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.

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[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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[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.

pressure, a capillary was detached by fusing off without admitting air and used for X-ray analysis while the water content of the clay was determined on the main sample in the manner previously described.

The capillaries were made of Pyrex tubing drawn down to a rectangular cross-section with the walls as thin as possible and the longer edge of the rectangle about 0.5 mm. in length. They were sealed to larger tubing which in turn was connected to the adsorption apparatus through a ground joint and a stopcock. The arrangement was such that the set of capillaries could be rotated in a vertical plane by means of the ground joint and thus either immersed in the constant temperature bath or raised into the air temporarily for the removal of a single capillary by fusion as required.

The X-ray camera used for the diffraction measurements was a 10-cm. vacuum camera which had been developed for the measurement of long spacings in clays and soaps.[6] The glass capillary containing the clay sample was mounted in a vertical position against a lucite window machined to a thickness of 0.002 mm. with the broad face of the rectangular capillary perpendicular to the X-ray beam. Nickel-filtered copper Kα radiation of 1.54 Å. was used. The X-ray tube was run at 30 kv. and 15 milliamperes. The X-ray beam was collimated by 2 slits placed approximately 20 cm. apart. Exposure times varied from 10 to 48 hours depending upon the thickness of sample and glass capillary. Kodak Industrial X-ray film, Type K was found to give the highest speed. These simultaneous determinations of vapor pressure, water content and *c*-axis spacing were made on sodium, cesium, calcium and barium montmorillonites.

Results

The desorption isotherms of water vapor at 20° on the mono- and divalent montmorillonites are shown in Figs. 1 and 2, respectively. The isotherms show that the exchangeable ion influences the amount of water adsorbed at a given pressure, as well as the general shape of the isotherm.

The amounts of water adsorbed at a given pressure are in the order to be expected from considerations of the size and charge of the exchangeable ions except in the case of Rb and Cs. The differences between these two ions and K are much less than for the other monovalent ions and it would, in fact, be expected that K, Rb and Cs, being monovalent and relatively large, would show low hydrations and therefore be approximately equivalent in water adsorption. Such was found to be the case for kaolinite.[4]

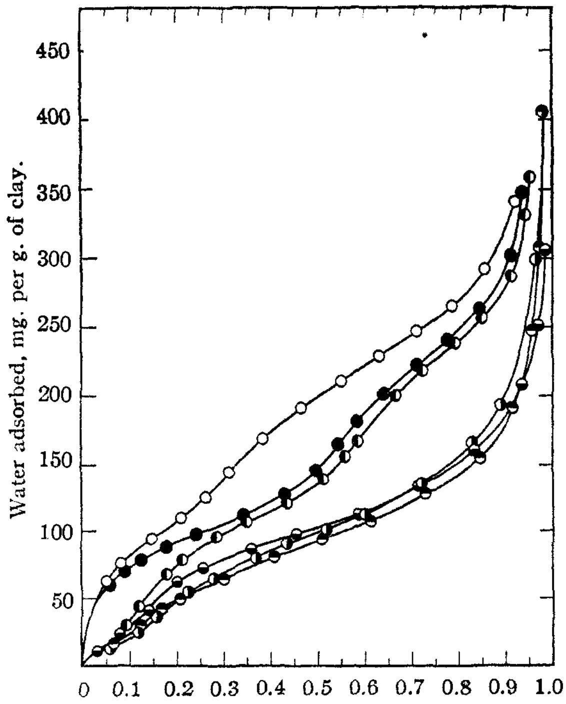

Fig. 1.—The desorption of water on monovalent montmorillonites at 20°: ○, H; ●, Li; ◐, Na; ◑, K; ◓, Rb; ◒, Cs.

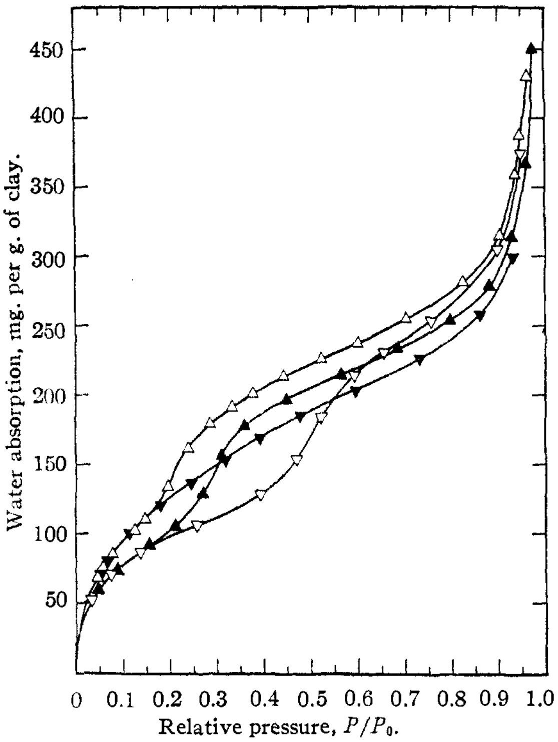

Fig. 2.—The desorption of water on divalent montmorillonites at 20°: ▼, Mg; △, Ca; ▲, Sr; ▽, Ba.

The deviations from the normal order in the case of Rb and Cs montmorillonite, though small, are nevertheless greater than experimental error. No explanation for this is apparent at present but it may be of interest to point out that these same two ionic modifications also give anomalously large nitrogen surface areas. The data are shown in Table II.

Table II

Nitrogen Surface Areas

Ion	Surface area ($m.^2/g.$)
H	44.7
Li	41.0
K	48.5
Rb	64.2
Cs	108
Ba	42.4

Nitrogen adsorption presumably measures only the external surface of aggregates of ultimate platelets, since nitrogen does not cause expansion of the montmorillonite lattice. The aggregates in the case of the dry Rb and Cs clays used in the nitrogen adsorption measurements were therefore smaller than in the case of the other ions. However, the water desorption isotherms were measured by de-

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(6) C. S. Benz, W. Courchene, A. G. Keenan and L. A. Wood, to be published.

sorption from samples nearly saturated with water so that any aggregate structure present in the dry clay would be expected to have been obliterated by penetration of water into the lattice.

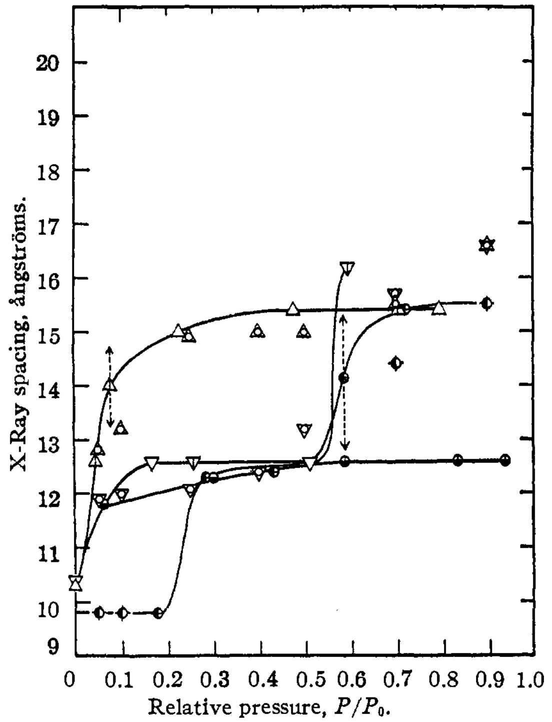

Fig. 3.—X-Ray spacing in montmorillonites as a function of relative pressure: Na: ⊖, desorption; -ϕ-, data of H., N. and A.[7] Cs: ⊖, adsorption; ⊕, desorption; Ca: △, adsorption; ∠|∖, desorption; ◬, data of H., N. and A.[7] Ba: ▽, adsorption; ∇|7, desorption; ⩔, data of H., N. and A.[7]

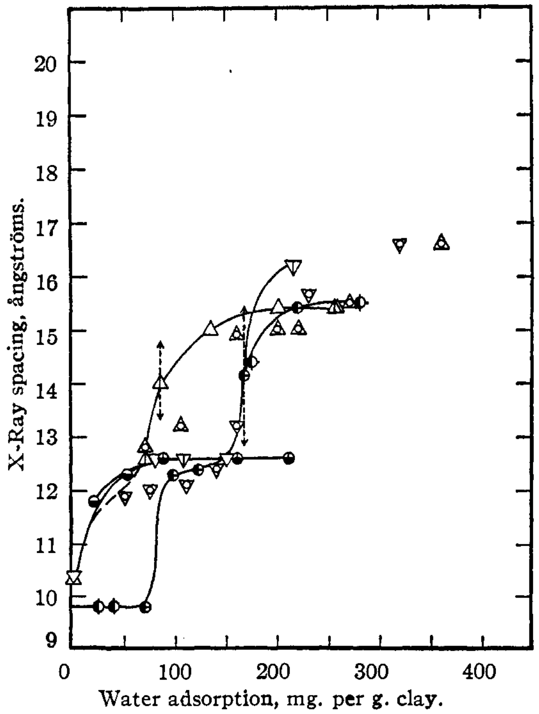

Fig. 4.—X-Ray spacing in montmorillonites as a function of water content: Na: ⊖, desorption; -ϕ-, data of H., N. and A.[7] Cs: ⊖, adsorption; ⊕, desorption; Ca: △, adsorption; ∠|∖, desorption; ◬, data of H., N. and A.[7] Ba: △, adsorption; ∇|7, desorption; ⩔, data of H., N. and A.[7]

Graphs of the *c*-spacing of the lattice plotted against relative pressure and against water content are given in Figs. 3 and 4, respectively. There seems to be no correlation between the observed spacing and whether it was obtained on an adsorption or a desorption curve. Figures 3 and 4 also contain the data of Hendricks, *et al.*[7] The agreement between the two sets of data is quite satisfactory.

Application of the BET Theory to Water Adsorption.—The water desorption data are shown plotted according to the BET equation in Fig. 5.

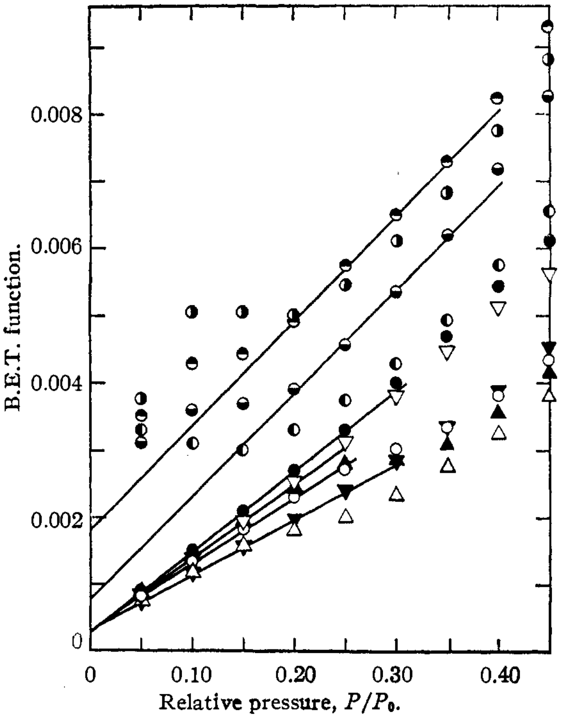

Fig. 5.—BET plots for desorption of water on montmorillonites: ○, H; ●, Li; ◐, Na; ◑, K; ⊖, Rb; ⊖, Cs; ▼, Mg; △, Ca; ▲, Sr; ▽, Ba.

In the case of these particular samples, neither the Na nor K gave straight lines. The BET parameter x_m calculated in the normal manner is given in column 2 of Table III. The range of points included in the calculation is indicated by the straight lines in Fig. 5.

TABLE III

RELATIVE IONIC HYDRATIONS AS COMPARED TO RB AND CS

Ion	x_m, mg./g.	x_m minus av. for Rb and Cs	Molecules of water per exchangeable ion
H	100	40	3
Li	80	20	1
Rb	57		
Cs	62		
Mg	120	60	8
Ca	120	60	8
Sr	90	30	4
Ba	90	30	4

In the previous work on kaolinite,[4] it was found

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

possible to calculate a value for the hydration of the exchangeable ions, *i.e.*, for the number of water molecules clustered around each exchangeable ion. This was arrived at by a comparison of adsorptions on kaolinite samples of different ultimate particle size. It was concluded from the data that the lithium ion, presumably because its size was just right, fitted into the kaolinite lattice and was sterically hindered from influencing the adsorption of water.

A similar procedure is not possible in the case of montmorillonite nor does it seem permissible to assume without experimental verification that lithium ion behaves in the same manner on montmorillonite as it does on kaolinite. An approximate calculation of ionic hydration on montmorillonite can be made, however, by assuming that the Rb and Cs ions are not hydrated, due to their large size and consequent low polarizing power. In the case of kaolinite,[4] these two ions showed the lowest hydration numbers of all the ions studied (about 1 molecule of water per ion), with the exception of lithium ion where a specific factor was operating. The average x_m for Rb and Cs is therefore taken to be the adsorption due to the montmorillonite lattice surface alone and has been subtracted from each of the x_m values for the other ions to give the values shown in column 3 of Table III. These entries therefore represent water adsorption in mg./g. of clay due to hydration of the exchangeable ions, on the basis of the assumptions stated above. The values can be converted to molecules of water per exchangeable ion since the exchange capacity of the clay is known (0.83 meq./g.). These values are shown in column 4 of Table III.

Discussion

The X-ray diffraction data in Figs. 3 and 4 show horizontal sections in three regions: (1) just under 10 Å., (2) between 12 and 13 Å. and (3) between 15 and 16 Å. The accepted interpretation[8] is that these represent spacings in the direction of the *c*-axis for dry montmorillonite and lattices expanded by the presence of one and two layers of water molecules, respectively. The most significant feature of the present X-ray data is the absence of spacings which do not correspond to integral numbers of layers of water molecules between the clay platelets. The only two points which do fall between values for integral layers were actually diffuse bands covering the spacings indicated by the dotted lines in Figs. 3 and 4. This substantiates the conclusion of Bradley, *et al.*[8] that in the case of H montmorillonite the spacing between platelets does not change continuously with water content but only spacings corresponding to integral layers of water molecules between platelets are found. The present results also generalize this conclusion to include the other ions studied.

A comparison of the water desorption isotherms, Figs. 1 and 2, with the X-ray spacings, Figs. 3 and 4, brings out some interesting correlations. In general, a change in the numbers of layers between platelets occurs at the same relative pressure or water content as that at which a change in the slope of the isotherm is taking place. Though the correspondence is not exact, it seems quite definite that the changes in the slopes of the isotherms are due to layer formation between the platelets, as was previously assumed.[3]

The differences in the water desorption isotherms may be explained on the basis of ionic hydration effects. In the case of the monovalent montmorillonites (Fig. 1), it is evident that the water adsorption decreases with increasing size of the exchangeable ions, the differences being negligible for the three largest ions. If in the case of the divalent ions (Fig. 2), the steeply descending portions of the isotherms near the center of the graph represent water coming out of the second adsorbed layer, it is seen that the energy with which this water is held varies inversely with the radius of the ion.

The hydration numbers of the exchangeable ions on montmorillonite, given in column 4 of Table III, are only approximations because of the assumptions necessary in calculating them. The numbers are, however, of a reasonable order of magnitude and the interesting point is that they place the ions in the same order as was previously obtained on kaolinite.[4] This, moreover, is the order that would be predicted from a consideration of ionic size and charge. Such correlations indicate that even in the case of a system as complicated as an expanding-lattice clay, the BET theory, to a first approximation at any rate, is measuring some fundamental property.

The results obtained in the present work agree quite well with those of Hendricks, *et al.*,[7] except for H and Na montmorillonites. The latter authors postulated that neither of these ions hydrated. The present work shows that although Na is slow to hydrate, it hydrates almost as strongly as Li once the plates are separated. The H montmorillonite also shows a very strong hydration even at low relative pressures. The results obtained in the present work seem to be more in agreement with what would be expected for the H and Na ions. The results with Na and Ca montmorillonite are also in good agreement with those of Mering.[9]

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(8) W. F. Bradley, R. E. Grimm and G. L. Clark, *Z. Krist.*, **97**, 216 (1937).

(9) J. Mering, *Trans. Faraday Soc.*, **42B**, 205 (1946).