EQUILIBRIUM THEORY OF THE KAOLINITE–WATER SYSTEM AT LOW MOISTURE CONTENTS, WITH SOME REMARKS CONCERNING ADSORPTION HYSTERESIS

by

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ABSTRACT

A MICROSCOPIC theory of the kaolinite–water system is presented, based upon the assumption that the clay–water interaction may be envisioned as partly hydration of the exchangeable cations and partly adsorption by the oxygen and hydroxyl surfaces. The theory treats exchangeable cation hydration quantum-mechanically as an ion-dipole phenomenon and considers water adsorption by the mineral surface as a problem in hydrogen bonding. A statistical mechanical model incorporating the quantum-theoretical results is then invoked to find the contribution of each component interaction to the initial portion of the adsorption isotherm for homoionic kaolinite. Good agreement between the theoretical calculations and available experimental data is achieved for water vapor adsorption by Li-, Na-, K-, and Mg-kaolinite, without the use of *ad hoc* empirical parameters. The concordance, in turn, is used to suggest that the basis for adsorption hysteresis in kaolinite–water vapor systems is the irreversible transition: mineral surface water → cation hydration water.

INTRODUCTION

IT IS well known that water vapor interacts to a significant degree with dry kaolinite. Perhaps the clearest non-calorimetric demonstration of this fact is the convex form of the adsorption isotherm at low relative vapor pressures, which immediately suggests that the initially adsorbed water molecules bind even more tenaciously to the clay than they do among themselves. Though simple, this qualitative hypothesis is not at all easy to elaborate in a rigorous manner, chiefly because experimental data that can be used to advantage in the development of a microscopic physical model are almost non-existent. This is not to say that a dearth of purely thermodynamic evidence on the kaolinite–water vapor interaction exists (see, for example, Martin, 1962), but

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that the physical meaning of such information is uncertain since the phenomenon under consideration is not reversible. On the other hand, the development of a microscopic theory of the kaolinite–water system should not be intractably difficult. Because irreversibility is not an inherent property of molecular behavior, the microscopic theories of equilibrium and non-equilibrium phenomena possess a common quantum-theoretical foundation. The equilibrium theory thus can serve as a convenient starting point for the formulation of the much more complicated non-equilibrium theory. Such has been the case, for example, with the theory of ferromagnetism. In a similar way, the possibility that a microscopic equilibrium theory of the kaolinite–water system may result in a successful qualitative study of the problem of adsorption hysteresis will be exploited in the present paper.

To simplify our task as much as possible, we shall examine only the clay–water interaction at low moisture contents, where hysteresis effects are minimal. The total interaction will be divided into three component interactions: exchangeable cation hydration, oxygen surface adsorption, and hydroxyl surface adsorption.* These interactions, again consistent with the restriction to low water contents, will be considered independently, according to the following general procedure. A fundamental differential equation is written down for each interaction after an appropriate potential energy function has been postulated. This equation, the time independent Schrödinger equation of quantum mechanics, is then solved in order to get numerical estimates of the permitted energy states for a system interacting as considered. The energy states form an integral part of the next step, which is the development of a statistical mechanical model. The statistical mechanical equations, in turn, permit the calculation of important macroscopic quantities. In particular, we shall examine the influence of each of the three component interactions on the adsorption of water vapor by homoionic kaolinite. From a comparison between our theory and available experimental adsorption data we may be able to come to some conclusions regarding the microscopic nature of the kaolinite–water vapor system and the causes of the adsorption hysteresis it exhibits.

THEORY OF EXCHANGEABLE CATION HYDRATION

The most general and rigorous theoretical treatment of exchangeable cation hydration should take into account both the interaction of water molecules with the ion and the interaction of the ion with the clay mineral. In the absence of detailed information on the microscopic level concerning the latter phenomenon, the development of a theory of ion hydration is

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* It does not follow necessarily that we are neglecting the interaction of water with the edges of particle aggregates. If the particle edges are made up of local oxygen and hydroxyl surface arrays, the description of the water-edge surface interaction may be included in the present theory. It may also be that the edge surfaces make up only a small fraction of the total surface area (Martin, 1959), in which case the problem is vitiated.

indeed a formidable problem unless simplifying assumptions can be made. To this end we shall suppose that the state of water molecules bound to an exchangeable cation shows no explicit dependence upon the way the cation binds to the clay mineral surface. This hypothesis implies the unproven contentions that (a) the process of ion hydration requires an amount of work (done against the potential field binding the ion to its adsorption site) that is much smaller than the ion dehydration energy, and that (b) the bonding of the ion to the clay mineral has negligible covalent character. The theory to be developed here, therefore, must be said to yield an upper limit for the strength of the exchangeable cation-water interaction.

When a single water molecule is near an exchangeable cation, the polar properties of the molecule are likely to play a dominant role in the resulting interaction. Thus it is to be expected that the potential energy function describing the system has approximately the form (Sposito, 1965, pp. 49f)

$$U(\theta, r) = \frac{z^2 e^2 a}{6\epsilon^2 r_e^4} \left[\left(\frac{r_e}{r}\right)^{12} - 3 \left(\frac{r_e}{r}\right)^4 \right] - \frac{ze\mu}{\epsilon r^2} \cos \theta \qquad (1)$$

where r is the distance separating the cation and the water molecule, r_e is the equilibrium separation in the absence of dipole-cation interactions, ze is the charge on the cation, ϵ is the dielectric constant of the water molecule arising from electronic and nuclear polarizations alone, a is the polarizability of the water molecule, μ is the dipole moment of the water molecule, and θ is the angle between the coulomb field vector of the cation and the dipole moment vector of the water molecule. The three terms in equation (1) represent repulsive, ion-induced dipole, and ion-dipole interactions, respectively. A more accurate potential function would take into account ion-quadrupole and, perhaps, even ion-octupole interactions as well; but these are of minor significance compared to the ion-dipole interaction. Besides the cation-dipole interaction, the internal motions of the water molecule must be considered in setting up the Schrödinger equation. These are: rotation about the axis of symmetry and vibration of the nuclei relative to the center of mass of the molecule. The complete time-independent Schrödinger equation for an exchangeable cation and a single water molecule of total energy E then may be written as

$$- \frac{\hbar^2}{2\mu_o} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \phi^2} \right\}$$

$$+ \left\{ \frac{z^2 e^2 a}{6\epsilon^2 r_e^4} \left[\left(\frac{r_e}{r}\right)^{12} - 3 \left(\frac{r_e}{r}\right)^4 \right] - \frac{ze\mu}{\epsilon r^2} \cos \theta \right\} \psi(\boldsymbol{r}, \phi, \boldsymbol{q_1}, \boldsymbol{q_2}, \boldsymbol{q_3})$$

$$- \frac{\hbar}{2I} \frac{\partial^2 \psi}{\partial \phi^2} - \sum_{l=1}^{9} \left\{ \frac{\hbar^2}{2} \frac{\partial^2 \psi}{\partial q_l^2} - \frac{1}{2} \lambda_l q_l^2 \psi \right\}$$

$$= E \psi(\boldsymbol{r}, \phi, \boldsymbol{q_1}, \boldsymbol{q_2}, \boldsymbol{q_3}) \qquad (2)$$

where $\hbar$ is Planck's constant divided by 2π, μ_0 is the reduced mass of the cation-water molecule system, I is the equilibrium moment of inertia of the

water molecule about its axis of symmetry, ϕ is the angle of rotation about that axis, q is the normal displacement vector for the three nuclei in the water molecule relative to their center of mass, and λ is the square of the angular normal vibration frequency of the water molecule. The absolute value of the square of the wave function ψ is interpreted as a probability distribution function of the coordinates r, ϕ, q_1, q_2, and q_3. Equation (2) is immediately separable into thirteen differential equations of the second order whose separation constants, save for the one appearing in the equation in the coordinate ϕ, are equal to the components of the permitted energy states of the system. Eleven of the equations are easily solved (Herzberg, 1945, pp. 204 ff; Sposito, 1965, pp. 52 f). The remaining pair are

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\,\theta\,\frac{dp}{d\theta}\right) + \left\{\frac{2\mu_0 r_e^2}{\hbar^2}\,E_\theta - \frac{k^2}{\sin^2\theta} + \frac{2ze\mu\mu_0}{\epsilon\hbar^2}\cos\,\theta\right\}P(\theta) = 0 \qquad (3)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{z^2e^2a\mu_0}{3\epsilon^2 r_e^4\hbar^2}\left[\left(\frac{r_e}{r}\right)^{12} - 3\left(\frac{r_e}{r}\right)^4\right]$$
$$- \frac{2\mu_0}{\epsilon\hbar^2}\left[E_T - \left(\frac{r_e}{r}\right)^2 E_\theta\right]R(r) = 0 \qquad (4)$$

where E_θ is the angular component of E_T, the total energy of the cation-dipole interaction, and k^2 is the integral separation constant for the equation in the ϕ coordinate. Equations (3) and (4) are solved approximately by expanding, in Taylor series, $\cos\,\theta$ to second order in θ and $[(r_e/r)^{12}-3(r_e/r)^4]$ to second order in $(r - r_e)$ (Sposito, 1965, pp. 53–66). For the total energy of the system one then finds

$$\left.\begin{aligned}
& E = E_l + E_m + E_p + E_p, \qquad E_p = \hbar^2\,p^2/2I \\
& E_l = \frac{\hbar^2}{6\mu_0 r_e^2}\left\{\left(5l^2 - \frac{6ze\mu\mu_0}{\epsilon\hbar^2}\right) + \left[\left(5l^2 - \frac{6ze\mu\mu_0}{\epsilon\hbar^2}\right)^2\right.\right. \\
& \qquad\qquad\qquad\qquad \left.\left. - \frac{36z^2e^2\mu^2\mu_0^2}{\epsilon^2\hbar^4} + 96l^2\,\frac{ze\mu\mu_0}{\epsilon\hbar^2}\right]^{1/2}\right\} \\
& E_m = \sum_{i=1}^{3}(m_i + \tfrac{1}{2})\,h\nu_i \qquad E_n = \frac{-z^2e^2}{3\epsilon^2 r_e^4} + (n + \tfrac{1}{2})\,h\nu_e
\end{aligned}\right\} \qquad (5)$$

where

$$\nu_e = \frac{1}{2\pi}\frac{ze}{\epsilon r_e^3}\left(\frac{48a}{\mu_0}\right)^{1/2}$$

is the vibration frequency of the cation-dipole system along the radial coordinate, ν_i is the ith normal vibration frequency of the free water molecule, and the integers l, m, n, and p are subject to

$$1 \leqslant l < \frac{1}{4}\left(\frac{6ze\mu\mu_0}{\epsilon\hbar^2}\right)^{1/2}; \quad 0 \leqslant m \leqslant \infty; \quad 0 \leqslant n \leqslant \infty; \quad -\infty \leqslant p \leqslant \infty$$

A statistical mechanical model of exchangeable cation hydration may be developed next by considering the cations as independent entities and the water molecules binding to them to be mutually noninteracting. The latter assumption is reasonable since the molecules cannot hydrogen bond to one another if they are strongly oriented about the cation. Now suppose there are M independent, distinguishable cations, each capable of binding up to m water molecules. The grand canonical partition function for this system is (Hill, 1960, p. 131)

$$\Xi\,(T,\,M,\,\mu) = \exp\,(-\,\Omega_s/kT) = \sum_{N=0}^{\infty} Q_N\,(T,\,M)\,\lambda^N \tag{6}$$

where

$$\Omega_s = U_s - S_s T - \mathscr{N}_s \mu \tag{7}$$

is the grand canonical potential* (U being the internal energy, S the entropy, T the absolute temperature, $\mathscr{N}$ the mole number, and μ the chemical potential), k is Boltzmann's constant,

$$\lambda = \exp\,(\mu_P/kT)$$

is the absolute activity, μ_P is the chemical potential per molecule, N is the number of water molecules, and

$$Q_N\,(T,\,M) = \sum_{\{a_S\}} M!\,\frac{[q(S,\,T)]^{a_S}}{a_S!} \tag{8}$$

In equation (8), a_S is the number of cations binding s water molecules, the sum $\sum_{\{a_S\}}$ being over all possible sets of the a_S such that

$$\sum_{s=0}^{m} a_S = M$$

is fulfilled and $q(s,\,T)$ is the partition function for the interaction of s water molecules with a cation. Using equation (8), the multinomial theorem, and the conservation condition

$$\sum_{s=0}^{m} Sa_S = N$$

equation (6) may be written

$$\exp\,(-\,\Omega_S/kT) = \sum_{\{a_S\}} M!\,\frac{[q(s,\,T)\,\lambda^s]^{a_S}}{a_S!} = \left[\sum_{s=0}^{m} q(s,\,T)\,\lambda^s\right]^{M} \tag{9}$$

* The thermodynamic meaning of equation (7) is that Ω_S represents the difference between Ω for a system, at temperature T, composed of water vapor and an interfacial condensate ("adsorbed water") in a volume V at chemical potential μ and Ω_V for a system composed of water vapor alone in the same volume at the same chemical potential (Sposito, 1965, Chap. 1). Thus $\Omega_S = \Omega - \Omega_V$, $U_S = U - U_V$, etc., refer essentially to thermodynamic properties engendered by the presence of an interfacial condensate.

Since the water molecules do not interact with one another,

$$q(s, T) = \frac{m!}{s! \, (m - s)!} \, [q(T)]^s \tag{10}$$

where $q(T)$ is the partition function for the single water molecule-cation interaction:

$$q(T) = \sum_{l=1} e^{-El/kT} \sum_{m=0} e^{-Em/kT} \sum_{n=0} e^{-En/kT} \sum_{p=0} e^{-Ep/kT} \tag{11}$$

where the E are components of the permitted energy states of the system, calculated from equation (5). Thus, with the binomial theorem, equation (9) can be written in the form

$$\Omega_S = - \, kT \ln [1 + q(T) \, \lambda]^{mM} \tag{12}$$

differential form of equation (7) shows that

$$\mathscr{N}_S = - \left(\frac{\partial \Omega_s}{\partial \mu} \right)_{T, \, M} = N_S/N_0$$

where N_0 is Avogadro's number. Therefore,

$$\frac{N_S}{mM} \equiv \theta = \frac{q(T) \, \gamma}{1 + q(T) \, \lambda} = \frac{q(T) \exp (\mu^0 p/kT) \, P/P_0}{1 + q(T) \exp (\mu^0 p/kT) \, P/P_0} \tag{13}$$

since, for microscopic equilibrium,

$$\lambda(\text{interfacial condensate}) = \lambda(\text{vapor}) = \exp (\mu^0 p/kT) \, P/P_0$$

In equation (13), μ_p^0 is the chemical potential per water molecule in the ideal vapor and P/P_0 is the relative vapor pressure. The equation itself has the form of the well-known Langmuir adsorption isotherm.
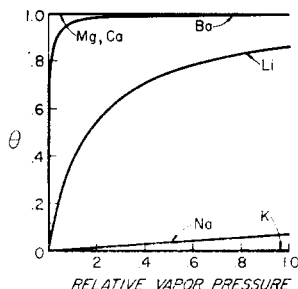

FIG. 1. Reduced theoretical adsorption isotherms at 25°C for six cation-water vapor systems.

Figure 1 shows plots of equation (13) for six exchangeable cation–water systems at 25°C. The values of $q(T)$ and μ_p^0 were calculated on an IBM 7090 digital computer using equations (5) and (11), the statistical mechanical definition of μ_p^0 (Hill, 1960, pp. 166 f), and the physical constants listed in Table 1. It can be seen that Mg^{2+} and Ca^{2+} ions have complete monolayer

TABLE 1.—PHYSICAL CONSTANTS USED IN THE THEORY OF THE
KAOLINITE–WATER VAPOR INTERACTION

Symbol	Value	Source
μ	1.854×10^{-18} esu-cm	Sposito, Appendix II
a	1.510×10^{-24} cm^3	Sposito, Appendix II
ε	3.1 cgse	Auty and Cole
I	2.947×10^{-40} g-cm^2	Herzberg
$h\nu_1/k$	$5239°$K	Herzberg
$h\nu_2/k$	$2288°$K	Herzberg
$h\nu_2/k$	$5388°$K	Herzberg
$h\nu_{H1}/k$	$4524°$K	Ockman
$h\nu_{H2}/k$	$2366°$K	Fox and Martin
$h\nu_{H3}/k, h\nu_H/k$	$4690°$K	Fox and Martin
$h\nu/k$	$5252°$K	Ledoux and White
$h\nu_0/k$	$149.6°$K	
E_{vw}	-760 cal	Rowlinson
E_{HB}	-5.75 kcal	Sposito
R_e	2.73Å	Sposito
$r_{H2}O$	1.33Å	Rowlinson
r_{Li}^+	0.60Å	Pauling
r_{Na}	0.97Å	Ahrens
r_K^+	1.33Å	Ahrens
r_{Mg}^{2+}	0.66Å	Ahrens
r_{Ca}^{2+}	0.99Å	Ahrens
r_{Ba}^{2+}	1.34Å	Ahrens

hydration shells at all measurable relative vapor pressures. The shell for Ba^{2+} ion is complete when p/p_0 is 0.2. However, Li$^+$ ion is able to hydrate only to the extent of 0.86 monolayer over the entire range of relative pressures, while Na$^+$ and K$^+$ remain virtually unhydrated. The results, except for those on Li$^+$–H$_2$O, are in good qualitative agreement with the conclusions of Martin (1959) and Jurinak (1963), who studied the adsorption of water vapor by homoionic kaolinite. The experimentally observed behavior, toward water vapor, of exchangeable Li$^+$ on kaolinite is anomalous in that this ion evidently is able to remain unhydrated because of some unknown, specific cation-clay mineral bonding mechanism (Keenan *et al.*, 1951; Martin, 1959). Apparently this mechanism is less operative if, before contact with water vapor, the sample of kaolinite is degassed at 25°C under a pressure of 10^{-5} mmHg (Kohl *et al.*, 1964) than if it is degassed at 65° or 70°C under the same pressure (Martin, 1959; Jurinak, 1963): in the former case ion hydration appears to be taking place by at least 0.2 relative vapor pressure. This behavior, of course, is more in agreement with what is shown in Fig. 1. On the other hand, since the explanation suggested for the hydration behavior of exchangeable Li$^+$ involves a violation of one of our basic assumptions, that there is no explicit dependence of the state of cation hydration upon the cation-clay mineral bonding mechanism, it is not surprising that

the present theory fails to predict directly what is observed in practice. Moreover, the fact that the ions Na^+, K^+, and Li^+ (in certain instances) do finally hydrate on kaolinite at relative pressures near one (Martin, 1959; Jurinak, 1963) is no contradiction of the theory, because the exchangeable cations on a wet clay interact directly with the mineral surface hydration water rather than with water vapor. For such an interaction, equation (2) must be replaced by a many-body Schrödinger equation which includes intermolecular potential functions for the water molecules as well as the cation-water potential function. It is clear that the expression for the energy states will have a form much different from that of equation (5) and that the results obtained here are not applicable.

THEORY OF MINERAL SURFACE HYDRATION

Adsorption by the Oxygen Surface

The interaction between water vapor and the mineral surface of kaolinite may be viewed essentially as a problem in hydrogen bonding. For, a water molecule confronted by the oxygen or the hydroxyl surface of the clay should behave not very differently from the way water molecules do in general behave when near oxygen or hydroxyl atoms. It would seem that at low water contents the configuration in which two hydrogen bonds are formed is the one of lowest potential energy for the binding of a single water molecule with an oxygen surface. An arrangement both geometrically simple and compatible with the structure of the kaolinite surface is shown in Fig. 2. For an intramolecular bond angle of $109.5°$ and a hydrogen bond length of $2.8\,\text{Å}$, the distance between points of contact of the water molecule with the surface hexagonal array is $4.54\,\text{Å}$—close to the $4.85\,\text{Å}$ separating the centers of next-nearest-neighbor oxygen atoms ($2.8\,\text{Å}$ in diameter).
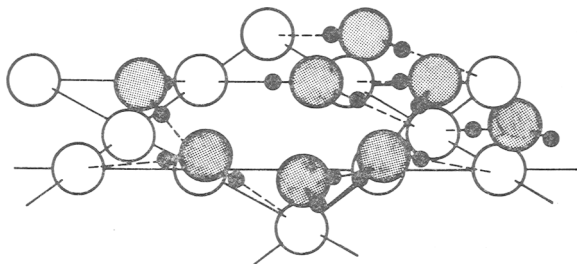

FIG. 2.—Postulated arrangement of water molecules in the first adsorbed layer on an oxygen surface.

The Schrödinger equation describing the interaction between a single water molecule and the oxygen surface will contain terms representing the motion of the hydrogen atoms in the water molecule, both in their intramolecular vibrations and their bonding to the kaolinite oxygen atoms, and

terms for the van der Waals interaction between molecular and crystalline oxygen atoms. A straightforward but tedious analysis shows that the hydrogen bonding contributes just one energy state to the interaction (Sposito, 1965, pp. 84–88). The intramolecular vibrations may be dealt with as before. The van der Waals interaction leads to an equation similar to equation (4), but with an inverse sixth power attraction term; the analysis, however, proceeds in the same way as for that equation. The total energy of the system is then found to be

$$E = E_r + E_s + 2E_{HB}$$
$$= \sum_{j=1}^{3} (r_j + \tfrac{1}{2}) h\nu_H j + 2E_{vw} + (2s + 1) h\nu_0 + 2E_{HB} \tag{14}$$

where E_{vw} is the potential minimum van der Waals energy,

$$\nu_0 = \frac{1}{2\pi R_e} \left(\frac{-144\,E_{vw}}{m_0} \right)^{1/2}$$

R_e being the equilibrium separation of a water molecule from a surface oxygen atom and m_0, the mass of an oxygen atom; ν_{Hj} is the jth normal vibration frequency of the hydrogen-bonded water molecule, E_{HB} is the dissociation energy of the hydrogen bond (without van der Waals energy contributions), and the r and s are integers subject to $0 \leqslant r \leqslant \infty$, $0 \leqslant s \leqslant \infty$.

Because the water molecules depicted in Fig. 2 are mutually non-interacting, the statistical mechanical model developed in the foregoing section may be used in the present case by identifying M as the number of surface oxygen atoms (with $m = 1$). The resulting adsorption isotherm is identical in form with equation (13).

Adsorption by the Hydroxyl Surface

As with the water molecule binding to an oxygen surface, the configuration of lowest potential energy for the water–hydroxyl surface interaction would seem to be the one in which two hydrogen bonds are formed. The monolayer structure suggested in Fig. 3 features two molecule-surface bonds and is such as not to place too great a strain on the water molecule. The Schrödinger equation for this system is much the same as that for the water–oxygen surface association, but for one important exception: in order to describe the water–hydroxyl surface interaction the model system must include the adsorbent. This is made necessary by the fact that hydrogen bond formation involves the clay structure hydroxyls, rather than those of the water molecule. The total energy of the system turns out to be

$$E = E_m + E_s + 2E_{HB} + E_t$$
$$= \sum_{i=1}^{3} (m_i + \tfrac{1}{2}) h\nu_i + 2E_{vw} + (2s + 1) h\nu_0 + 2E_{HB} + (t + \tfrac{1}{2}) h\nu_H \tag{15}$$
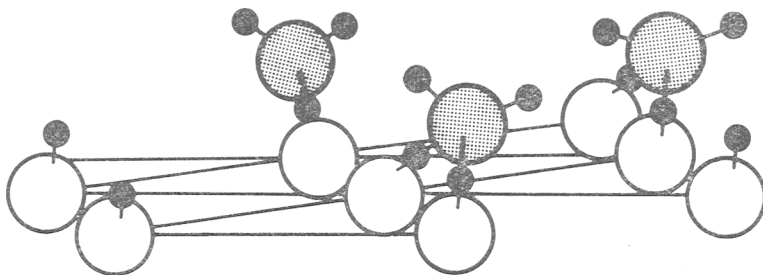
FIG. 3.—Postulated arrangement of water molecules in the first adsorbed layer on an hydroxyl surface.

where the first four terms have their previous meanings and ν_H is the vibration frequency of the hydrogen-bonded clay structure hydroxyls. The statistical mechanical analysis given earlier is again applicable if M is considered to be the number of pairs of surface hydroxyls and the microscopic equilibrium condition

$$\lambda(\text{interfacial condensate} + \text{kaolinite}) = \lambda(\text{vapor}) + \lambda(\text{kaolinite})$$

is imposed. The adsorption isotherm is then

$$\theta = \frac{q(T) \exp \left[(\mu^0 p + \mu H)/kT\right] P/P_0}{1 + q(T) \exp \left[(\mu^0 p + \mu_H)/kT\right] P/P_0} \tag{16}$$

where μ_H is the (additive) contribution of the non-hydrogen-bonded surface hydroxyls to the chemical potential of kaolinite:

$$\mu_H = \frac{h\nu}{2kT} + \ln \left[1 - \exp\left(- h\nu/kT\right)\right]$$

where ν is the vibration frequency of the free surface hydroxyl atoms.

Figure 4 shows plots of equations (13) and (16) for systems at room temperature. The values of $q(T)$, $\mu_p{}^0$ and μ_H were calculated as before on the
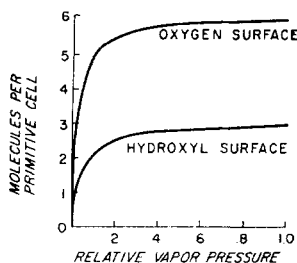

FIG. 4.—Theoretical adsorption isotherms at 25°C for the mineral surface-water vapor system.

IBM 7090 using the physical constants in Table 1. The data given there for the ν_{Hj} are actually the vibration frequencies observed for ice, used as a first approximation. It is apparent from the figure that both kinds of mineral surface have a relatively high affinity for water vapor: monolayers on the two are essentially complete by 0.4 relative vapor pressure.

APPLICATION OF THE THEORY TO THE KAOLINITE–WATER SYSTEM

We shall now undertake a detailed calculation on the kaolinite–water vapor system using the results obtained during our studies of exchangeable cation and mineral surface hydration.

Mg-Kaolinite

According to theory, each exchangeable cation on Mg-kaolinite is hydrated by at least six water molecules* at all measurable relative vapor pressures. Therefore, the contribution of exchangeable cation hydration to the adsorption isotherm (at low water contents) is a constant. The contributions from mineral surface hydration may be obtained from Fig. 4 and a knowledge of the appropriate M values. The value of M for the hydroxyl surface will be assumed to be half that for the oxygen surface. The latter figure is calculated by subtracting from the total surface area of the clay the surface area taken up by the trios of water molecules (16.7 Å² per trio) forming the lower half of the cation hydration octahedra and dividing this figure by two, then by the area per adsorption site (7.65 Å²).
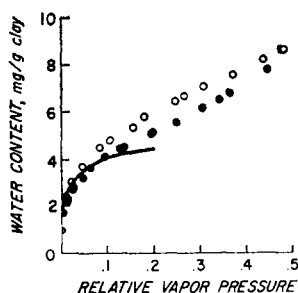

FIG. 5.—Water vapor adsorption (●) and desorption (○) isotherms for Mg-kaolinite at room temperature (Martin, 1959). The line represents the theoretically calculated isotherm.

Figure 5 displays a portion of the adsorption and desorption data obtained by Martin (1959) at 25.5°C for Mg-kaolinite. The line through the datum points was calculated using Figs. 1 and 4 and the values 0.027 me/g and

* The radius ratio of the magnesium ion with the water molecule predicts octahedral coordination in the hydrate.

13 m²/g reported by Martin as the cation exchange capacity and specific surface area of his sample. Since the present theory may tend to overestimate somewhat the strength of the exchangeable cation-water vapor interaction, as mentioned earlier, it seems proper to conclude that the theoretical curve in Fig. 5 conforms with the *adsorption isotherm* for relative pressures in the range $0 \leqslant p/p_0 \leqslant 0.1$.

The success of our theory for Mg-kaolinite leads us to conclude that the exchangeable Mg^{2+} ions hydrate fully upon the first exposure of the clay to water vapor, while the initial layer of mineral surface water fills in more slowly as the relative vapor pressure increases. Because the calculated adsorption isotherm was derived from an equilibrium theory, it would seem that irreversibility in the Mg-kaolinite–water vapor interaction does not exert too important an influence at low relative pressures. On the other hand, Martin's work (1959) showed in a direct way that hysteresis in kaolinite–water vapor systems is related to exchangeable cation hydration. Thus, it may be that in the present case hysteresis comes about through hydration of the exchangeable cations beyond the initial, *reversibly added* amount of six water molecules per ion. However, the additional cation hydration water cannot come for long from the vapor phase, since direct access to the latter would be prevented by the multilayers building up on the mineral surface with increasing relative vapor pressure. The newly acquired cation hydration water, therefore, must be taken largely from the mineral surface water itself. Now, this speculation lies comfortably within the general model of hysteresis developed by Everett and co-workers (1952, 1954). According to Everett, hysteresis in surface phenomena occurs whenever at least two different states are accessible to the adsorbate molecules, the transition from state to state being irreversible in the thermodynamic sense. On Mg-kaolinite, the two states may be designated as cation hydration and mineral surface hydration; the irreversible transition is evidently

$$\text{mineral surface water} \rightarrow \text{cation hydration water} \qquad (17)$$
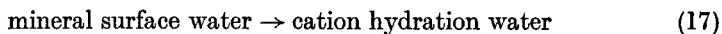
It is not hard to see that if the cation hydration water does not return to its former state at the same relative vapor pressure at which it was formed, the desorption isotherm will lie above the adsorption isotherm, as is always observed. More remains to be said, but first let us turn to other examples of the kaolinite–water vapor system in order to verify the suppositions advanced thus far.

K- and Na-Kaolinite

Martin's data (1959) indicate that water vapor adsorption by K-kaolinite is completely reversible in the range of relative pressures $0 \leqslant p/p_0 \leqslant 0.2$. This fact suggests that the exchangeable potassium ions are always unhydrated at low relative pressures, in agreement with what is predicted in Fig. 1. Therefore, the initial part of the adsorption–desorption isotherm for

K-clay should be calculable by using Fig. 4 with the method and data given in the preceding section. There is, however, no correction to the total surface area for ion hydration water as in the case of Mg-kaolinite.* The theoretical curve together with Martin's data are shown in Fig. 6. The good agreement between experiment and theory is convincing evidence that the water vapor–mineral surface water transition is reversible and that the *irreversible* transformation of the latter water is correctly portrayed in the expression (17).

What is observed experimentally for the K-kaolinite–water vapor system is also found when the clay is saturated with Na^+ ions, but over a smaller range of relative pressures. Thus an adsorption-desorption isotherm can be predicted for Na-kaolinite in precisely the same way as done for K-kaolinite if the very small amount of Na^+ ion hydration water is ignored. The result is shown in Fig. 7. That a single theoretical adsorption isotherm satisfactorily describes the reversible behavior in both K- and Na-kaolinite–water vapor systems is again compelling evidence in support of our hypothesis on the cause of adsorption hysteresis.
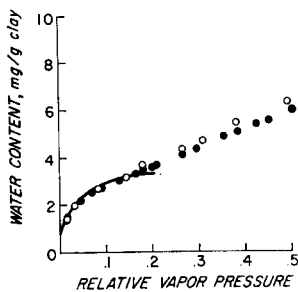

FIG. 6.—Water vapor adsorption (●) and desorption (○) isotherms for K-kaolinite at room temperature (Martin, 1959). The line represents the theoretically calculated isotherm.
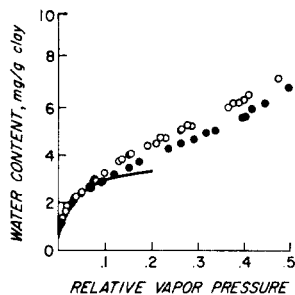
FIG. 7.—Water vapor adsorption (●) and desorption (○) isotherms for Na-kaolinite at room temperature (Martin, 1959). The line represents the theoretically calculated isotherm.

Li-Kaolinite

The anomalous hydration behavior of the exchangeable cations on Li-kaolinite, noted earlier, can provide a unique test of our theory. The experimental adsorption data evidently should follow the same theoretical curve as do the data for K- and Na-kaolinite, while the desorption isotherm should, at its lower end, follow the theoretical curve to which the adsorption data would have conformed had the exchangeable ions hydrated as expected. A little care is required when computing the desorption isotherm because the M values for mineral surface adsorption will each be increasing as the

* The exchangeable cations are assumed to lie in the cavities of the oxygen surface and thus to take up no space on the planar faces of the kaolinite crystal.

relative pressure decreases, depending upon the extent to which the Li^+ ion has dehydrated. One may then follow the usual procedure, at each point on the desorption curve subtracting from the total surface area the area taken up by the octahedrally coordinated ion hydration water, and then dividing by $2 \times 7.65 \text{Å}^2$ to get M for the oxygen surface. This done, the curves in Fig. 8 are obtained, which, except for their behavior at the lowest relative vapor pressures, tend further to substantiate our point of view.
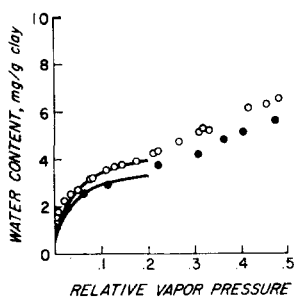

FIG. 8.—Water vapor adsorption (●) and desorption (○) isotherms for Li-kaolinite at room temperature (Martin, 1959). The lines represent the theoretically calculated isotherms.

CONCLUSIONS

It would be naive to claim that the present theory gives a completely satisfactory account of the kaolinite–water vapor interaction. Undoubtedly the rather close agreement between the theory and experiment is in part the result of a fortuitous mutual cancellation of errors in principle and application. However, it does seem reasonable to conclude that, *at low moisture contents*, the exchangeable cation-water interaction is to a large degree an ion-dipole phenomenon, and that strong hydrogen bonding plays a major role in determining the configuration of water molecules on the mineral surface of kaolinite. The extent to which this statement applies to adsorbed water at moderate and high relative vapor pressures is not known with certainty at the present time. Indeed, a detailed solution of the problem requires no less than a microscopic non-equilibrium theory. The theory should include, in a natural way, the transition postulated to be the cause of adsorption hysteresis. This problem seems exceedingly difficult to resolve at the present time. One reason for this, as suggested in the Introduction, is that the bulk of the literature on clay–water vapor systems has been pre-occupied with questionable thermodynamic studies rather than with experiments whose results demand a strictly microscopic interpretation. More work, for example, is needed on the structure of adsorbed water, perhaps along the lines of the X-ray diffraction studies carried out by Longuet-Escard *et al.* (1960). A calorimetric study of the process of irreversible ex-

changeable cation hydration on monovalent ion-saturated clays would seem useful, as would be estimates of the amount of cation hydration water as a function of relative vapor pressure. The latter information might be obtained using nuclear magnetic resonance techniques. It is to be hoped that, with this kind of empirical background, a strong and convincing hypothesis can be found to guide the theory of clay–water systems to a successful conclusion.

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