Movement and Equilibrium of Water in Soil Systems as Affected by Soil-Water Forces

PHILIP F. LOW, Professor of Soils, Agronomy Department, Purdue University, Lafayette, Indiana

Introductory Remarks by Chairman

It is always a special pleasure to peruse a paper in which theory and experimental data are well balanced and combine to form a lucid picture of the phenomena under investigation. Grateful acknowledgment is given to Professor Low for contributing a paper of this quality to this Symposium. Of particular interest is the experimental proof of the lesser density of water held on the planar surfaces of montmorillonite clay particles. This finding falls well in line with the evidence on "icebergs" available on other including biologic systems. It is hoped that Professor Low will extend his investigations to systems involving other clay minerals. It would be of particular theoretical and practical interest to find out to what extent in a clay-water suspension the lesser density of the water layers around planar surfaces may be offset by the known electrostriction effect of the exchangeable cations.

• THE INTERACTION between water and soil minerals is an intriguing problem of fundamental significance. The solution of this problem must be obtained before many practical problems in agriculture, soil engineering and related fields can be solved. Therefore, the author and his colleagues have studied the forces between water and soil minerals, especially the clays, and their influence on water movement and equilibrium. This paper summarizes the results and conclusions to date.

Following the thermodynamic methods of Willard Gibbs, it is possible to show (5) that Φ , the total potential of a constituent,¹ can be divided into μ , the chemical potential, and θ , the positional potential; thus,

 $\Phi = \mu + \theta \qquad (1)$

The chemical potential is the chemical free energy per mole and depends on the intrinsic nature and state of the constituent; whereas, the positional potential is the poten tial free energy per mole and depends on the position of the constituent in an external force field or force fields. Obviously, the distinction between internal force fields, which influence the chemical potential, and external force fields, which influence the positional potential, is arbitrary. For this discussion an external force field will be any force field which extends over a region which is large compared to the size of a molecule.

WATER MOVEMENT

Since Φ is a measure of the escaping tendency of the constituent, assume that the gradient of Φ is the force tending to cause movement. If it is further assumed that the frictional forces are proportional to v, the steady-state velocity, can be written Equation 6.

$$v = -k \frac{d\Phi}{dx}$$

where k is the transmission constant. When the right hand side of Equation 1 is sub-

(2)

¹ The total potential is identical to \overline{F} , the partial molar free energy, but the former term will be used here because it is more descriptive.

stituted for Φ Equation 2 becomes

$$\mathbf{v} = -\mathbf{k} \left[\frac{\mathrm{d}\,\boldsymbol{\mu}}{\mathrm{d}\mathbf{x}} + \frac{\mathrm{d}\,\boldsymbol{\theta}}{\mathrm{d}\mathbf{x}} \right] \tag{3}$$

But, in an ideal solution,

$$d\mu = \overline{v} dP - \overline{s} dT + \frac{RT}{N} dN \qquad (4)$$

where \overline{v} , \overline{s} and N are the partial molar volume, partial molar entropy and mole fraction of the constituent respectively, P is the pressure, T is the absolute temperature and R is the molar gas constant. Therefore, showing

$$\mathbf{v} = -\mathbf{k} \left[\overline{\mathbf{v}} \, \frac{\mathrm{dP}}{\mathrm{dx}} - \overline{\mathbf{s}} \, \frac{\mathrm{dT}}{\mathrm{dx}} + \frac{\mathrm{RT}}{\mathrm{N}} \, \frac{\mathrm{dN}}{\mathrm{dx}} + \frac{\mathrm{d\theta}}{\mathrm{dx}} \right] \quad (5)$$

In this equation each of the terms can be regarded as a force tending to cause water movement with respect to a particular frame of reference. If the frame of reference is not the same for the different forces they will not have the same transmission constant. In particular, the mole fraction term represents an "osmotic force" tending to cause water movement with respect to the dissolved solutes. Unless the dissolved solutes are stationary relative to the soil particles this term must be excluded from the brackets and assigned a different transmission constant. Of course, if the soil solution is homogeneous, dN = 0 and the term drops out.

From Equation 5 several equations applicable to the movement of water in soil may be obtained. If the temperature is uniform, free salts are absent or are uniformly distributed, and the only force field present is the gravitational field, dT = o, dN = oand $d\Phi = Mg dh$ so that

$$\mathbf{v} = -\mathbf{k} \,\overline{\mathbf{v}} \left[\frac{\mathrm{d} \mathbf{P}}{\mathrm{d} \mathbf{x}} + \mathbf{p} \,\mathbf{g} \,\frac{\mathrm{d} \mathbf{h}}{\mathrm{d} \mathbf{x}} \right] \tag{6}$$

In these equations M is the molecular weight of water, g is the acceleration due to gravity, h is the height above datum and P is the density of the water. Since Q, the volume flow, is equal to vA, where A is the cross-sectional area of the pores, write

$$Q = -k\overline{v}A \left[\frac{dP}{dx} + \rho g \frac{dh}{dx} \right]$$
(7)

which is a form of the Darcy equation.

If the soil water is moving in the vapor phase under conditions of uniform temperature and pressure and if the gravitational field is ignored, Equation 5 reduces to

$$\mathbf{v} = -\frac{\mathbf{k}\mathbf{R}\mathbf{T}}{\mathbf{N}} \frac{\mathbf{d}\mathbf{N}}{\mathbf{d}\mathbf{x}} \tag{8}$$

In this equation p, the partial pressure of the water vapor, can replace N because p = NP. Thus,

$$v = -\frac{kRT}{p}\frac{dp}{dx}$$
 (9)

The number of water molecules dn, crossing the area A in time dt is²

$$dn = \frac{p}{RT} vA dt$$
 (10)

When Equation 9 and 10 are combined the result is

$$\frac{dn}{dt} = -kA \frac{dp}{dx}$$
(11)

²Note that p/RT = c, where c is the concentration of water molecules.

56

This equation is a form of Fick's law for diffusion.

For water flow in soils it is often impossible to assess separately the contributions of the last two terms on the right hand side of Equation 5. This is especially true when the water moves in films along the solid-liquid interfaces where both microscopic concentration gradients and force field gradients exist. In this event there is no longer any advantage in separating Φ into its component parts. Instead, we use the expression

$$\Phi = \Phi^0 + RT \ln a \tag{12}$$

where Φ^0 is the total potential of the water in the standard state and \overline{a} is the total activity (5) of the water. The value of Φ^0 depends on the pressure and temperature; whereas, the value of \overline{a} depends on the concentration of the constituent, the degree of interaction with neighboring molecules or ions and the nature and magnitude of any force fields which are operative. When the right hand side of Equation 12 is substituted for Φ in Equation 2 and the temperature held constant, the following is obtained

$$v = -k \left[\overline{v} \frac{dP}{dx} + RT \frac{d(\ln \overline{a})}{dx} \right]$$
 (13)

But π , the osmotic pressure, can be related to a by the equation

$$\overline{\mathbf{v}} \pi = -\mathbf{R} \mathbf{T} \ln \mathbf{a}$$
 (14)

As a result,

$$\mathbf{v} = -\mathbf{k}\overline{\mathbf{v}} \left[\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}\mathbf{x}} - \frac{\mathrm{d}\pi}{\mathrm{d}\mathbf{x}} \right]$$
(15)

This equation was tested experimentally and was found to be valid (7).

WATER EQUILIBRIUM

When equilibrium is attained the velocity of the water is zero and Equation 5 becomes

$$\overline{v} dP - \overline{s} dT + \frac{RT}{N} dN + d\theta = o$$
 (16)

which can be integrated between the reference phase, indicated by the zero superscript, and any other phase at the same temperature, to give

$$\overline{\mathbf{v}}$$
 (P - P⁰) = RT ln $\frac{N^0}{N}$ - (θ - θ^o) (17)

Now, the first term on the right hand side of this equation is related to the difference in the concentrations of solutes in the two phases. When the appropriate substitutions (6) are made Equation 17 can be written

$$\mathbf{P} - \mathbf{P}^{\mathbf{0}} = \mathbf{RT} \Sigma (\mathbf{m_s} - \mathbf{m_s}^{\mathbf{0}}) - \frac{(\theta - \theta^{\mathbf{0}})}{\overline{\mathbf{v}}}$$
(18)

where m is the molar concentration of any ionic or molecular species designated by the subscript s.

To apply Equation 18 to the swelling of clays, let the symbols without superscripts refer to the median plane between two parallel clay plates and the symbols with zero superscripts to the external solutions. Then, the pressure difference $(P - P^0)$ is equal to the hydrostatic replusive force which tends to separate the plates and cause swelling. From the equation it is evident that this force results, not only from the difference in ion concentration between the median plane and the external solution, but also from the difference in the potential energy of the water between these two phases. The question now arises as to whether clay-water forces exist which lower the potential energy of the water in the interfacial region relative to that in the external solution. The following paragraphs will be devoted to a discussion of the evidence in favor of such forces. Obviously, if they exist, they will influence water movement as well as water equilibrium. An attempt was made by Hemwall and Low (4) to assess qualitatively the importance of the terms in Equation 18. It seemed reasonable to assess the importance of the first term by altering the number and dissociation of the adsorbed cations and by measuring the resultant change in swelling. These cations are responsible for the difference in ion concentration between the interplate and external solutions. It seemed reasonable also to assess the importance of the second term by altering the adsorptive forces between clay and water and measuring the resultant change in swelling. These adsorptive forces would account for any difference in the potential energy of water between the two regions. Treatments were designed, therefore, to alter or eliminate separately the degree of cation dissociation and the adsorptive forces between clay and water. Swelling measurements were made before and after the treatments. In addition, water in the clay which remained unfrozen at -5 C was determined. Unfrozen water and clay swelling should be related since the same forces are probably responsible for both.

Wyoming bentonite clays were prepared which were saturated with Na, with a mixture of Na and Th and with Th only. Thorium was used because each tetravalent Th ion would replace four monovalent Na ions and would likely be dissociated less than the Na ions. Therefore, the number of osmotically active, adsorbed ions should be great-



from 1.05 me. per gm to 0.98 me. per gm.

est on the Na-clay, less on the Na-Th-clay and least on the Th-clay. Electrophoretic measurements and potentiometric and conductometric titrations indicated that such was the case. An X-ray pattern of a rehydrated sample of the Th-clay showed that the individual layers of the clay were only partially expanded.

A portion of the Na-clay was treated with dimethyldichlorosilane which, according to Rochow (10), reacts with the adsorbed water on the clay to form a polymerized monolayer in which methyl groups are exposed at the new surface formed. Since any surface made up of methyl groups is hydrophobic, it was felt that this treatment would eliminate any clay-water forces which might exist. The Na-clay adsorbed 0.253 gm of silane per gm of clay. A subsequent X-ray analysis disclosed, however, that no interlayer adsorption of silane occurred. Consequently, clay-water forces were eliminated at external surfaces only. Ion dissociation was also eliminated at these surfaces because the electrophoretic mobility of the silaned clay was zero and the cation exchange capacity was reduced

The apparatus used for obtaining swelling pressures and the results obtained will not be discussed here except to say that the non-silaned clays swelled in the expected order, namely, Na-clay>Na-Th-clay>Th-clay. The dilatometer used to determine unfrozen water at -5.0 C was the same as that of Buehrer and Rose (2). It should be mentioned that, with the dilatometer method, unfrozen water is the water which does not exhibit the normal volume expansion associated with freezing. Consequently, any adsorbed water with a structure which is less dense than that of pure water might freeze, but still appear partly as unfrozen water. The experimental data are shown in Figure 1.

The data in Figure 1 have a direct bearing on the existence of clay-water forces. A calculation shows that, if all the exchangeable and free ions were concentrated in the unfrozen water on any of the clays, the ion concentration would not be sufficient to prevent freezing at -5 C. This would be true even if all the exchangeable ions were completely dissociated, which is unlikely. Therefore, it is safe to conclude that the un-

frozen water was due to clay-water forces and not to a depression of the freezing point by the dissolved solutes.

At the water contents used in the freezing studies the Na-clay was not at maximal swelling because the addition of more solution to the system formed a new gel of larger volume. This was true in the presence or absence of dioxane, which has an inhibitory effect on hydrogen bonding and was added to reduce any hydrogen bonding which might occur between clay and water. The addition of more solution not only increased swelling but, as shown in Figure 1, unfrozen water also. If the curve for Na-clay in 0.001 N NaCl is extrapolated to the water content at maximal swelling (7.6 gm of water per gm of clay) it can be seen that, at this water content, there would be approximately 1.4 gm of unfrozen water per gm of clay, representing a water layer about 16 A thick. In the presence of dioxane this layer would be a little thicker, a fact which indicates that this reagent did not interfere with clay-water forces but with the hydrogen bond formation in ice. Apparently, unfrozen water increases with swelling because the force fields become more effective with increasing interplate distance.

The silaned Na-clay, the Na-Th-clay and the Th-clay were at maximal swelling at all the water contents used in the freezing studies. A clear supernatant liquid was used as the criterion for maximal swelling. Note that, for these clays, increasing the water content had relatively little effect on the unfrozen water. Since, unfrozen water at -5.0 C increased with an increase in swelling but remained unchanged when swelling was at a maximum, it is evident that the amount of unfrozen water and the degree of swelling are related. Additional evidence for this relationship is provided by the fact that, for the non-silaned clays, the unfrozen water sequence was the same as that for the swelling sequence, i.e., Na-clay > Na-Th-clay > Th-clay. However, it should be observed that the silaned Na-clay, with only internal surfaces available for adsorption, and the Th-clay, with mostly external surfaces available for adsorption, contained the same amount of unfrozen water. Internal surface area far exceeds external surface area. Therefore, it appears that clay-water forces are more extensive at external surfaces than at internal surfaces.

If clay-water forces exist they should alter the structure of the adsorbed water and, thereby, change its density. Consequently, experiments were conducted on the density of water adsorbed on Wyoming bentonite saturated with either K, Na or Li ions. In the first of these experiments (8) \bar{v}_W , the partial specific volume of water (volume per gm of the last increment), was determined in different suspensions at 25 C by a pycnometer method. Suspension densities for K-, Na - and Li-clay in water were obtained at different clay concentrations. Then a graph of ρ , the suspension density, against c, the clay concentration, was made for each clay and the value for \bar{v}_W at any concentration was calculated by the equation

$$\overline{v}_{W} = \frac{1}{\left[\rho - c \frac{d\rho}{dc}\right]}$$
(19)

All the terms in this equation were obtainable from the aforementioned graphs, one of which is shown in Figure 2.

From Figure 2 it is obvious that the plot of ρ against c produced a straight line. The equation for this line is

$$\rho = c \left(\frac{dP}{dc}\right) + \rho_0 \qquad (20)$$

where P_0 is the density of pure water. Substituting the right hand side of Eq. 20 for P in Eq. 19 shows that the partial specific volume of the water is the same as that for pure water at all the clay concentrations employed. The same was true for the Na-clay and the Li-clay. Since the interplate distance at the highest clay concentration (the concentration at maximal swelling) was about 168 A, it can be concluded that, for these clays, water had its normal density at 84 A from the clay surface.

In the second experiment on adsorbed water density (1) pastes of K-, Na - and Liclay were compressed between a column of mercury and a porous, stainless-steel filter. The mercury was confined in a capillary, as was the water which was forced through the filter. Thus, the change in volume of the clay paste and of the expressed water could be observed simultaneously. From these observations, and from the weight of water in the paste at the termination of the experiment, it was possible to plot the volume of the clay paste against the weight of water in the paste. Since, the slope of the resulting line at any water content is equal to the partial specific volume of the water at that water content, and since density is the reciprocal of the partial specific volume, water densities could be obtained at several water contents for each of the three homoionic clays. The results are shown in Figure 3. In this figure dis-



Figure 2. Plot of suspension density against clay concentration for K-bentonite at 25 C.

a "broken down ice structure" in which there is a tendency for each water molecule to bond itself tetrahedrally to four neighboring water molecules. The bonds are continually breaking and reforming so that, on the average, each molecule is bonded to less than four neighbors and has other neighbors at various distances. When ions are added to water its loosely co-ordinated structure is disrupted and a closer packing (increase in density) of water molecules results. In general, the disrupting effect is least with small ions and greatest with large ones. Extending these ideas to the clay-water system, one is compelled to ascribe the observed decrease in density to the influence of the clay surface and not to the adsorbed ions. Therefore, it is

tances from the clay surface were calculated by assuming a surface area of 8×10^6 cm² per gm and an average water density of unity.

From Figure 3 it is at once apparent that the water density decreased continuously from > 60 A to <10 A from the surface. At a distance of about 10 A the density decrease is of the order of 2 to 3 percent. At all distances the water density was less than that of normal water which has a density of 0.9970 at 25 C and of 0.9999 at 1 C. Evidently, the nature of the adsorbed ion influences the water structure. At water contents below about 4.0 gm of water per gm of clay the clays decreased the water density in the order Na-clay > Li-clay > K-clay. At higher water contents the order is reversed for the Na- and Li-clay. In addition, there was a more rapid decrease of water density with proximity to the surface at 1 C than at 25 C.

An explanation for the observations made in Figure 3 can be based on the current ideas of the structure of water and ionic solutions. Water can be regarded as



proposed that the "broken down ice structure" of water is stabilized by the polarizing influence of the negatively charged clay surface or by hydrogen bonding to this surface. It is not to be inferred that the stabilized structure is rigid but only that a more regular ordering of the water molecules exists. In this structure, as in water, the ions exert a disrupting influence, probably by decreasing the extent of hydrogen bonding. This influence appears to be in the order K>Li>Na. Hence the structural development of the adsorbed water should be greatest on the Na-clay, less on the Li-clay and least on the K-clay. Support is given to the proposed order of structural development by evidence, which will be referred to later, that the activation energy for ionic movement in this water is greatest for Na, less for Li and least for K. Also, as in water, a decrease in temperature results in an increase in structural regularity. In the adsorbed water this is manifested by a density decrease.

The above results show that the density of the adsorbed water structure is less than that of pure water up to distances greater than 60 A but not exceeding 84 A. A reasonable conclusion, therefore, is that the clay-water forces responsible for this structure extend 60 to 84 A from the surface. For these clays 84 A was the half-distance between adjacent clay layers at maximal swelling. When one realizes that a very large force is required to sensibly alter the structure of water (e.g., a pressure of 200 atmospheres increases the density of water by only 1 percent) it becomes evident that the forces referred to may be of considerable magnitude.

The experiments of the preceding sections throw light on experiments conducted in

this laboratory several years ago", and vice versa. In the earlier experiments, samples of K-, Na-and Li-clay were suspended in solutions of different salt concentration. In each case, the salt was the chloride of the cation with which the suspended clay was saturated. The resulting suspensions were put in centrifuge tubes and immersed in a constant temperature bath at -50 C for 12 hours. At the end of this time if the suspensions were not frozen they were diluted slightly with the appropriate chloride solution and returned to the bath for another 12-hour period. This process was continued until freezing occurred. The clay concentration was recorded for each suspension which froze. In addition, the zeta potential of each clay was determined at each salt concentration. The results for the Na-clay are shown in Figure 4. Analogous results were obtained for the K-clay and Li-clay.

From Figure 4 it is clear that the concentration of clay in suspension at freezing was related to the zeta potential of the suspended particles; as the zeta potential increased, indicating an increase in cation dissociation, the clay concentration at freezing decreased, and vice versa. But the observed clay concentrations at freezing were not the equilibrium values be-



Figure 4. Zeta potential and freezing concentration of Wyoming bentonite as a function of sodium chloride concentration.

cause none of the suspensions contained enough exchangeable ions and free salt to lower the freezing point more than a fraction of a degree. In addition, there was very little unfrozen water in the frozen suspensions. Apparently, the particles in suspension affected the supercooling of the suspension; the degree of supercooling being a function of the concentration and zeta potential of the suspended particles. Supercooling was enhanced by the particles because particle-free solutions of the same salt concentrations froze with little or no supercooling under the same conditions. Also, in most suspensions the particle concentration had to be reduced before freezing occurred.

The contribution of the clay particles to supercooling cannot be attributed to the

³ Deming, John M. Forces involved in the swelling of clays. Unpublished Ph.D. Thesis Purdue University. 1951.

influence of the exchangeable ions because supercooling was not affected directly by the addition of electrolytes. Further, Dorsey (3) has shown that electrolytes have a negligible effect on supercooling. Consequently, the observations reported here can be attributed to clay-water forces which promote supercooling and become more effective as the zeta potential goes up. These facts elicit the following proposals: (a) the water structure formed as a result of the clay-water forces is not identical with that of ice; otherwise, there would be no supercooling, (b) an increased dissociation of ions from the clay surface is conducive to the structural development of the adsorbed water; either the disruptive effect of the ions is lessened or the intensity of the claywater interaction is increased as the ions become distributed through a larger volume. Clay-water interaction would be increased by increased ionic dissociation if this interaction was due to the polarizing effect of the electric field at the particle surfaces. Support is given to proposal (1) by the fact that, in the dilatometer work, it was difficult to supercool suspensions of the silane-treated clays. Recall that the silane treatment eliminated clay-water forces at external surfaces. Now let us examine additional evidence for proposal (2).

In the dilatometer work on unfrozen water in clay systems, the Th-clay was not only undissociated but adsorbed Th ions in excess of its inherent exchange capacity (zeta potential =+53.8 mv.); it contained relatively little unfrozen water. ⁴ The Na-Th-clay was slightly dissociated (zeta potential = -17.6 mv.) and contained more unfrozen water. The Na-clay was largely dissociated (zeta potential = -35.0 mv.) and contained the most unfrozen water. In addition, external surfaces accounted for more unfrozen water than did internal surfaces. Ionic dissociation should extend farther, i.e., the ionic atmosphere should be more diffuse, at external surfaces. Hence, the dilatometer work supports proposal (2).

Recently, the author (9) used the same clays as those employed in the water density research to obtain the mobilities and activation energies for movement of the adsorbed ions. A Na-clay, which was saved from another experiment, was also used. The results are shown in Table 1.

Clay ^a	Ionic Mobility at 25 C.	Ionic Activation Energy	Ionic Dissocia- ation	Density of Adsorbed Water at 25 C.	Structural Development of Water
	sq. cm./ volt/sec.	cal./ gm. ion	(relative)	gm./cc.	(relative)
K-clay	0.000051	4037	++	0.981 ^b	+
Na-clay	0.000069	4486	+++	0.972	+++
Li-clay	0.000057	4358	++	0.975	++
Na-clay	0.000132	5157	++++	-	

TABLE 1

NATURE OF WATER ADSORBED ON CLAYS IN RELATION TO THE ELECTROCHEMICAL PROPERTIES OF THE EXCHANGEABLE IONS

^aThe first three clays were prepared from $< 2.0 \mu$, columnated Wyoming bentonite by titration. The last clay was prepared from $< 0.2 \mu$, electrodialyzed Wyoming bentonite by titration.

^D These values are for a distance of 10 A. from the clay surface.

In Table 1, the data in columns 2, 3 and 5 were obtained experimentally. The data in column 4 were obtained by using the following relationship between U, the ionic mobility, and E, the activation energy, $U = \alpha_{\beta} Be^{-E/RT}$ (21)

* The relatively small amount of unfrozen water on this clay was due partly to its lack of interlayer expansion.

where a is the degree of ionic dissociation, β is a geometry factor for movement in the porous clay-water system, B is a constant which is dependent on the distance between successive equilibrium positions of the ion, R is the molar gas constant and T is the absolute temperature. Values of B were assumed to be the same as those in solution, namely, 0.252 for K, 0.389 for Na and 0.484 for Li. The value of β was assumed to be the same for all systems since the clay was packed the same in each one. The data in column 6 were obtained by regarding the water density as a criterion of structural development, the less the density, the greater the structural development.⁵

The activation energy for ionic movement is equal to the sum of the energies expended by the ion in pushing back molecules to form a hole and in breaking bonds with the clay and neighboring water molecules so that it can move into the hole thus formed. Therefore, one would expect the activation energy to go up with an increase in the coherence of the water structure.⁹ Evidently, this is what happened, as indicated by the data in the table. But, activation energies and the degree of ionic dissociation were in the same order. A reasonable conclusion is that the water structure became better developed as the degree of ionic dissociation increased. Here also, the evidence supports proposal (2).

The nature of the exchangeable cation should have an effect on the structural development of the adsorbed water. In solutions, ions disrupt the water structure in the order K > Na > Li. It would be expected that this order would obtain for clay-water systems as well. Apparently it does because, even though the K- and Li-clay were equally dissociated, there was less structural development in the adsorbed water on the former than on the latter. Structural development of water was greatest on the Na-clay because this clay was the most dissociated.

In summary, it appears that clay-water forces are responsible for the development of a water structure at the clay-water interface. This structure extends upwards of 60 A. from the clay surface and becomes less regular, and probably more fluid, with distance from the surface. This adsorbed water structure and that of ice are not identical but are similar in that both are less dense than normal water. Very likely, both owe their coherence to hydrogen bonds. Structural development in the adsorbed water is enhanced by ionic dissociation from the clay surface, possibly because the disruptive effect of the ions is less when they are distributed over a larger volume and not concentrated at the surface where the structure is "anchored." The disruptive effect of the ions is probably in the order K > Na > Li when they are equally dissociated.

If clay-water forces give rise to a more regular water structure in the vicinity of the clay mineral surfaces, they must also increase the viscosity of the water near these surfaces. Since water tends to move toward regions of low potential energy, it should accumulate in the interfacial regions between clay and water, the extent of the accumulation being proportional to the magnitude of the forces. For the same reason, these forces should affect such soil properties as swelling, aggregation and compaction. In addition, they should be effective in preventing the freezing of water. Thus, it is reasonable to believe that soil- and clay-water forces affect the movement and equilibrium of water in soil systems.

REFERENCES

1. Anderson, Duwayne M. and Low, Philip F. "The Density of Water Adsorbed by Lithium-, Sodium- and Potassium-Bentonite." Soil Sci. Soc. Amer. Proc. Vol. 22, No. 2, (in press).

2. Buehrer, T.F. and Rose, M.S. "Studies in Soil Structure V: Bound Water in Normal and Puddled Soils." Ariz. Agr. Expt. Sta. Tech. Bull. 100. (1943).

3. Dorsey, Ernest, N. "The Freezing of Supercooled Water." Amer. Phil. Soc. Trans. 38:248-328. (1948).

4. Hemwall, John B. and Low, Philip F. "The Hydrostatic Repulsive Force in

³ Note that if all the hydrogen bonds in water were broken and the water molecules became close-packed, the water density would be 1.84.

[°] For example, one would expect a much greater activation energy for ionic movement in ice than in water.

5. Low, Philip F. "Force Fields and Chemical Equilibrium in Heterogeneous Systems with Special Reference to Soils." Soil Sci. 71:409-418. (1951)

6. Low, Philip F. and Deming, John M. "Movement and Equilibrium of Water in Heterogeneous Systems with Special Reference to Soils." Soil Sci. 75:187-202. (1953)

7. Low, Philip F. "Effect of Osmotic Pressure on Diffusion Rate of Water." Soil Sci. 80:95-100. (1955).

8. Low, Philip F. and Anderson, Duwayne M. "The Partial Specific Volume of Water in Bentonite Suspensions." Soil Sci. Soc. Amer. Proc. Vol. 22, No. 1, (in press).

9. Low, Philip F. "The Mobilities of Exchangeable Alkali Metal Cations in Bentonite-Water Systems." Soil Sci. Soc. Amer. Proc. (in press).

10. Rochow, E.G. "Chemistry of the Silicones." John Wiley and Sons, New York. (1951)