Application of Electrostatic Models to the Colloidal Behavior of Plate-shaped Particles

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The approach to many colloidal problems has usually been based on the equilibrium assumption, that is, of a Boltzmann distribution of ions around the macromolecular surface in question. It would appear however, that certain electrostatic models may give only an approximate but yet more useful description of systems which possess some symmetry. The two methods are in a way analogous to the equilibrium and orbit theories of plasma physics.

While the use of electrostatic models seems to be valid only for perticle-particle separations which are no greater than 20 to 30Å, it is precisely in this region that the equilibrium approach fails catastrophically.

The idea of specific attractive forces between the counter ions and charged macromolecules was first proposed by Langmuir.[1] He first considered the colloid system as a whole instead of the two interacting particles. This approach has been severely criticised by Verwey and Overbeek (Ref. 2, p. 195). Actually, as will be seen in the present work, where two particles are considered with the aid of an electrostatic model, fairly good results are obtained.

Langmuir[1] believed that unipolar coacervation was due to Coulomb forces and suggested that a repulsive force, possibly hydration, was needed in order to counter-balance the tendency of the colloid system as a whole to contract under the influence of attractive Coulomb forces. This casts serious doubt on the exact role of the long-range London-van der Waals attractive force.

That this repulsive force has eluded most investigators has been due mainly to two factors: The belief that the Boltzmann distribution of ions always exists, and the gross simplification of treating the macromolecule either as a conductor or as a point charge. It is well known that, even for fairly ideal systems, such as are found in the gas phase, the first assumption has been found to fail. Now, to regard the macromolecule as a point charge means to ignore the important surface and dipole effects, while the assumption that it is a conductor is equivalent to assigning a value of infinity to the dielectric constant. This last factor will be shown to be of considerable importance.

As has been pointed out by McEwan[3] and Norrish[4], for small separations of two large plate-shaped particles the counter ions may be

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[1] I. Langmuir, *J. Chem. Phys.*, **6**, 873 (1938).

[2] E. J. W. Verwey and J. T. G. Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier Publishing Co. Inc., New York (1948).

[3] D. M. MacEwan, *Nature*, **162**, 935 (1948).

[4] K. Norrish, *Discussions Faraday Soc.*, **18**, 120 (1954).

regarded as being ordered between the particles. The counter ions may, therefore, be considered to a first approximation as having specific areas of interaction with additive effects, quite analogous to the specific orbits describing the interactions in plasma physics. Derjaguin[5] makes a similar assumption concerning the volume elements of polarization which he justifies for small particle-particle separations. The main requirement for this model to hold is that the macromolecules should have relatively large surface areas per counter ion. While edge effects are important, montmorillonite or vermiculite platelets with surface areas of the order of millions of square angstroms[6] should be very suitable systems for treatment in the crystalline region of swelling.

Recently Jordine, Bodman and Gold[6] and Jordine[7] have applied the method of the electrostatic images of an infinite dielectric slab to montmorillonite systems. Only an approximate solution was obtained, however, since several terms were ignored. A rigorous solution of a point charge located between two charged slabs of dielectric will now be given. It will be seen that a repulsive image force arises quite naturally, and in such a way as to contribute to a minimum in the potential energy curve. A major problem, however, is that of assigning the correct effective dielectric constant to the intervening solvent medium. Nevertheless, as in Ref. 6 and Ref. 7, dielectric saturation has been taken into account.

The problem will be solved for the midway position[*1] of the charge between the dielectric slabs. It will also be outlined how a generalised crystal lattice theory of images can be developed to treat the system as a whole without making any assumptions concerning specific areas of interaction by the interlayer ions.

Lastly, a detailed theory of the mechanism of swelling will be proposed.

A Statement of the Problem of the Point Charge between Two Charged Dielectric Slabs (Montmorillonite, Vermiculite, Mica). — As a starting point for the model, consider that in Fig. 1 of Ref. 6 another platelet is placed symmetrically so as to form a plane ($-2D$, yz). This will be quite similar to Norrish's model (Ref. 4, Fig. 8) except that the platelets are not regarded as conductors.

In terms of electrostatics, the problem may be stated as the interaction between two dielectric interfaces and an array of charges. Thus, we have for $x<-2D$ and $x>0$ two regions mL and mR respectively of the dielectric constant K_m, while there is for $-2D<x<0$ a region w of the dielectric constant K_w. A set of point charges is located along the plane $x=-D$, and the interfaces $x=-2D$ and $x=0$ have a uniform surface charge of density, σ. We shall, for purposes of simplification in what follows, regard the interaction of the point charges as additive and, hence, consider only a given point charge e^* located at $(-D, 0, 0)$. In other words, we will consider a cell model, as has been discussed in the introduction.

A Solution of the Problem.—The differential equations which must be solved to obtain the potential V and, hence, the electrostatic energy of interaction are:

$$\nabla^2 V=0 \tag{1}$$

in the regions mL and mR and

$$\nabla^2 V=-\frac{4\pi}{K_w}\sum_{j=1} e_j^*\delta(x+D)\delta(y-y_j)\delta(z-z_j) \tag{2}$$

in the region w.

Since we are interested in a single cell, we may consider only one point charge; therefore, Eq. 2 may be written as:

$$\nabla^2 V=-\frac{4\pi}{K_w}\sum e_j^*\delta(x+D)\delta(y)\delta(z) \tag{3}$$

In addition to satisfying Eqs. 1 and 2, the potential must satisfy the usual electrostatic boundary conditions at the interfaces and at infinity.[6]

Since Eqs. 1 and 2 are linear, by a well-known theorem the potential can be written as $V=V_i+V_\sigma$, where V_i denotes the potential due to the point charge and its images, and V_σ, that due to the surface charge. We can choose V_σ as follows:

$$\left.\begin{aligned} V_\sigma&=\frac{2\pi\sigma x}{K_w} && -D<x<0\\ &=-\frac{2\pi\sigma x}{K_m} && 0<x<\infty\\ &=-\frac{2\pi\sigma(2D+x)}{K_w} && -2D<x<-D\\ &=\frac{2\pi\sigma(2D+x)}{K_m} && -\infty<x<-2D \end{aligned}\right\} \tag{5}$$

Strictly speaking, since the platelets are only effectively infinitive, V_σ must be cut off for x at a value sufficiently large so that it tends to zero as x tends to ∞.

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[5] B. V. Derjaguin, ibid., **18**, 85 (1954).

[6] E. St. A. Jordine, G. B. Bodman and A. H. Gold, *Soil Sci.*, **94**, 371 (1962).

[7] E. St. A. Jordine, ibid., **96**, 149 (1963).

[*1] In a forthcoming paper (Hurst and St. A. Jordine, *J. Chem. Phys.*, **41**, November 1 (1964)) it is shown that the midway position is favored energetically. See also experimental studies by Brown.[8]

[8] G. A. Brown, *Mineralog. Soc. Gr. Britain Clay Mineral Bull.*, **4**, 109 (1950); Quoted in R. E. Grim, "Clay Mineralogy," McGraw-Hill Book Co. Inc., New York, Toronto, London (1953), p. 134.

Applying the method of images in dielectrics we get, for the potential due to the ion and its images in w, mL and mR respectively:

$$V_w - V_\sigma = \sum_{n=0} \frac{\alpha^n e^*/K_w}{\sqrt{[x+(2n+1)D]^2+y^2+z^2}} + \sum_{n=1} \frac{\alpha^n e^*/K_w}{\sqrt{[x-(2n-1)D]^2+y^2+z^2}} \tag{6}$$

$$V_{mL} - V_\sigma = \sum_{n=0} \frac{\alpha^n 2e^*/(K_w+K_m)}{\sqrt{[x-(2n-1)D]^2+y^2+z^2}} \tag{7}$$

$$V_{mR} - V_\sigma = \sum_{n=0} \frac{\alpha^n 2e^*/(K_w+K_m)}{\sqrt{[x+(2n+1)D]^2+y^2+z^2}} \tag{8}$$

where

$$\alpha = (K_w - K_m)(K_w + K_m)^{-1}$$

Having obtained the potential functions for the various regions we can now obtain the energies of interaction, designated U_w and U_m.

With the aid of Green's theorem (Ref. 9, p. 160) the energy may be written in general as:

$$U_w = \frac{K_w}{8\pi} \iiint (\nabla V_w)^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z = -\frac{K_w}{8\pi} \Sigma \iint V_w \frac{\partial V_w}{\partial n_i} \mathrm{d}s_i \tag{9}$$

$$U_m = \frac{K_m}{8\pi} \iiint (\nabla V_m)^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z = -\frac{K_m}{8\pi} \Sigma \iint V_m \frac{\partial V_m}{\partial n_i} \mathrm{d}s_i \tag{10}$$

The significant interaction-energy terms will be those arising from the following cross terms:

a) The real charge with all the images. These are images with respect to the real charge; hence, the integration is only over the surface of the real charge.

b) An image with the successive image induced by it. The first image functions as a virtual charge and as such has an integrable surface.

c) Cross interaction between the two symmetric image sets, but not between images within a given set located behind a platelet or slab.

d) Interaction between images on the left with the free charge or the slab on the right, and vice versa. These terms are quite symmetric.

e) Interaction between the real point charge and the free charge on the two surfaces.

f) Interaction between the free charges on the two platelets. This is a more difficult problem then it would appear; hence, it will be treated in conjunction with e).

g) For the energy of the field in the platelets, the interaction terms follow from the equations for V_{mR} and V_{mL}. The terms involving the surfaces of the images are, as in d), fictitious and, hence, zero.

On carrying out the appropriate integrations and putting $e^* = ze$, we obtain:

$$U_w = \frac{z^2e^2}{2DK_w} \left\{ -\left(2 + \frac{1}{2|1-\alpha^2|}\right) \ln (1-\alpha) + \frac{1}{|1-\alpha^2|} \left(\frac{1}{2} \ln (1+\alpha) - \alpha - \frac{\alpha^3}{3}\right) - \alpha \right\} + \frac{ze\pi\sigma}{K_w} \sum_{n=1} (\alpha^n [\sqrt{(2n+1)^2D^2 + ze/2\pi\sigma} - (2n+1)D) + \frac{ze\pi\sigma}{2K_w} (\sqrt{D^2 + ze/2\pi\sigma + D}) \quad \text{ergs/ion} \tag{11}$$

and

$$U_m = \frac{2ze\pi\sigma}{(K_w+K_m)} \sum_{n=0} (\alpha^n [\sqrt{(2n+1)^2D^2 + ze/2\pi\sigma} - (2n+1)D) \quad \text{ergs/ion} \tag{12}$$

The total electrostatic energy of interaction, designated U_E, is:

$$U_E = U_w + U_m \tag{13}$$

In view of the discussion following Eq. 5, it can be shown that, when $2D \to \infty$, the last two terms of Eq. 11 become:

$$\frac{ze\pi\sigma}{K_w} \sum_{n=0} (\alpha^n [\sqrt{(2n+1)^2D^2 + ze/z\pi\sigma} - (2n+1)D) \tag{14}$$

Thus eliminating the problem of an energy term which becomes indefinitely large as $2D$ increases.

The Mechanism of Swelling and the Role of the Hydration Energy of the Interlayer Ions. — Before applying Eq. 13 to obtain potential energy curves, it is necessary to consider the mechanism of expansion. According to Barshad,[10-12] in the dry montmorillonite, vermiculite, or other expanding clay mineral the platelets are sandwiched together, with interlayer ions present in the cavities of the oxygen framework which forms the boundary of the platelets. It is known that the presence of the interlayer ions is essential to swelling, and that this process is dependent on the size and charge of the ion. An important role is also played by the dielectric constant of the solvent medium. In the crystalline region of swelling a few essential things seem to cccur. Firstly, the solvent molecules, those of water,

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[9] J. Jeans, "Mathematical Theory of Electricity and Magnetism," 5th ed., Cambridge University Press, Cambridge, England (1960).

[10] I. Barshad, *Am. Min.*, **34**, 675 (1949).

[11] I. Barshad, *Soil Sci. Soc. Am., Proc.*, **16**, 176 (1952).

[12] I. Barshad, *Clays and Clay Technology, California Div. of Mines, Bull.*, **169**, 70 (1955).

for instance, must be adsorbed to the external surface of the crystal; thereafter water molecules penetrate the platelets with the concomitant removal of the ions from the cavities of the platelets and the subsequent coordination of the water molecules by the ions.

In terms of solid state physics, the foregoing process may be considered to be the creation of negative holes in the montmorillonite crystal as a result of the removal of the ions from the cavities. The interlayer ion now functions as a nucleus for the coordination of water molecules to give a heterogeneous crystal of montmorillonite-water. The creation of holes in the montmorillonite and the movement apart of the platelets require energy which must be yielded to the montmorillonite. On the other hand, the incorporation of water into the crystal requires that the water molecules release energy. The processes are, therefore, seen to be complementary, the ions being the main intermediary agents, extracting energy from the water molecules to be yielded to the montmorillonite and to contribute to the swelling potential. All this may be stated more concisely; swelling or crystal growth is a consequence of a defect or imperfection in the montmorillonite crystal. The foregoing essentially describes the process in the region of platelet separation, $0 \leqslant 2D \leqslant 5.4\text{Å}$, corresponding to two complete and continuous monomolecular layers of water between any two platelets.

In order to relate the energy extracted from the water molecules to the hydration energy of the ion, it is necessary to consider the following equation of Bernal and Fowler$^{13)}$ for the hydration energy of an ion with a valence z and a radius r:

$$U_h=\frac{(K_w-1)z^2e^2}{2K_wR_z}+(nP_{(r,z)}-u_w) \qquad (15)$$

where the symbols have the some meaning as in Ref. 13. The first term in the above equation arises quite logically from the general electric field equations, while the second terms is an empirical relation representing the potential energy change of the water molecules due to coordination by an ion. The term due to the electric field equations has already been partially computed in the general expression for U_w, that is, Eq. 11. In addition, the diameter $2R_z$ of the saturation sphere which is the lower boundary of integration takes values such that it coincides with $2D$. From Table VII of Ref. 13, $2R_z=5.8$, 7.2 and 9.2 Å for $z=1$, 2 and 3 respectively. This would make the first term zero, since the platelet separation $2D$ corresponds to the upper boundary or the physical infinity. Thus, the first term is, for practical purposes, zero. Herein could lie a partial explanation for the lower heats of the solution of ions when bound to montmorillonite reported by Janert.$^{14)}$ It must also be borne in mind that some of the energy abstracted from the polar solvent is yielded to the montmorillonite crystal. Jordan,$^{15)}$ for example, showed that even after the separation of 12 Å had been attained it was still necessary to add polar solvents to commercial montmorillonite-organic complexes in order to obtain further expansion and gelation. This would suggest an energy requirement of the montmorillonite before extensive separation can occur. As has been shown by Barshad,$^{11)}$ the dielectric constant of the solvent plays a key role. Other factors, such as the size and type of interlayer ions and solvent molecules, are also important, as has been shown by Granquist and McAtee.$^{16)}$ Whatever the interlayer ion may be, it appears that the solvent should have a high dielectric constant and the ability to solvate the interlayer ion, thus releasing energy, as has been discussed above.

There is no rigorous way of representing the mutual potential energy of the coordination of the water molecules by the ion. Intuitively, this may be represented by an integral function, such as:

$$(nP_{(r,z)}-u_w)=(nP_{(r,z)}-u)\int_0^\infty f(\rho)\,\mathrm{d}\rho$$

Clearly, $f(\rho)=e^{-\rho}$

Proceeding in this empirical manner, the contribution to the total potential energy of the system at any interplatelet separation $2D$ may now be defined as:

$$U_C=(nP_{(r,z)}-u_w)\frac{\int_{D-1}^{D} f(\rho)\,\mathrm{d}\rho}{\int_0^\infty f(\rho)\,\mathrm{d}\rho} \qquad (16)$$

$$=(nP_{(r,z)}-u_w)\int_{D-1}^{D} e^{-\rho}\,\mathrm{d}\rho$$

Since $f(\rho)=e^{-\rho}$,

$$U_C=(nP_{(r,z)}-u_w)(e-1)e^{-D}; \quad (D \geqslant 1) \qquad (17)$$

The interpretation of Eqs. 16 and 17 is that the fraction of the energy under the curve between $(\rho-1)$ and ρ contributes to the potential energy at $\rho=D$. In a way, the function bears some similarity to a Dirac δ-function.

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13) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

14) H. Janert, *J. Agri. Sci.*, **24**, 136 (1934): Quoted in R. E. Grim, "Clay Mineralogy," McGraw-Hill Book Co. Inc., New York, Toronto, London (1953), p. 187.

15) J. W. Jordan, *J. Phys. & Colloid Chem.*, **53**, 194 (1948).

16) W. T. Cranquist and J. L. McAtee, *J. Colloid Sci.*, **18**, 409 (1963).

There should also be a term similar to $(nP_{(r,z)}-u_w)$ for the energy yielded to the montmorillonite platelets in order to remove the ion from the cavity. This term could be developed empirically as above for U_C, but the sign should be negative. An attempt is now being made to estimate this term theoretically. A possibility exists, however, of estimating its value experimentally. If, for example, montmorillonite flakes of varying ratios of high to low hydration energy ions such as K^+; Na^+K^+; Li^+Cs^+; Li^+ are prepared and then allowed to swell, there may exist a critical ratio of ions at which the interplatelet separation takes a value $\geqslant 9$ Å. In this way the critical average hydration energy per ion could be obtained and related to the crystal energy term. This term should to all appearances be much less than $(nP_{(r,z)}-u_w)$ for most ions possessing large hydration energies, but it would never be completely satisfied for those ions with relatively small hydration energies.

Potential Energy Curves and Extensions.— Except for the unknown term describing the energy of creating a hole in the montmorillonite platelets, it is now possible to obtain potential energy curves from Eq. 13 and its sum with Eq. 17. These are shown below in Figs. 1, 2 and 3 for $z=1$, 2 and 3 respectively. The numerical values of the various parameters in Eqs. 13 and 17 are given in Ref. 7 and 13 respectively.

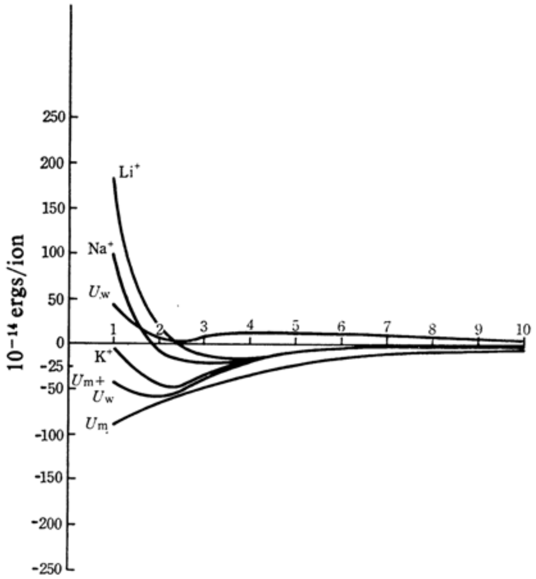

Fig. 1. Energy of interaction between two faces of montmorillonite and monovalent interlayer ions in relation to distance of separation, calculated for varying values of K_w as in Eqs. 13 and 14.

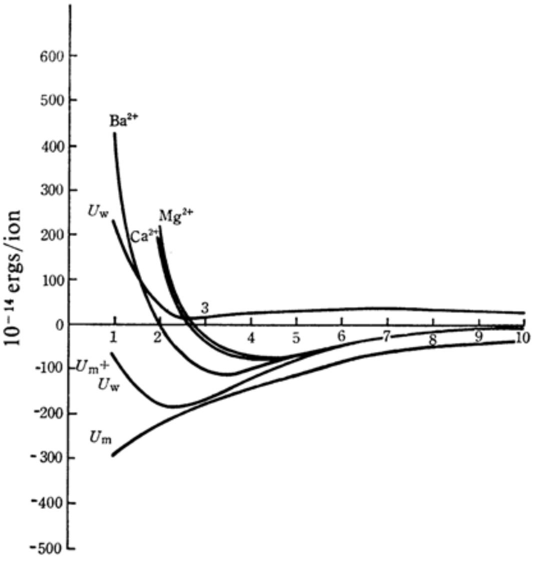

Fig. 2. Energy of interaction between two faces of montmorillonite and divalent interlayer ions in relation to distance of separation, calculated for varying values of K_w as in Eqs. 13 and 14.

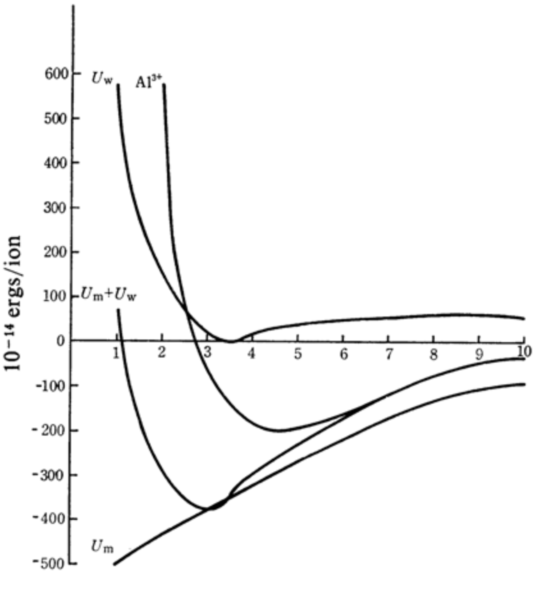

Fig. 3. Energy of interaction between two faces of montmorillonite and trivalent interlayer ions in relation to distance of separation, calculated for varying values of K_w as in Eqs. 13 and 14.

It must be stressed that Eq. 13 is not strictly valid except for $2D \geqslant 5$ Å, since the development postulates two complete and continuous monomolecular layers of water, one on either side of the interlayer ion. In addition, Eq. 17 is completely empirical.

It may be noted that, if the first term in the image series is taken, Eq. 11 reduces to:

$$U_w = \frac{K_w - K_m z^2 e^2}{(K_w + K_m) K_w 2D} + \frac{\pi \sigma z e}{2K_w}\left(\sqrt{D^2 + ze/2\pi\sigma + D}\right) \tag{18}$$

This expression, which is the first order approximation, yields a curve quite similar to that given by Ref. 15, Eq. 8 in Ref. 6, Fig. 2. If, now, the platelets were replaced by uncharged conductors U_w would reduce to:

$$U_w = -\frac{z^2 e^2}{2DK_w} \ln 2 \tag{19}$$

This result indicates that the energy for small D would always be attractive if the montmorillonite platelets are assumed to be conductors.

From Eqs. 11 and 19 it is clear that the image problem we have solved is essentially that of a one-dimensional ionic crystal lattice. With extensions for computing the lattice sums, it is possible to extend this to a two-dimensional lattice and thus treat several ions and their images as one system. This would indeed yield a more rigorous solution to the problem. For the present, however, Eq. 13 is adequate for both montmorillonite and vermiculite systems.

Lastly, the problem as solved represents the case for two dielectric faces or for two slabs of an infinite thickness. In the work referred to in Footnote *1, a solution is given which takes into account the thickness of the platelets, giving a small correction term to the energy.

Discussion

From Eq. 13 and its representation in Figs. 1, 2 and 3, it would appear that the electrostatic energy of interaction is such a function of the distance as to exhibit a minimum or an energy well. This minimum arises from the combined effects of dielectric image or polarisation energy terms and Coulombic terms. The experimental values of the equilibrium separation for some of the various ionic forms of montmorillonite are given in Ref. 4 as $D=1.9$ Å for Cs^+, $D=2.5$ Å for K^+, $D=6$ Å for Li^+, and $D=4.5$ Å for Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+} and Al^{3+}. It would appear from the curves of Eq. 13 in the figures that some other repulsive energy term must be operative. After adding U_C to U_E, the total potential energy curves are obtained for the various ions. As was anticipated, the best agreement seems to be obtained for Al^{3+}, since the larger the surface element $ze/2\sigma$ the more ideal the image model becomes. From the depth of the minimum in the total potential energy curve for Al^{3+}, the binding energy is seen to be about 30 kcal. per mole of ions, a value which is about sixteen per cent that of the sodium chloride crystal. These correlations indicate conclusively why aluminum-montmorillonite does not exhibit macroscopic swelling. On the other hand, the curves for Li^+ and Na^+ show binding energies of the order of 3 to 4 $\boldsymbol{kT}$. Such minima are shallow enough to permit macroscopic sweelling, as experiment confirms.4)

Since the binding energies of the various ions determine the potential energy of the surface, this feature may have general biochemical implications. In Figs. 1 and 2 there is a marked difference between the biologically important ions, such as K^+, Na^+, Mg^{2+} and Ca^{2+}, and Li^+ and Ba^{2+}. Thus, K^+ and Ca^{2+}, which assist in maintaining the osmotic and structural integrity of living cells, have high binding energies and would thus maintain the surface in a state of stable potential energy. Of course, at the other extreme is Cs^+, which would virtually immobilise the surface. Ca^{2+} has perhaps ideal properties for biological functions in that, while it facilitates a good turnover of water, it also has a high binding energy. This could explain its well-known regulatory influence on, for example, the uptake of some other ions by excised plant and animal tissues. These correlations cannot be taken too far, but there does seem to be some relationship between these properties and the potential energy spectrum displayed in the figures.

From the curves representing U_m, U_w and U_E, it may be seen that in the region of separation under study U_m is the leading term of U_E for $z=1, 2$ and 3 respectively. This evidence does seem to favor the theory of swelling proposed, that there is an energy requirement of the montmorillonite platelets which must be satisfied by cooperative processes between the solvent medium, the interlayer ion, and the platelets before any appreciable expansion can proceed. It may be noted that, if the platelets were conductors U_m would be zero.

In Figs. 1, 2 and 3 the curves of Eqs. 11, 13 and 13+17 all have the typical appearance of potential energy curves for molecular systems. The explosion to a gel by montmorillonite or vermiculite crystals may be regarded as the probability of skating out of the energy well. There is, therefore, a statistical problem concerning a distribution function for the number of platelets which escape the barrier to demonstrate macroscopic swelling. This is borne out by the X-ray date of Norrish (Ref. 4, Fig. 2) and Norrish and Rausell-Colom (Ref. 17, Fig. 3). It is well to note that the expansion of the first few platelets will act as a trigger mechanism for others, leading to an explosive avalanching process.

Let us consider now the mechanism of this explosive process, known as macroscopic swelling.[4] In an earlier section of this work, an approximation was made in computing the energy terms, e) and f); as soon as the interlayer ions lose their ordered arrangement, the shielding effect is considerably reduced and f) is no longer zero. In other words, the free surface charges of a like sign on adjacent platelets repel each other, since, as has been pointed out earlier, they now act as sinks for sources at infinity. Support for this proposal is found in Ref. 17 and in Weies' work.[18] These workers have shown that, within certain limits, the macroscopic swelling for a variety of clay minerals with various interlayer ions is greater and more explosive the greater the surface charge density. In the second instance, the authors, by perturbing the mobile interlayer ions of lithium-vermiculite with an electric field of a few V./cm., stimulated lithium-vermiculite to exhibit macroscopic swelling almost instantaneously. These crystals thereafter exhibited unexplained electrical properties similar to those described by Garrent and Walker.[19]

Before giving an explanation to the electrical phenomena in 18, it is of interest to describe briefly the procedure for preparing what appears to be lithium-vermiculite. By applying much higher voltages for short intervals to a native sodium-vermiculite crystal immersed in water, the crystal was stimulated to swell some three to four times its original volume within a few minutes. The water was then replaced by a dilute lithium chroride solution, and the perturbation field was maintained for a few more minutes. The crystal was then left overnight in lithium chloride solution, a procedure which is perhaps not essential. It would appear, therefore, that the laborious method of prolonged heat treatment used by many workers in preparing lithium-vermiculite can be simplified. The heat serves largely to increase the ionic conductivity as it would for any ionic crystal lattice. The swollen sodium-vermiculite, when left for a few hours in air, always contracted to one-and-a-half times its original thickness.

The explanation for all these electrical phenomena seems to lie in a model presented in Ref. 6, that is, the consideration of the vermiculite platelets with the interlayer ions as a pile of plate-shaped conductors. If an electric field is now applied, the mobile interlayer ions or positive charge carriers migrate in the direction of the field and can thus be replaced by other positive-charge carriers. This perturbation destroys the equilibrium distribution of the ions over the surface; hence, towards the anode there is an increased interaction between the surface charge of adjacent platelets leading to repulsion and the growth of the crystal. By applying an a. c. field of a sufficiently low frequency, the mechanical response time of the system could be determined. Preliminary studies by the authors suggest a value of 0.06 sec. The possibility of a permanent dipole moment may be ruled out since there is no preferential direction in the plane of the crystal for growth. It follows the field completely.

Conclusion

The general theory of images in dielectrics has yielded results which convincingly support Langmuir's[1] preliminary ideas. All the evidence from theory and from current experimental knowledge suggests that, within the limits set by the type and size of solvent and interlayer ion, the swelling and many other colloidal properties of clay minerals are wholly determined by the electrical properties of the system. The influence of the surface density of the charge on the swelling, which was reported in Refs. 17 and 18, points to the fact that double-layer theory should not be applied without reservations to clay mineral systems. As further proof of the importance of the dielectric constant of the medium between the platelets, a comparison may be made of Table VII of Ref. 11 and Table I of Ref. 18. Here it is seen that a calcium-saturated montmorillonite immersed in a mixture of octanol and *n*-pentane gives almost the same X-ray spacing as a montmorillonite saturated with *n*-octylammonium ions in a mixture of *n*-octanol and *n*-octylamine. This result would indicate that, in this range of dielectric constants of the solvent, the alkylammonium ions behave much like any other ions; support is also given to Barshad's[11] proposal regarding the formation of complexes between the solvent and the platelets of montmorillonite. Moreover, these complexes should be regarded as heterogeneous crystals.

Finally, Figs. 1, 2 and 3 provide convincing evidence that the image model describes the system adequately.

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17) K. Norrish and J. A. Rausell-Colom, *Clays and Clay Minerals*, **10**, 123 (1963).

18) A. Weies, ibid., **10**, 191 (1963).

19) W. G. Garret and G. F. Walker, ibid., **10**, 557 (1963).

Summary

The method of images in dielectrics is applied to a model consisting of two infinite dielectric slabs and a point charge. When specific effects of the ions such as hydration energies are taken into account, the model describes the electrical aspects of the swelling of the clay minerals satisfactorily. In addition, a detailed theory of the mechanism of swelling is proposed and is shown to be favored by preliminary experimental studies of vermiculite.

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Appendix I

In order to demonstrated further the agreement between theory and experiment, we may compare Barshad's (Ref. 20, Figs. 2 and 3) experimental results for ΔF_w with its equivalent, $\partial(U_C+U_w)/\partial D$, or even ΔF_m (Ref. 20, Fig. 6) with $\partial U_m/\partial D$. Though the units are different, the respective families of curves can be shown to be identical except for units and scale. The units used in Ref. 20 are not obvious, hence no exact comparison can be made until they are clarified and converted to ours. Both experiment and theory agree that the free-energy change of the water is a path of decreasing potential energy as D increases, while for the montmorillonite it is a path of increasing potential energy, rapidly approaching zero from negative values. The total potential energy, U_C+U_E, will, therefore, tend to demonstrate a minimum followed by a maximum as D increases. These features can be deduced from the potential energy curves and expressions. The value of D at the maximum increases as the valence of the ions increases. For monovalent ions the maximum occurs at about $D=9\,\text{Å}$, whereas for polyvalent ions it is greater. This is not surprising, since no polyvalent ion exhibits macroscopic swelling (at least as far as current experiments indicate).

Appendix II

The case of the added electrolyte has already been treated,*1 but experimental evidence can be presented to show that excess salt exerts only a secondary influence on the swelling process. In Figs. 5 and 7 of Ref. 4, which depict the experimental X-ray spacings of sodium-montmorillonite in sodium chloride solutions and water respectively, similar progressive interlayer separations of $2D=0$, 9 and 30 Å are demonstrated.

Clearly, though the added electrolyte can inhibit swelling, the primary mechanism of the swelling process is essentially due to the counter ions which neutralise the charge on the platelets. This is the basis of the theory developed in this work.

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20) I. Barshad, ibid., **8**, 84 (1960).