 is expected. The principal effect of reducing the CEC appears to be a concomitant reduction in the integrated intensities of the D_2O absorptions, although caution is required in making this interpretation directly from Figure 2 because the mass densities of the montmorillonite films were not always equal (Table 1). A more quantitative comparison can be made by computing the corrected absorbance ratio, $A'd_0/A_0d'$, where A is the integrated absorbance between 2000 and 2800 cm^{-1} , d is the clay film density, 0 refers to the Na-montmorillonite film, and $'$ refers to a Na/Li-montmorillonite film. The value of A for each spectrum was determined gravimetrically after a baseline had been estimated by drawing a smooth

Table 2. Relative integrated absorbance of D_2O on the clay films compared with the relative cation-exchange capacity.

Clay film sample no.	Relative integrated absorbance ¹	Relative CEC
1	1.00	1.00
2	0.86	0.81
3	0.50	0.58

¹ Estimated precision of $\pm 15\%$ based on replicate measurements made on different films, 2000 to 2800 cm^{-1} region.

curve connecting the absorbance at 2000 cm^{-1} to that at 2800 cm^{-1} , with the slopes of the curve at the connecting points matching those of the spectral profile. The corrected absorbance ratio is compared to the CEC ratio of the clays in Table 2. Within the estimated precision of the A/d measurement ($\pm 15\%$), and the extent that A/d is proportional to the water content of the clay film, it can be concluded from Table 2 that reducing the CEC reduces water content proportionately. This same effect was observed by Calvet and Prost (1971, Fig. 9) for Li-saturated Camp Berteau montmorillonite.

The effect of reduced CEC and water content on the basal plane spacing of the montmorillonites is illustrated in Figure 3. The Na-montmorillonite hydrated at 50% RH shows a diffractogram peak centered at 12.1 Å, which corresponds to an interlayer spacing large enough to accommodate one monolayer of adsorbed water, i.e., the spacing expected for Na-montmorillonite at 50% RH (Mooney *et al.*, 1952). On the other hand, the 58% CEC Na/Li-montmorillonite shows a more asymmetric diffractogram peak at 11.3 Å, indicating that the clay contains some collapsed interlayers even under 50% RH. This result is in agreement with the data of Brindley and Ertem (1971), who found that heated Na/Li-Wyoming montmorillonite ceased to expand fully in water after the CEC was reduced from 0.9 mole charge/kg to below about 0.6 mole charge/kg. However, the same clay that did not expand fully in water did expand to give a basal spacing of 17.1 Å in ethylene glycol. This result also was confirmed in the present study, where it was found that both of the montmorillonites described in Figure 3 gave basal spacings of 17.2 Å in ethylene glycol with sharp, symmetric diffractogram peaks. If the 11.3-Å basal spacing observed in Figure 3 for the Na/Li-montmorillonite under water vapor reflects a random mixture of collapsed (9.6-Å) and expanded (12.1-Å) interlayers, then the fraction of collapsed interlayers can be estimated to be about 30%. This result, in turn, suggests that the water content of the 58% CEC Na/Li-montmorillonite should be about 70% of that of the Na-montmorillonite hydrated under the same conditions, if the expanded interlayers in the former clay retained normal solvation properties. The data in the third row of Table 2 indicate that the water content drops to about 50% of the maximum instead of 70%.

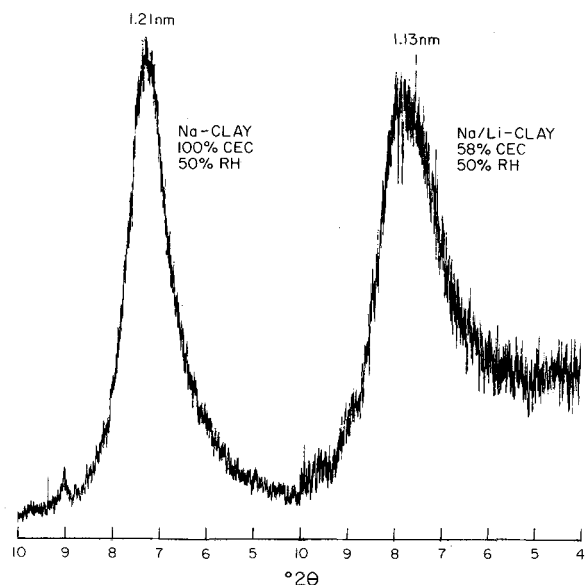


Figure 3. Unsmoothed X-ray powder diffractograms for Na-montmorillonite and 58% CEC Na/Li-montmorillonite under H_2O vapor at 50% RH (CuK α radiation) (1 nm = 10 Å).

Near-infrared spectra

The near-IR diffuse reflectance spectra of the Na-montmorillonite film under H_2O vapor at 65% RH and of the 58% CEC Na/Li-Montmorillonite film under H_2O vapor at 56% RH are shown in Figure 4. The principal

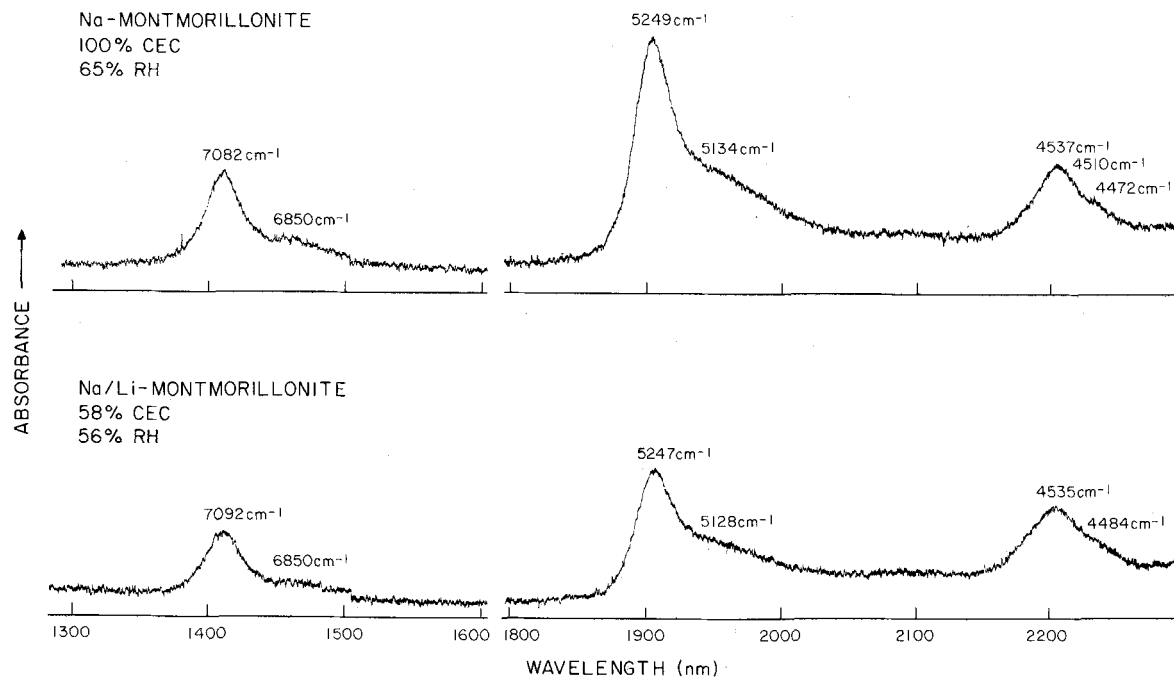


Figure 4. Unsmoothed near-IR diffuse reflectance spectra of Na-montmorillonite and 58% CEC Na/Li-montmorillonite under H_2O vapor at about 60% RH. Instrumental settings for the spectra were: period, 4; scan rate, 0.25 nm s $^{-1}$; 20 nm nm $^{-1}$; absorbance $\times 1$.

Table 3. Principal absorptions and their assignments in the near-IR spectra of the montmorillonite films.

Wavelength ¹ (nm)	Wave number ¹ (cm $^{-1}$)	Band assignment ²
2232 (sh) ³	4480	$\nu_{OH}^* + \delta_{AlMgOH}^* = (3625 + 851) \text{ cm}^{-1}$
2217 (sh)	4510	$\nu_{OH}^* + \delta_{AlFeOH}^* = (3625 + 885) \text{ cm}^{-1}$
2205	4535	$\nu_{OH}^* + \delta_{Al_2OH}^* = (3625 + 918) \text{ cm}^{-1}$
1949 (sh)	5130	$\nu_{OH} + \delta_{H_2O}$
1905	5250	$\nu_{OH} + \delta_{H_2O}$
1460 (sh)	6850	$2\nu_{OH}$
1410	7090	$2\nu_{OH}$

¹ Rounded values which reflect experimental precision.

² Asterisk indicates a clay structural hydroxyl group; band assignments for adsorbed water are based on Buijs and Choppin (1963).

³ sh = shoulder feature.

features of the near-IR spectrum of Na-montmorillonite, which has not been published heretofore, are summarized along with band assignments in Table 3. The assignments of the peak and shoulder features near 2205 nm are consistent with near-IR spectra and band assignments made by Prost (1982) for Na-hectorite and by Cariati *et al.* (1981) for Ca-montmorillonite, although the assignment of a band at 2354 nm (4248 cm $^{-1}$) to $\nu_{OH} + \delta_{AlMgOH}$ by the latter authors appears to be impossible numerically. As noted by Prost (1982), the peaks near 5250 and 7090 cm $^{-1}$ in Figure 4 are believed to correspond to combinations of the peaks at 2685 and 1205 cm $^{-1}$ in Figure 2 (e.g., $(2685 + 1205) \times 1.36 =$

5290 cm^{-1}). Similarly, the shoulder features near 5130 and 6850 cm^{-1} correspond to combinations of the peaks at 2510 and 1205 cm^{-1} in Figure 2. The relative prominence of the peaks near 5250 and 7090 cm^{-1} is the result of the fact that the molar absorptivity of strongly hydrogen-bonded OH groups in water is nearly three orders of magnitude smaller in the near-IR region than it is in the fundamental region (Luck, 1974, Ch. III.3). Thus, the absorptions of weakly hydrogen-bonded OH groups are relatively enhanced in the near-IR region.

A comparison of the two IR spectra in Figure 4 shows that the wavenumbers of the principal absorptions do not shift as the CEC of the montmorillonite is reduced. The only significant change appears in the intensities of the absorptions assigned to adsorbed water molecules. Because these water molecules are solvating the exchangeable cations, their IR spectra should decrease in intensity as the CEC is reduced, just as was observed for the spectra of adsorbed D_2O in the fundamental region. The close similarity in overall line shape between the spectra in Figure 4 suggests also that the spatial arrangement of the adsorbed water molecules is not altered significantly by a reduction in CEC.

CONCLUSIONS

The spectra in Figure 1A suggest that, as the relative humidity of water adsorbed by Na-montmorillonite increases from near zero to about 50%, the exchangeable cations move out of the ditrigonal cavities in the clay surface to positions in the interlayer space where they are solvated by water molecules. This displacement of the exchangeable cations must be regarded as an initial step in the process of dissociation away from the clay surface. Although it cannot be stated that complete dissociation of the Na ions must follow this initial step as the water content of the clay increases, it can be concluded that solvation of the Na ions occurs readily at relatively low water contents. The concept that Na ions are fixed permanently in the ditrigonal cavities of the clay surface in aqueous suspensions appears to be untenable.

In addition, both the quantity of adsorbed water and its structural characteristics appear to be related directly to the presence of exchangeable Na ions. The similarity of the fundamental and near-IR spectra of adsorbed water on montmorillonites of varying charge points clearly to the major role the exchangeable cations play in organizing the water structure. At monolayer surface coverages or less, and on the time scale over which IR spectroscopy can probe a molecular environment, it appears that adsorbed water on Na-montmorillonite is primarily solvation water of the exchangeable cations, with the silicate surface playing a lesser role in determining the arrangements of the water molecules.

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Резюме—Инфракрасные спектры (ИК) были получены в основной и ближней инфракрасной области для Na-насыщенного Уаеминского монтмориллонита и Na/Li-насыщенных Уаеминских монтмориллонитов с уменьшенным зарядом, уводенных в присутствии водяного пара о 50% относительной влажности и отводенных в состоянии вакуума. Изменения интенсивностей изгибающих колебаний структурных групп OH, особенно группы MgAlOH, наблюдались для Na-монтмориллонита после дегидратации глины. Этот результат рассматривался как доказательство того, что обменные ионы Na теряют сольватационную воду и осаждаются в двухтригональных кавитациях на поверхности глины, когда она осушается. Для Na/Li-монтмориллонитов, интенсивность изгибающих колебаний структурных OH также уменьшалась из-за миграции Li⁺ в октаэдрический слой. Основные ИК спектры D₂O, адсорбированный монтмориллонитом, показали характеристическую абсорбцию при 2685, 2510, 2400, и 1205 см⁻¹, интенсивность которой уменьшалась пропорционально катионообменной способности. Этот результат, вместе с подтверждающими данными рентгеновских порошковых диффрактограмм и данными спектров (диффузионного отражения ближней ИК области) воды адсорбированной глинами указывают на то, что обменные катионы из Na-монтмориллонита были диссоциированы с поверхности глины в то время, как она уводилась. Эти катионы играли значительную роль в организации структуры адсорбированной воды при низких ее содержаниях. [E.C.]

Resümee—Infrarot (IR)-Spektrien im Bereich der Grundschnwingungen und im nahen Infrarot wurden für Na-gesättigten Montmorillonit von Wyoming und für Na/Li-gesättigte Montmorillonite von Wyoming mit reduzierter Ladung, die bei einem Wasserdampfdruck von 50% relativer Feuchtigkeit hydratisiert und im Vakuum dehydratisiert wurden, gefahren. Bei dem Na-Montmorillonit wurden Veränderungen bei den Intensitäten der strukturellen OH-Knickmoden, vor allem der MgAlOH-Gruppe, beobachtet, wenn der Ton dehydratisiert wurde. Dieses Ergebnis wurde als Beweis dafür interpretiert, daß austauschbare Na-Ionen ihr Solvatationswasser verlieren und sich in die ditrigonalen Hohlräume auf der Tonoberfläche anlagern, wenn sie getrocknet wird. Bei den Na/Li-Montmorilloniten nahmen die strukturellen OH-Knickmoden bei der IR-Intensität ebenfalls ab, da das Li⁺ in die Oktaederschicht wandert. Die Spektren im Bereich der Grundschnwingungen im IR von an den Montmorillonit adsorbiertem D₂O zeigen charakteristische Adsorptionsbanden bei 2685, 2510, 2400, und 1205 cm⁻¹, deren Intensitäten proportional mit der Kationenaustauschkapazität abnehmen. Dieses Ergebnis zusammen mit den Ergebnissen aus den Röntgenpulverdiffraktogrammen und den Ergebnissen aus den diffusen Reflexionsspektren im nahen IR von an Tonen adsorbiertem H₂O deuten darauf hin, daß sich die austauschbaren Kationen am Na-Montmorillonit von der Tonoberfläche dissoziieren, wenn diese hydratisiert wird, und somit eine wichtige Rolle dabei spielen, welche Struktur des adsorbierten Wassers sich bei niedrigen H₂O-Gehalten bildet. [U.W.]

Résumé—La montmorillonite-Na du Wyoming et les montmorillonites-Na/Li de charge réduite ont été étudiées par spectroscopie infrarouge (IR) et proche infrarouge (PIR) à des teneurs en eau correspondant à des pressions relatives de vapeur d'eau de 0 et 50%. On observe pour la montmorillonite-Na des modifications dans les intensités des modes de vibration de déformation des OH de structure en particulier des groupes OH liés au couple Mg-Al lorsqu'on déshydrate l'argile. On interprète ce résultat comme la preuve que les ions Na⁺ échangeables perdent leur eau d'hydratation et se logent dans les cavités ditrigonales à la surface de l'argile lorsqu'on déshydrate celle-ci. L'intensité des bandes de déformation des groupes OH diminue aussi dans le cas des montmorillonites-Na/Li parce que les ions Li⁺ migrent dans les cavités octaédriques libres. Le spectre infrarouge de D₂O adsorbée sur les montmorillonites est formé des bandes à 2685, 2510, 2400, et 1205 cm⁻¹ dont l'intensité diminue avec la capacité d'échange. Ce résultat, conforté par les mesures faites par diffraction des RX et par les spectres de réflexion diffuse dans le domaine proche infrarouge de l'eau adsorbée par les argiles, indique que les cations échangeables de la montmorillonite-Na sont dissociés de la surface de l'argile lorsqu'elle s'hydrate et qu'ils jouent un rôle déterminant dans l'organisation de l'eau adsorbée des systèmes peu hydratés.