JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 74 MARCH 22, 1952 NUMBER 6

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Adsorption of Water Vapor by Montmorillonite. I. Heat of Desorption and Application of BET Theory[1]

BY R. W. MOONEY, A. G. KEENAN[2] AND L. A. WOOD

Repeated adsorption–desorption measurements of water on montmorillonite showed that the desorption isotherm was reproducible whereas the adsorption isotherm depended on the initial water content. Heats of desorption were calculated from the Clausius–Clapeyron equation and give evidence of discrete layer formation. Application of the BET theory leads to a novel interpretation of the monolayer capacity. The results are correlated with the known structure of montmorillonite.

In a previous paper[3] an application of the BET theory[4] to the adsorption of water vapor and nitrogen by a series of homoionic kaolinites was found to give information concerning the degree of hydration of exchangeable ions on the clay surface. It was found possible to correlate the results with the size and the charge of the exchangeable ion. Since kaolinite is a non-expanding lattice type clay, the adsorption of both water vapor and nitrogen presumably takes place on essentially the same surface. This would not be the case for the montmorillonite used in the present research since it is well known that when water is adsorbed by montmorillonite, it enters between the ultimate plates, which are about 10 Å. in thickness, as well as being adsorbed on the outer surfaces of aggregates of plates.[5,6] It is doubtful, on the other hand, that nitrogen molecules are able to enter between two adhering plates, but are adsorbed only on the outer surfaces of the aggregates.[7,8]

Because of this added complication in the case of montmorillonite, an extensive series of adsorption–desorption cycles was carried out with water vapor on several homoionic montmorillonites. These results, together with some heat of desorption data obtained by use of the Clausius–Clapeyron equation, are reported in the present paper. The influence of the exchangeable ions on water adsorption and the degree of swelling as measured by X-ray diffraction are reported in the following paper.

Experimental Details

The montmorillonite used in these experiments was a Wyoming Bentonite, obtained from the American Colloid Company[9] under the name "Volclay," SPV grade, 200 mesh. X-Ray diffraction spectra, obtained in another study, revealed no impurities in observable quantities. The exchangeable ions on the natural montmorillonite were chiefly calcium, magnesium and sodium, and the clay had a base exchange capacity of 0.90 milliequivalent per g. Hydrogen montmorillonite was prepared by electrodialyzing the natural clay as described previously[3] in the case of kaolinite. Sodium montmorillonite was prepared by titrating a suspension of the electrodialyzed material to *p*H 7 with sodium hydroxide.

Each of the samples was dried to constant weight (0.01% loss in weight per day) under high vacuum at 70°, a procedure found to be gravimetrically equivalent to drying in air at 140°. The apparatus and procedure were the same as described previously.[3] The nitrogen adsorption isotherms were determined in the usual manner,[10] and the surface area available to the nitrogen was calculated by the BET method.

For the determination of the heat of desorption, the desorption of water vapor by a sample of sodium montmorillonite was measured at both 0 and 20°. The desorption at 0° was carried out with the sample bulb surrounded with cracked ice and water in a dewar flask.

Reproducibility of Isotherms.—The measurements of the water adsorption by montmorillonite yielded complex results due to the complicated nature of the water adsorption processes in the expanding lattice structure. The isotherms

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[1] Part of this work was carried out under contract to the Corps of Engineers, United States Army as part of a project under the direction of Professor B. K. Hough, School of Civil Engineering, Cornell University. Acknowledgment is also made to Mr. David L. Tornburg for his valuable technical assistance in many ways, including measurement of the nitrogen isotherms.

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[3] A. G. Keenan, R. W. Mooney and L. A. Wood, *J. Phys. Colloid Chem.*, **55**, 1462 (1951).

[4] S. Brunauer, P. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[5] U. Hofmann, K. Endell and D. Wilm, *Z. Krist.*, **86**, 340 (1933).

[6] W. F. Bradley, R. E. Grim and G. L. Clark, *ibid.*, **97**, 216 (1937).

[7] S. B. Hendricks, R. A. Nelson and L. T. Alexander, THIS JOURNAL, **62**, 1457 (1940).

[8] B. Makower, T. M. Shaw and L. T. Alexander, *Proc. Soil Sci. Soc. Am.*, **2**, 101 (1937).

[9] 363 West Superior St., West Chicago, Illinois.

[10] W. Barr and V. Anhorn, *Instruments*, **20**, 454 (1947).

for samples of natural, hydrogen and sodium montmorillonite are plotted in Figs. 1, 2 and 3, respectively. Marked hysteresis was evident in each of the initial adsorption–desorption cycles. Following the first cycle, a second adsorption run was begun without any intermediate drying of the clay. In the case of the natural montmorillonite, a third cycle was carried out. On the second and following adsorption branches, only a few points were taken and the sample then equilibrated with saturated water vapor.

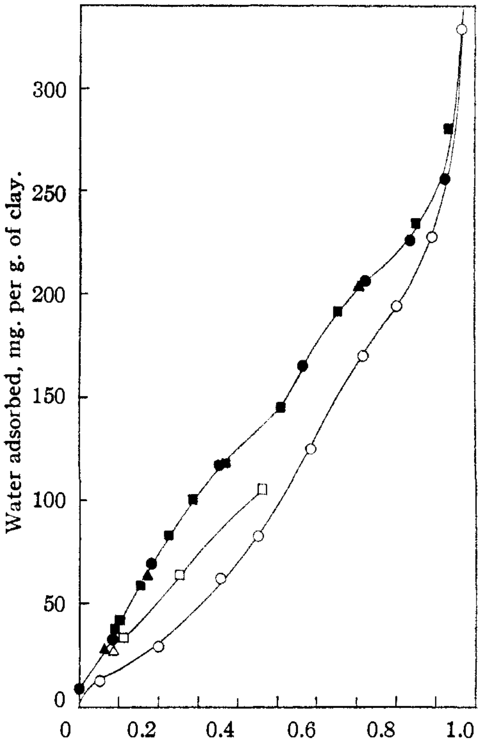

Fig. 1.—The adsorption of water on natural montmorillonite at 20°: ○, first adsorption; ●, first desorption; △, second adsorption; ▲, second desorption; □, third adsorption; ■, third desorption.

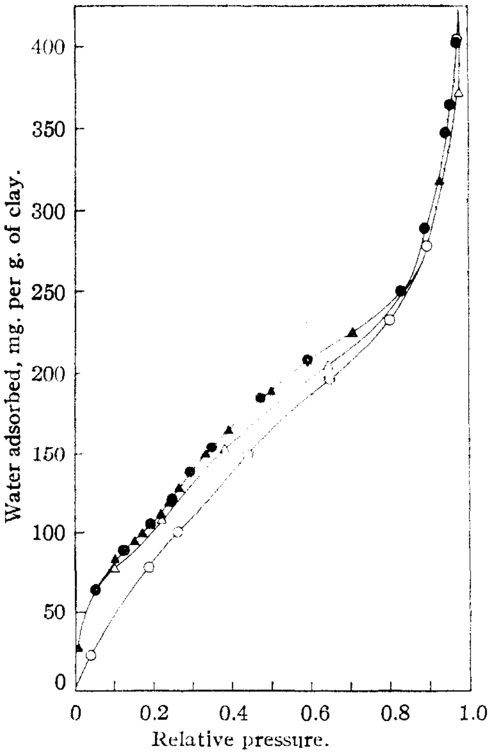

Fig. 2.—The adsorption of water on hydrogen montmorillonite at 20°: ○, first adsorption; ●, first desorption; △, second adsorption; ▲, second desorption.

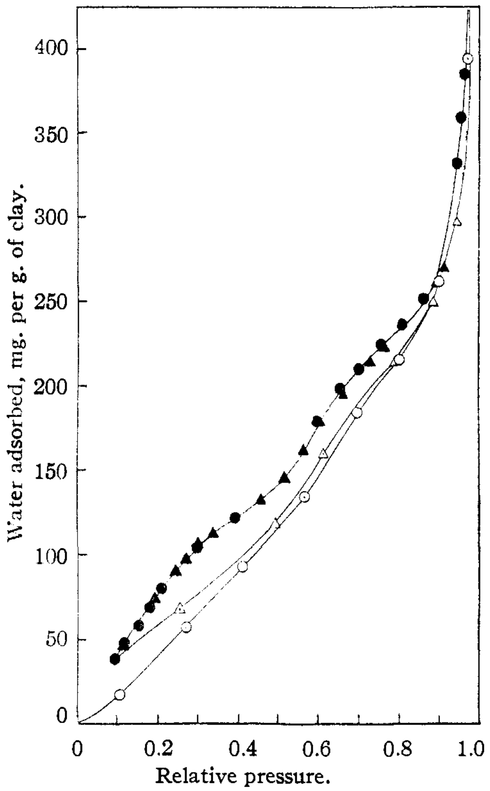

Fig. 3.—The adsorption of water on sodium montmorillonite at 20°: ○, first adsorption; ●, first desorption; △, second adsorption; ▲, second desorption.

In no case was the original adsorption isotherm retraced and in general the adsorption curves appeared to depend on the initial water content at which the adsorption was begun. On the other hand, the desorption curves were reproducible provided the relative pressure on the preceding adsorption curve was carried up as high as the final steeply-rising section. If desorption was begun before the adsorption had been carried this far, then the desorption would follow the usual "scanning" curve across the hysteresis loop.

A possible explanation of the non-reproducibility of the adsorption curve may be that when adsorption is begun on a practically dry clay, surface heterogeneities cause the system to be very sensitive to slight variations in the amount of residual water present. When desorbing from an almost saturated clay, slight variations in water content are no longer significant.

In order to determine whether the adsorption curve failed in reproducibility because of a slow approach to equilibrium, the variation of the adsorption at constant pressure was studied over a long period of time. With a sample of hydrogen montmorillonite, it was found that at a relative pressure of 0.65, about 90% of the water was taken up in the first few minutes, and the increase in total adsorption from the end of 24 hours to 10 days was only 0.31%. The addition of air to a pressure of 1 mm. to the vacuum system prior to admitting the water vapor slowed the process so that only 70% of the final amount was taken up in the first 24 hours. With sodium montmorillonite, the increase in water adsorbed from the end of 24 hours to 21 days was 0.14% at a relative pressure of 0.70. Because of the reproducibility of the desorption curves, and for other reasons discussed below, it was believed that they more properly represented the equilibrium values than the adsorption curves. It is apparent that none of the isotherms fit exactly into any of the five standard classifications proposed by Brunauer, *et al.*[11]

Nitrogen areas were also determined for each of the clays. The nitrogen adsorptions were reversible, showed no hysteresis, and the BET function yielded excellent straight-line plots in the applicable pressure range. The surface areas available to nitrogen are given in Table I and were reproducible to within 0.3 m.^{2}/g. on the same sample. The previous history of the samples was clearly important, since, for example, the electrodialysis process for converting the natural to the hydrogen montmorillonite increased the nitrogen area by 50%. Such observations are in accord with Hendricks, Nelson and Alexander's picture[7] of montmorillonite, which assumes that the nitrogen adsorption occurs on the "external surface area of the organized montmorillonite crystals," which they estimate to contain fifty to a hundred layers. The increase of nitrogen surface area on electrodialysis can be reasonably ascribed to a slight breaking up of these "organized crystals," resulting from the mechanical agitation of the suspension or from the removal of ions involved in the binding of the individual plates into organized crystals.

Heat of Desorption.—The desorption isotherms at 0 and 20° on a sample of sodium montmorillonite are shown in Fig. 4. The two isotherms roughly parallel one another with adsorption at 0° being always greater than the adsorption at 20°. This would be expected for physical adsorption. The isosteric heat of desorption was computed from the Clausius–Clapeyron equation.

$$E = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{p_1}{p_2}$$

A graph of the resulting heat of desorption against water content is shown in Fig. 5. It is evident that there are two kinks in the curve corresponding to regions of relatively small rate of change of heat of desorption with change in water content. These occur at approximately the water contents corresponding to one and two layers of water on the surface, respectively.

Application of the BET Theory to Water Adsorption.—The desorption data were converted to the BET function and found to give straight lines well within experimental precision in the usual range of relative pressures from 0.05 to 0.35. The lines for the natural and hydrogen montmorillonites are shown in Fig. 6. The sodium montmorillonite gave a line which was almost identical with the natural and with even less scatter of the points. In Table I are given the values of the parameter x_m which in the BET theory represents the weight of water required to cover the surface with a monomolecular layer. Using the normal

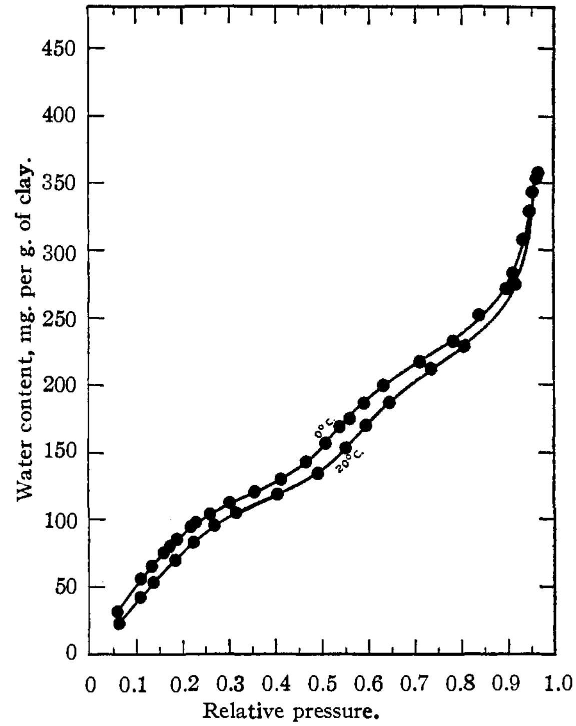

Fig. 4.—The desorption of water on sodium montmorillonite at 0 and 20°.

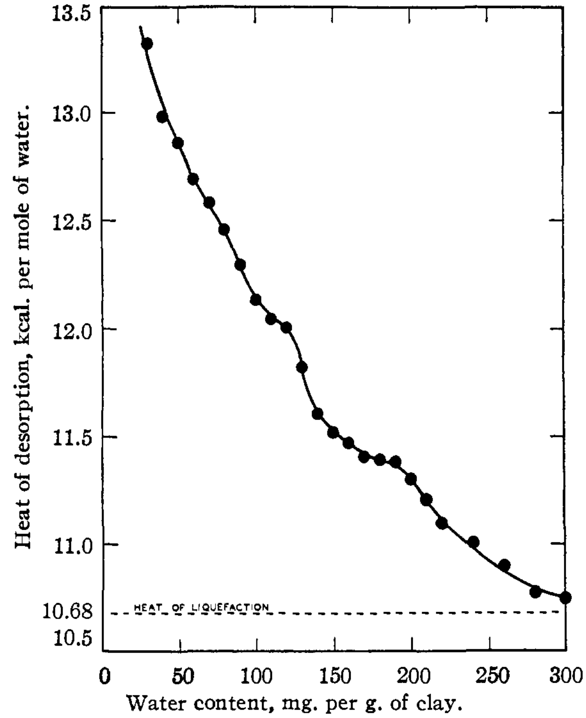

Fig. 5.—The heat of desorption of water on sodium montmorillonite.

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(11) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, THIS JOURNAL, **62**, 1723 (1940).

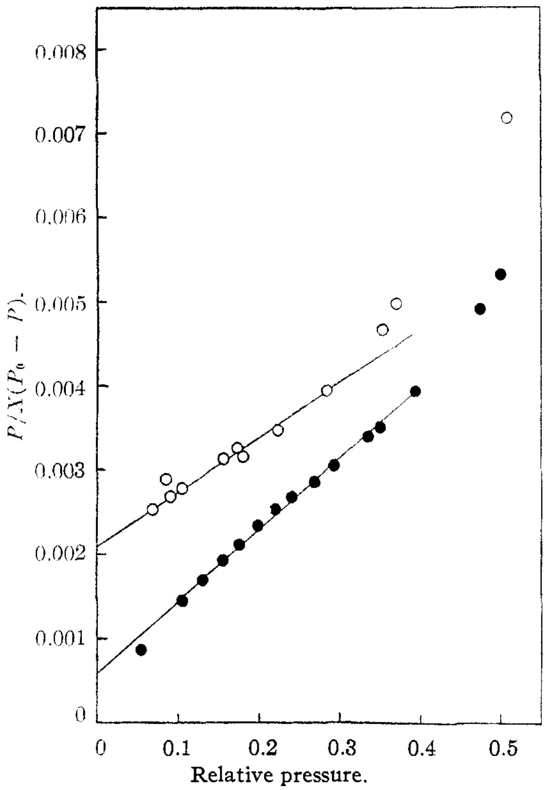

Fig. 6.—BET plots for the desorption of water on montmorillonite: ○, natural montmorillonite; ●, hydrogen montmorillonite.

packing area of water in physical adsorpion,[12] 10.8 Å.^{2} per molecule, the equivalent surface areas were calculated and are given in Table I.

TABLE I

SURFACE AREAS OF MONTMORILLONITES

Exchangeable ion	Water adsorption x_m (mg./g.)	Water adsorption Equivalent area (m.^{2}/g.)	Nitrogen area (m.^{2}/g.)	Total surface area (m.^{2}/g.)
Natural	117	422	27	817
Hydrogen	111	400	40	760
Sodium	122	440	33	847

The water adsorption "areas" of about 400 m.^{2}/g. admit of an interesting interpretation. They correspond to x_m values of slightly more than 100 mg./g. The X-ray data of others[6,7] and that reported in the following paper indicate that not more than one layer of water molecules is present between the platelets at this water content. This immediately suggests, therefore, that in the case of the expanding-lattice clay, montmorillonite, the BET theory gives not the monolayer capacity on each surface of the expanded platelets but the adsorption when only one layer of molecules occurs between each pair of platelets (plus the small contribution from a monolayer on edges and external surfaces).

This interpretation is consistent with the known structure of montmorillonite. The plates are undoubtedly held together by strong forces since the energy of adsorption of nitrogen and many other gases is insufficient to bring about separation. When water molecules penetrate between the plates, it seems reasonable to suppose that the plates first separate only enough to admit one layer of molecules, and when this layer is filled completely, a second layer may begin forming.

On the basis of this interpretation of x_m, the values of the surface areas should be calculated in a somewhat different manner from the usual one. The nitrogen area presumably gives the external area, while the water monolayer value of about 400 m.^{2}/g. represents the external area plus half the interior area. Thus the true total surface area is obtained by subtracting the nitrogen area from twice the water monolayer area. This yields values in the region of 800 m.^{2}/g. as shown in the last column of Table I.

If it is assumed that the montmorillonite plates are so large that the area on the edges is negligible compared with the faces, then the surface area may be calculated from the constitution of the unit cell. Using $Al_{3.34}Mg_{0.66}Si_8O_{20}(OH)_4H_{0.66}$ as the formula of the unit cell of hydrogen montmorillonite, and a and b dimensions of 5.14 and 8.90 Å., respectively, an area of 766 m.^{2}/g. is obtained. For the sodium clay, the value is 749 m.^{2}/g. The fact that these values are in general agreement with those deduced from the water desorption lends support to the interpretation of the water data given above. The slightly higher value obtained by experiment for sodium montmorillonite may indicate some hydration of the exchangeable ions.

Discussion

The application of the BET theory to an expanding lattice clay is, of course, open to some question, but it is believed that the usual requirements are reasonably well fulfilled. Equilibrium is relatively rapidly attained and the desorption data yield an essentially linear BET function in the usual pressure range. Precedents for using the desorption isotherm are discussed by Brunauer.[13] The question of whether or not the adsorption of water by montmorillonite is properly considered physical adsorption cannot be definitely answered, but Brunauer[14] considered that the adsorption of water by such materials is an ion–dipole interaction and is probably on the borderline between physical and chemical adsorption. The calculation of surface areas from water adsorption data must not be considered to yield exact values since the work on kaolinite[8] has shown that the packing area of water varied with the nature of the exchangeable ion. However, the variation in this factor is not nearly large enough to invalidate the general conclusions drawn above.

While the isotherms apparently do not fit the standard classifications,[11] they may be considered a combination of types I and II, combined in a way to yield the concave region (upward) between 100 and 200 mg./g. It is believed that this tendency of the curve to flatten represents the transition between the first and second layers between the plates.

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[12] P. H. Emmett and M. Cines, *J. Phys. Colloid Chem.*, **51**, 1248 (1947).

[13] S. Brunauer, "The Adsorption of Gases and Vapors," Vol. 1, "Physical Adsorption," Princeton University Press, Princeton, N. J., 1943, pp. 394 *et seq.*

[14] *Ibid.*, p. 334.

The monolayer alone would yield a type I isotherm. The X-ray data mentioned bear this out as well as the facts that this is observed at the water content approximately equal to x_m and to that computed from the unit cell.

These considerations imply completion of the first layer between the plates before the second begins forming. However, this results in an inconsistency in the values of the BET parameter C. The values of C computed for these isotherms range from 4 to 15, while according to the BET analysis values of C of 10 indicate some multilayer formation (24% at $x = x_m$) before the first layer is complete.[15] For substantial completion of the first layer before further layers commence, a value of C of 100 or more is required. This apparent discrepancy is resolved when it is realized that the water between the plates is not subjected to the collisions by the vapor molecules which are necessary to permit multilayer formation. On the outside portions of the aggregates, such processes operate, and there is consequently multilayer adsorption at these pressures, but this is masked in the measurements by the much greater quantity of water held between the plates.

Using the assumptions that the nitrogen adsorption measures only the outside surface area of the aggregates and that the water adsorption, as interpreted above, measures the total surface area of the individual plates, it may be calculated that there is 18, 25 and 29 times as much surface between the plates, as there is outside the aggregate, for the hydrogen, sodium and natural montmorillonite, respectively. The numbers of plates per aggregate in these clays are also 18, 25 and 29, if the areas of the edges are assumed negligible.

RECEIVED AUGUST 13, 1951

[15] T. L. Hill, *J. Chem. Phys.*, **14**, 286 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Adsorption of Water Vapor by Montmorillonite. II. Effect of Exchangeable Ions and Lattice Swelling as Measured by X-Ray Diffraction

BY R. W. MOONEY,[1] A. G. KEENAN[2] AND L. A. WOOD

Using the methods developed in previous publications, the effect of various exchangeable ions on water adsorption is correlated with their size and charge and a measure of the degree of hydration of the ions is obtained. Further correlation between the shapes of the isotherms, heats of desorption and X-ray diffraction data gives evidence that the adsorbed water is present in discrete monolayers.

In the preceding paper,[3] it was shown that in the adsorption of water vapor by the expanding-lattice clay, montmorillonite, the desorption branches of the isotherms were reproducible over two and three adsorption–desorption cycles provided the preceding adsorption had been carried as far as the steeply ascending portion of the curve approaching relative pressure unity. The adsorption branches of the isotherms were not reproducible and gave evidence that the surface condition of the clay in a relatively dry condition was very sensitive to slight unavoidable variations in water content. It is evident, therefore, that any interpretations concerning the adsorption of water on montmorillonite must be carried out using data from the desorption isotherm.

In the present paper results are reported of an investigation of the influence of exchangeable ions on the adsorption of water vapor by montmorillonite. An earlier paper[4] reported the results of a similar study on kaolinite. In the present instance, the water adsorption results are further correlated with a study of the expansion of the montmorillonite lattice using the X-ray diffraction method.

Experimental Details

The apparatus and general procedure for obtaining the isotherms have been described previously.[3,4] The homoionic montmorillonites were prepared by a slightly different method from that used before. A titration curve on the electrodialyzed montmorillonite was made using sodium hydroxide as the base.[5] The amount required to give a *p*H of 7.5 was taken as the base exchange capacity and was found to be 0.83 milliequivalent of cation per gram of clay. Accordingly 0.83 milliequivalent of each desired ion per gram of dry clay was added to a suspension of the clay in water.

The monovalent ions Li, Na, K, Rb and Cs were added as solutions of the hydroxides while the divalent ions were added in the form of solids, namely, magnesium carbonate, calcium oxide, strontium hydroxide and barium hydroxide. The solutions and solids were standardized by titrating aliquots with standard hydrochloric acid. After addition of the base in solid or solution form, the clay suspension was stirred continuously and the *p*H measured at 24-hour intervals until it remained constant. This required from one to two weeks. The final *p*H values for each ionic modification are given in Table I.

TABLE I

FINAL *p*H VALUES OF HOMOIONIC MONTMORILLONITES

Monovalent ions	*p*H	Divalent ions	*p*H
Li	7.9	Mg	8.0
Na	7.8	Ca	7.0
K	7.6	Sr	7.3
Rb	7.5	Ba	6.8
Cs	7.0		

In order to measure the *c*-axis spacing of montmorillonite by X-ray diffraction at a known water content and in equilibrium with a known pressure of water vapor, a slight alteration in the water adsorption apparatus was made. A set of very thin glass capillaries containing clay were attached as side arms to one of the regular water adsorption tubes. When equilibrium had been attained at any given

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[1] Proctor and Gamble Fellow, 1950–1951.

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[3] R. W. Mooney, A. G. Keenan and L. A. Wood, THIS JOURNAL, **74**, 1367 (1952).

[4] A. G. Keenan, R. W. Mooney and L. A. Wood, *J. Phys. Colloid Chem.*, **55**, 1462 (1951).

[5] The authors are indebted to Mr. Robert T. Martin of the Agronomy Department of Cornell University, for making this titration.