

NOTES

I.R. evidence for migration of protons in H- and organo-montmorillonites

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RUSSELL and Fraser (1971) demonstrated that, at low levels of hydration of various hydrogen montmorillonites, protons migrate towards incompletely neutralized OH groups coordinated to Mg and Al in the octahedral layer. They suggested that protons are principally associated with the negatively charged AlMgOH groups.

For the present study a sample of H-montmorillonite was prepared by passing a 1 per cent suspension of Na Wyoming bentonite through a protonated exchange column, and was stored in a refrigerator. An aliquot of this clay was partially converted into the Al form (designated H/Al) by heating at 90°C for 72 hr. Saturation of clay samples with Al was achieved by prolonged contact with 0.1 M solution of aluminum nitrate.

The 830-920 cm^{-1} region of the i.r. spectrum of an air dried film of freshly prepared H-clay (Fig. 1a) differs from that of all other montmorillonites examined (e.g. Figs. 1b and c). With all montmorillonites except H, three bands were observed in this region, at about 850, 890 and 920 cm^{-1} , which, following Russell and Fraser (1971), were attributed to AlMgOH, AlFe³⁺OH and AlAlOH librations respectively. Freshly prepared H-montmorillonite does not give rise to a distinct band at 850 cm^{-1} and the bands at 890 and 920 cm^{-1} are broad. These effects were reproduced with films of different thickness exposed to air humidity. This region of the spectrum remained unchanged on exposure of the sample to vacuum and heating up to 200°C, indicating that the effects are not due to differences in interlayer hydration. The spectrum also remained unchanged if the air-dried film was stored under refrigeration for 48 hr. However, if the film was left to stand in air at room temperature for the same period, a spectrum resembling that of H/Al or Al-montmorillonite was recorded (Fig. 1d). The band at 850 cm^{-1} also developed when the suspension of H-montmorillonite was stored under refrigeration for prolonged periods. After 1 yr it appeared as a shoulder and after 2 yr the spectrum was identical with that of Al-montmorillonite. The samples contained respectively 50 and 80 m-equiv of Al, exchangeable by LiCl, per 100 g of clay.

It is well known that H-montmorillonite is unstable, being partially converted to Al-montmorillonite and that this change is favored by increasing temperature. Since the band at 850 cm^{-1} was not observed with freshly prepared H-montmorillonite but did appear on aging, its absence seems to indicate protonation of the AlMgOH groups in H-clay while its appearance is diagnostic for aging of the clay. The fact that Russell and Fraser (1971) did observe bands at about 850 cm^{-1} with air dried samples of H-clay suggests that their specimens may have been partially converted into the Al form.

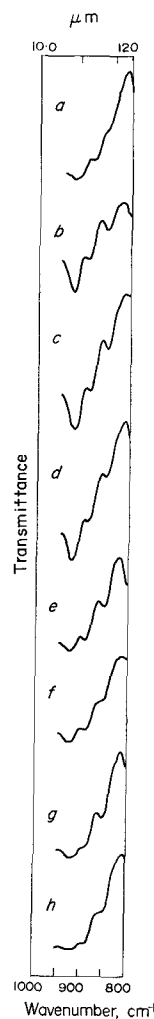


Fig. 1. The 800-950 cm^{-1} region of i.r. spectrum of (a) freshly prepared H-montmorillonite, (b) H/Al-montmorillonite (c) Al-montmorillonite (d) sample (a) after 48 hr under ambient conditions (e) sample (a) dipped in cyclohexylamine (f) sample (a) dipped in aniline (g) sample (a) immersed in aniline for 1 hr (h) sample (g) heated at 200°C under vacuum for 24 hr (the spectrum was taken at room temperature under vacuum).

Since sorption of organic material frequently involves proton transfer reactions, it seemed of interest to investigate the migration of protons in montmorillonites under the influence of organic bases. Mortland (1966) suggested that, on dehydration of protonated urea sorbed on montmorillonite, protons become dissociated from the organic cations and migrate into the lattice. No particular position was assigned to these protons. For the present study cyclohexylamine, a strong aliphatic base, and aniline, a weak aromatic one, were selected, because their reactions with montmorillonite had previously been investigated in some detail (Yariv *et al.*, 1968; Yariv and Heller, 1970).

If a sample of fresh H-montmorillonite is exposed to an organic base in molecular form, the band at about 850 cm^{-1} is restored, very rapidly with cyclohexylamine (Fig. 1e), but more slowly with aniline. On dipping the sample of H-montmorillonite in aniline, a weak band appears at 850 cm^{-1} (Fig. 1f) which increases considerably in intensity after 3 minutes of exposure and reaches its maximum value within 1 hr (Fig. 1g). This gradual development of the band at 850 cm^{-1} is probably due to the slow sorption of the weak base. A striking difference arises when the clay-organic associations are exposed to vacuum: with aniline treated samples the peak at 850 cm^{-1} is reduced in intensity at room temperature and becomes progressively weaker on heating (Fig. 1h). Some aniline is retained by the clay at least up to 200°C, partly in molecular form identified on the basis of the NH_2 stretching vibrations at 3320 and 3390 cm^{-1} , and partly as anilinium ions which give rise to a weak band at 1533 cm^{-1} . The band at 850 cm^{-1} reappears if the heated sample is exposed to ambient conditions for 24 hr. With cyclohexylamine the intensity of the band at 850 cm^{-1} remains unchanged on heating, at least up to 200°C under vacuum. A strong NH_3^+ deformation band at about 1500 cm^{-1} persists throughout, indicating the presence of cyclohexylammonium ions.

It appears that there is competition for the proton between the interlayer material and the clay sheets. In H-montmorillonite the AlMgOH groups are protonated and act as Brönsted acids. Organic bases become protonated on sorption by the clay but only strong bases retain most of the protons on heating under vacuum. The ability to retain protons under specified conditions may perhaps be used as a measure of the basicity of organic compounds in montmorillonite interlayers, but such basicity will not necessarily correspond to the basicity in other media.

On heating H, H(Al) or Al-montmorillonite to 200°C under vacuum, considerable changes were observed in the 800–950 cm^{-1} region of the i.r. spectra, as previously re-

ported by Russell and Farmer (1964) for variously substituted montmorillonites. The changes are completely reversed if the heated samples are dipped in either aniline or cyclohexylamine.

The presence of hydrated protons in clay interlayers may be inferred from the i.r. absorption band at about 1700 cm^{-1} , which characterizes both the H_3O^+ and H_5O_2^+ species (Gillard and Wilkinson, 1964). This band is pronounced in spectra of Al and H/Al-montmorillonite and is weak to absent in spectra of freshly prepared H-montmorillonite. On heating Al or H/Al-montmorillonite the band at 1700 cm^{-1} disappears, together with that at 850 cm^{-1} , indicating migration of protons from the interlayers into the clay sheets. This effect is reversed on cooling. The band at 1700 cm^{-1} also becomes weaker or disappears when amines are sorbed and protonated by the clay. It thus appears that the presence of hydrated protons in the clay interlayers does not necessarily lead to protonation of the AlMgOH -clays. Under ambient conditions this protonation was observed only with H-montmorillonite. The presence of Al in the clay interlayers seems to inhibit migration of protons from the interlayers into the clay sheets and this migration seems to occur only under vacuum or at elevated temperatures.

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