[CONTRIBUTION FROM THE ILLINOIS STATE WATER SURVEY]

Spectroscopic Studies of Base Exchange Materials*

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Previous investigations by means of X-ray studies[1] on montmorillonite have shown that water enters the clay lattice in a stepwise manner. Infrared studies in this Laboratory[2] have indicated that hydrated clay (montmorillonite) contains water in at least two forms and that drying eliminated one form before the other.

Another study of the hydration mechanism of these various montmorillonites has been made by Hendricks[3] by means of a differential thermal analysis and X-ray examination. Results obtained indicated that these montmorillonites could be placed in two classes with respect to water uptake. The first class consisted of the alkaline earth and Li^+ montmorillonites in which the cation was hydrated. In the second class, consisting of Na^+, K^+, Cs^+ and H^+ montmorillonite, the cation was not hydrated. Hendricks states "Although differential thermal analysis is a crude method of measuring no real physical constant of a system, it enables one to distinguish variations in the binding of water even though such variations might be very small."

These authors find[3] the amount of water taken up per gram by various montmorillonites at 30° and various humidities to be as shown.

TABLE I

WATER UPTAKE BY MONTMORILLONITES

Cation	(Relative humidity) 5%	 10%	 90%
	G. H_2O per G. of material		
H^+	0.045	0.075	0.36
Ca^{++}	.070	.105	.36
Mg^{++}	.085	.115	.34
Sr^{++}	.050	.085	.34
Li^+	.065	.085	.34
Ba^{++}	.050	.075	.32
Na^+	.025	.040	.28
K^+	.015	.030	.20
Cs^+	.02	.04	.18

Since base-exchange properties are dependent on hydration, especially in synthetic materials, we have extended the investigation to include a variety of substances in this class.

Taking the 3 mu absorption as a relative measure of water uptake as described in this paper in the following studies, we have the various ion clay salts arranged as follows: $Ca^{++} = Mg^{++} >> Li^+ > K^+ > Ba^{++} >> H^+ > Na^+ >> NH_4^+$. The general agreement with Hendricks' series is good, considering the difference in experimental method. The notable difference between the two sets of results is the shift of H^+ from one end of the series to the other at high humidity. The shift in the position of the K^+ is less striking and may be due to the wide difference in techniques. If the ions are arranged in the order of water uptake at 5 and 10% humidity, the H^+ is found between Ba^{++} and Na^+. It is not until 25% humidity is reached that the clay acid passes the Ba^{++} and Li^+ clay salts in water uptake.

Because it has not yet been possible to develop a technique whereby water uptake can be correlated quantitatively with infrared spectroscopic data, we cannot compare our findings directly with those of Hendricks, *et al.* The development of quantitative spectroscopic techniques now under way should lead to an interesting interpretation of these two series. Speculations at the present time seem unwarranted.

Experimental

A sodium montmorillonite described previously[2] and samples of Ball clay and Indianaite described in a previous paper[4] were furnished us by R. H. Bray, Asst. Chief, Soil Survey, Agri. Expt. Station, University of Illinois.

The following procedure was used in order to prepare samples of pure H^+, Li^+, K^+, NH_4^+, Ca^{++}, Mg^{++}, and Ba^{++} montmorillonites. First a sample of H^+ montmorillonite was prepared from the sodium montmorillonite.[5] The *p*H of a water suspension of this material was 3.5. Then samples of this material were treated with the hydroxides of the various cations mentioned above until a *p*H of 8 was reached. A Cameron *p*H meter was used for the *p*H determinations. Films were prepared by evaporation of a suspension of these materials on microscope cover slips floating on mercury. These films were made as nearly the same thickness as possible. This was accomplished by adjusting the thickness of the films until the intensities of light passing through the various films were identical in a definite region as registered by the thermocouple of the infrared spectrometer. Infrared absorption was determined on films hydrated for sixteen hours (A) and

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[1] Hofmann, Endell and Wilm, *Z. Krist.*, **86**, 340–348 (1933); Nagelschmidt, *ibid.*, **93**, 481–488 (1936); Hofmann and Bilke, *Kolloid Z.*, **77**, 238–251 (1936); Bradley, Grim and Clark, *Z. Krist.*, **A97**, 216–222 (1937).

[2] Buswell, Krebs and Rodebush, THIS JOURNAL, **59**, 2603 (1937).

[3] Hendricks, Nelson and Alexander, *ibid.*, **62**, 1457 (1940).

[4] Grim and Bray, *J. Am. Ceram. Soc.*, **19**, 307 (1936).

[5] Mattson, *J. Agri. Research*, **33**, 553 (1926).

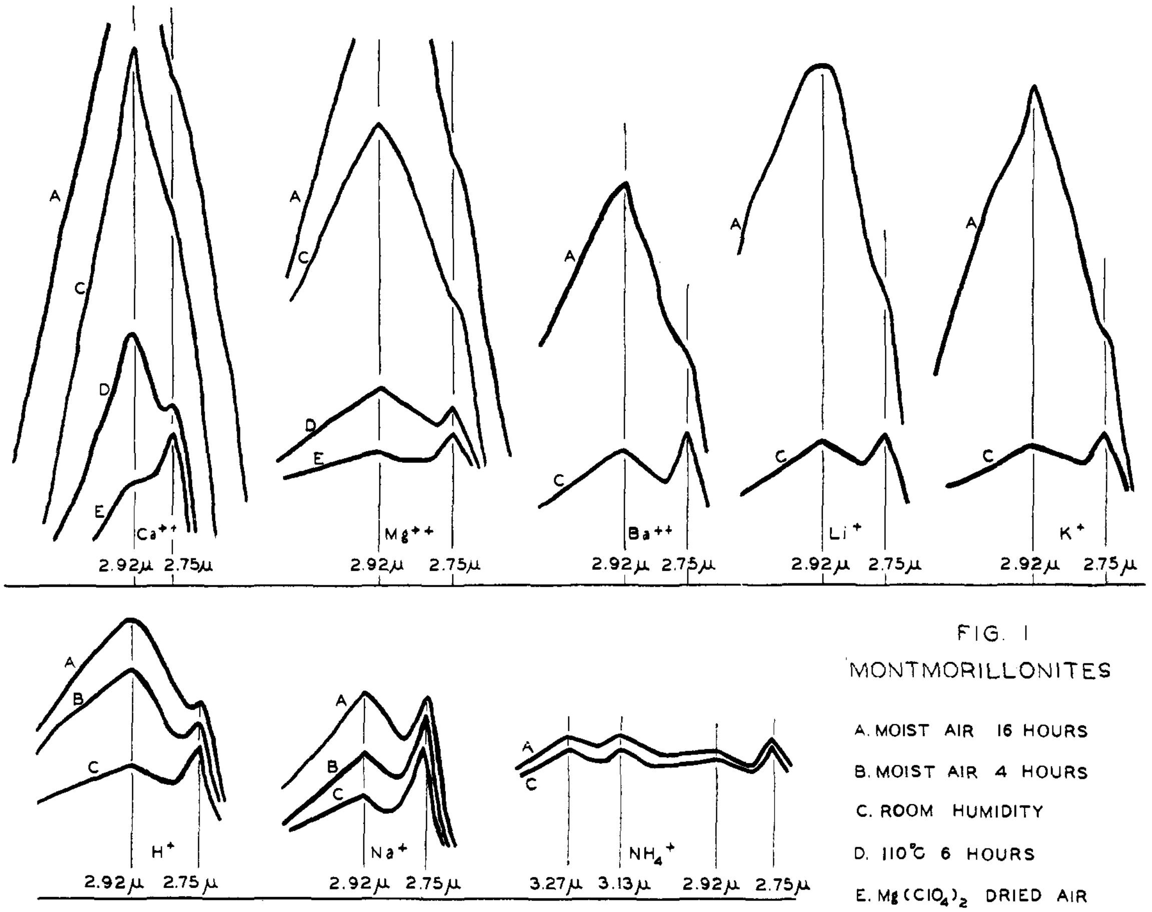

Fig. 1.—Montmorillonites.

four hours (B), respectively, over distilled water at 23° (21 mm. vapor pressure), films dried at room humidity (C), films dried at 110° for six hours (D), and films dried by passing dry air from a calcium chloride and magnesium perchlorate train through a cell containing the film (E).

Hydration of these films for periods longer than sixteen hours under the conditions mentioned produced no change in their absorption spectra, indicating that they had taken up a maximum amount of water at the sixteenth-hour hydration stage. These results are shown in Fig. 1.

We find that infrared absorption spectra of montmorillonites saturated with various cations show bands similar to those that have been observed previously[2] for the Na$^+$ montmorillonite: that is, the 2.75 mu (unbonded or free OH) and the 2.92 mu (bonded —OH) with similar effects due to hydration in greater or lesser degree. The height and breadth of the 2.92 mu band depends on the water content of the film. As will be noted below, it may become so broad as to nearly obscure the 2.75 mu band.

These montmorillonites saturated with various cations appear to fall into four classes with respect to water uptake. The first class consists of Ca^{++} and Mg^{++} montmorillonites, which take up a large amount of water. The Ca^{++} clay apparently takes up about the same as the Mg^{++} clay, as is apparent from spectra of the room humidity films and from films dried at 110° for six hours. It is to be noted that as the 2.92 mu band increases on hydration, it obscures the 2.75 mu band. Films of Ca^{++} and Mg^{++} montmorillonites take up so much water when hydrated over water at 23° for sixteen hours that they become opaque to our instrument in this region. Since each of these cations is highly hydrated[3] in the montmorillonites, this is the effect which would be expected.

In the second class, the Li$^+$, K$^+$ and Ba^{++} montmorillonites take up an appreciable amount of water, but not nearly as much as those of the first class. Using the room humidity films as a basis, the order of hydration of this class is Li$^+$ $>$ K$^+$ $>$ Ba^{++}. As the 2.92 mu band increases on hydration, it obscures the 2.75 mu band, as in the first class of montmorillonites. However, this effect is not as great as with the clays of the first class.

The third class includes the H^+ and Na^+ montmorillonites. Using the room humidity films as a basis, it is difficult to decide the order of absorption. However, on hydration over water at 23° for sixteen hours, a definite variation is noted. Using this as a basis, the order of the amount of water taken up is $H^+ > Na^+$. On hydration of the H^+ and Na^+ montmorillonite, the 2.92 mu band increases and the 2.75 mu band is partially obscured; but the effect is much less than is noted in the first two classes.

The fourth class consists of the NH_4^+ montmorillonite, which shows almost no increase in either the 2.92 or 2.75 mu bands on attempted hydration for sixteen hours or longer.

The variation in amount of water taken up by the various montmorillonites may be related to an actual difference in water required by the various cations for isomorphous replacement such as occurs in the zeolites. Pauling[6] states "The presence of definite available positions for occupancy by large cations or water molecules is clearly indicated by the formulas of such ismorphous pairs as natrolite and scolecite, differing in the replacement of $2Na^+ + 2H_2O$ by $Ca^{++} + 3H_2O$."

The placing of K^+ montmorillonite along with the Li^+ and Ba^{++} montmorillonites and above the Na^+ montmorillonite based on its water absorption capacity is seemingly in disagreement with the other data. The K^+ ion is less hydrated than the Na^+ ion in its solutions. This is shown by Jenny[7] in the following table.

	Li^+	Na^+	K^+	NH_4^+
Crystal lattice radii, Å.	0.78	1.01	1.30	1.43
Hydrodynamic radii, Å.	10.03	7.90	5.32	5.37

However we found, as stated above, that a film of Na^+ montmorillonite under the same conditions as one of K^+ montmorillonite apparently did not take up as much water as did the K^+ montmorillonite.

Absorption Spectrum of Ammonium Clays

The NH_4^+ montmorillonite offered interesting material for infrared study. Since the NH_4^+ ion is the only cation detectable in the infrared, it was decided to determine whether it gave a similar absorption spectrum when bound to a montmorillonite as when present as a purely inorganic salt, for example, an ammonium halide. Hence we first confirmed Pohlman's[8] work on the ammonium halides using an instrument of greater resolving power. We prepared our films in an improved, simplified manner. The dried gases of ammonia and the hydrogen halides were passed into a vacuum desiccator which was kept at a pressure of about 15 mm. A fog of the ammonium halide formed which was allowed to settle out on a 22 × 40-mm. cover glass. It was found after many attempts that the above conditions resulted in the formation of films of small enough particle size so that the reflection effect in the infrared was negligible. The crystals of the salt were barely discernible under a low-power microscope (about 1 mu). The ammonium chloride and ammonium bromide films showed a doublet at 3.20 and 3.30 mu. The ammonium iodide film showed broad absorption at 3.20 mu with a steep slope toward shorter wave lengths, and a more gradual one toward the longer wave lengths. These values agree with Pohlman's data.

The room humidity NH_4^+ montmorillonite showed bands at 2.75, 2.92, 3.13 and 3.27 mu. The first two bands are the unbonded and bonded —OH frequencies as found in all montmorillonites. The latter two bands, although rather broad, agree with the doublet observed in the case of the ammonium halides. No clear explanation of the greater separation of the doublet in the case of the montmorillonite has as yet offered itself. On hydration there was no appreciable change in the absorption spectrum, indicating that the NH_4^+ montmorillonite takes up only a small amount of water. The 5.56 mu singlet as found by Pohlman[8] for the ammonium halides was also detected in the NH_4^+ montmorillonite by means of a grating spectrograph previously described.[9] NH_4^+ montmorillonite films were also prepared by treatment of a H^+ montmorillonite film with dry gaseous ammonia and by base exchanging the H^+ ion with 10% ammonium chloride solution. Regardless of the method of preparation, the same absorption spectrum was obtained.

Hydration of Low Exchange Capacity Clays

In an attempt to correlate base-exchange capacity with hydration, films were prepared of clays of lower base-exchange capacity than the mont-

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(6) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, 2nd ed., pp. 386–387.

(7) Jenny, *J. Phys. Chem.*, **36**, 2217 (1932).

(8) Pohlman, *Z. Physik*, **79**, 394–420 (1932).

(9) Borst, Buswell and Rodebush, *J. Chem. Phys.*, **6**, 61 (1938).

morillonites. The base-exchange capacity of these clays was from 17 to 30 milliequivalents per 100 g., as compared to 85 milliequivalents per 100 g., for the montmorillonite. The mineral constitution and base-exchange capacity of these clays has been previously reported[4] by Grim and Bray.

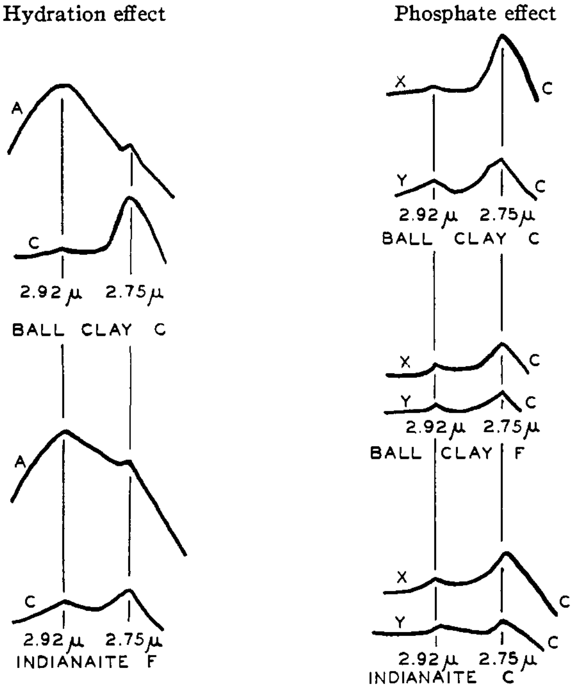
The clays used were a Ball clay C (C is a coarse colloid fraction of particles of 1.0 to 0.1 microns in diameter), Ball clay F (F is a fine colloid fraction of particles of 0.1 to 0.06 micron in diameter), and an Indianaite C and F. Regardless of particle size or mineral composition all these show considerably less absorption at 2.75 mu than do the montmorillonites. The 2.92 mu band is hardly noticeable in the case of room humidity films (C) of these low base-exchange capacity clays. On hydration (A) this band does not increase in intensity nearly as much as in the case of montmorillonites. These results are shown in Fig. 2 (hydration effect). These facts indicate that hydration can be correlated in some manner to base-exchange capacity, since the materials of lower base-exchange capacity show less bonded and unbonded—OH.

Effects of—OH Replacement on Absorption at 2.75 Mu

Certain of these clays allow replacement of—OH by phosphate.[10] A known amount of clay was shaken with a known amount of orthophosphoric acid solution. After shaking and filtering, the residual phosphate was determined on an aliquot portion and the fixed phosphate calculated by difference. The amount of phosphate fixed by the various clays was as follows

Indianaite C fixed 6850 p. p. m. P
Ball Clay F fixed 1800 p. p. m. P
Ball Clay C fixed 9050 p. p. m. P

The infrared absorption spectra of these phosphate treated clays (Y), Indianaite C and Ball Clay C and F, show a difference in the amount of unbonded—OH (2.75 mu) present. In the phosphate treated Indianaite C and Ball Clay C the area under the 2.75 mu peak is about 25% less than that under the same peak in the unphosphated clays (X). These results are shown in Fig. 2 (phosphate effect). Due to previously mentioned experimental difficulties exact quantitative data could not be obtained. However, the experimental data indicate that the previous assignment[2] of the 2.75 mu band to the unbonded —OH frequency was correct.



A. Moist air 16 hours.
C. Room humidity.
X. Unphosphated.
Y. Phosphated.

Fig. 2.—Ceramic clays.

Comparison of X-Ray Patterns of Natural and Artificial Exchangers

The application of data on clays to synthetic exchange materials would be desirable. Before doing so it seemed advisable to determine whether the synthetic materials showed crystalline structure and whether this structure, if present, showed any similarity to that of the natural clays. Since no data were available on this point, several commercial zeolites were obtained from the various companies producing them. X-Ray powder patterns were made for us by J. N. Mrgudich of the University of Illinois, Department of Chemistry. Nalcolite, Crystallite, R-P gel zeolite, Doucil No. 1, Federal Mineral and Decalso were studied and were shown to be definitely amorphous in structure. In this respect, then, synthetic "gel" materials differ from natural exchange materials. The synthetics also lose capacity on heating while the natural materials gain capacity on heating.

The powder pattern of a raw "greensand" which has extensive use as a water softener showed that it was definitely crystalline in structure—consisting mainly of glauconite, a mica-like silicate

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(10) Kurtz, "Phosphorus Fixation in Illinois Soils," Thesis, University of Illinois, 1940.

of Al, Ca, Fe, K and Mg. Since it is well known that heating this raw greensand increases its base-exchange capacity markedly, a sample of the raw material was heated in a muffle furnace at about 750° for two hours. The X-ray pattern of this heated glauconite of greater base-exchange capacity shows a definite precipitation of new particles of coarser grain size with the partial destruction of the glauconite structure. Thus, the increased base-exchange capacity may be due to these new particles formed on heating the greensand.

Conclusions

1. From our infrared absorption studies we can place the montmorillonites saturated with various cations (Ca^{++}, Mg^{++}, Li^+, K^+, Ba^{++}, H^+, Na^+, and NH_4^+) into four classes with respect to water uptake. The first class, one of extreme absorption, consists of the Ca^{++} and Mg^{++} montmorillonites. The second, of appreciable absorption, consists of the Li^+, K^+, and Ba^{++} montmorillonites; and the third class, H^+ and Na^+ montmorillonites, was one of slight absorption. The fourth, consisting of NH_4^+ montmorillonite showed almost no change on attempted hydration.
2. Similar studies of clays of low base-exchange capacity indicate that less bonded (2.92 mu) and unbonded (2.75 mu)—OH is present than in the case of the higher base-exchange montmorillonites.
3. The assignment of the 2.75 mu band to the unbonded—OH frequency is corroborated experimentally. Clays allowing replacement of structural—OH by phosphate show about 25% less absorption at 2.75 mu than do unphosphated clays.
4. The NH_4^+ montmorillonite showed a doublet at 3.13 and 3.27 mu characteristic of the NH_4^+ halides, which have a doublet at 3.20 and 3.30 mu.
5. X-Ray data show that the increased base-exchange capacity of greensand after heat treatment may be due to the formation of new particles.
6. X-Ray data show that the artificial gel zeolites are definitely amorphous while glauconite or greensand is crystalline in structure.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Halogen Acids to Olefins. XXVI. The Addition of Halogen Acids to Trichloromethylethylene

BY M. S. KHARASCH, E. H. ROSSIN AND E. K. FIELDS

The study of the effect of substituents on the direction of addition of halogen acids to ethylene compounds has interested chemists for many years. Better understanding of the factors which promote "normal" and "abnormal" additions now permits the correlation of the large body of known facts in an unambiguous manner. The data thus far accumulated indicate that in all "normal" additions where the double bond is not conjugated with the oxygen atom of a carboxyl group (as in acrylic acid) the halogen acid adds to produce a secondary or tertiary alkyl halide, rather than a primary halide. In the presence of oxygen and/or peroxides hydrogen bromide adds "abnormally" and an isomeric bromide is obtained.[1]

Recently, Robinson[2] suggested that it should be possible to predict the direction of addition of hydrogen bromide to olefins from a knowledge of the directing influence which the substituting groups exhibit when they are attached to the benzene nucleus. The ortho and para directing groups should promote addition in accord with the Markownikoff rule, whereas the reverse should be true of meta directing groups. In substantiation of this hypothesis Robinson cites the formation of 1,2-dibromopropane and β-bromopropionic acid in the reaction of hydrogen bromide with allyl bromide and acrylic acid, respectively.

The hypothesis of Robinson is most attractive, and, if correct, should be very useful, since there is available a great deal of information on the directing influence of groups when attached to a benzene nucleus.

It is, therefore, of interest to determine how generally Robinson's hypothesis is applicable. Acrylic and 1-carboxylic unsaturated acids, although they act in accordance with the proposed idea, are not critical test compounds, for they introduce

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[1] A comprehensive discussion and references are found in the review by Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

[2] Smith, *Chem. and Ind.*, **57**, 461 (1938).