

INFLUENCE OF ADSORBED WATER ON EXCHANGEABLE ION MOVEMENT

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ABSTRACT

The concept of activation energy for ion movement is discussed. It is shown that the activation energy for exchangeable ion movement is directly correlated with the specific volume of the adsorbed water, with the resistance to freezing of this water and with the activation energy for deuterium oxide diffusion in this water. Electrical interaction between ion and clay appears to have little effect on the activation energy. Consequently, it is concluded that the most important factor governing exchangeable ion movement in the pores of a clay-water system is the structure of the adsorbed water.

INTRODUCTION

When an ion moves through any fluid it must displace the molecules of the fluid. Consequently, the rate of ionic movement should be related inversely to the viscosity of the fluid. This relationship is expressed by the familiar Stokes-Einstein equation, viz.,

$$D = \frac{kT}{6\pi r\eta}, \quad (1)$$

in which D is the ionic diffusion coefficient, k is the Boltzmann constant, T is the temperature, r is the ionic radius and η is the viscosity of the fluid. A similar relationship obtains for the ionic mobility u . Now viscosity is a structure-sensitive property. Therefore, if the structure of the water near a clay surface is different from that of normal water, D and u for the ion should also be different. It is the purpose of this paper to show that exchangeable ion movement is indeed related to certain structure-sensitive properties of the clay adsorbed water.

RESULTS AND DISCUSSION

There are three factors which might cause the observed values of the diffusion coefficient and mobility of an ion in a clay-water system to deviate from those in aqueous solution. They are: the geometry of the

migration path, electrical interaction between the ion and clay particles and the afore-mentioned structural alteration in the adsorbed water. The dotted line in Fig. 1 depicts the path followed by an ion in moving a net distance L between points A and B in a clay-water system. Obviously, the presence of the plate-shaped particles reduces the cross-sectional area of the migration path and increases its tortuosity. Hence, the presence of the particles should tend to lower the ionic diffusion coefficient and mobility. Electrical interaction between the charge sites on the clay and the oppositely charged ion should do likewise. However, structural alteration

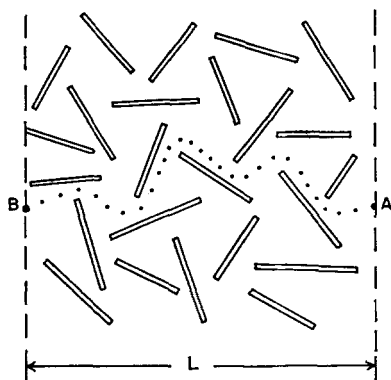


FIGURE 1.—Illustration of the geometry (tortuosity) of the migration path in a clay system.

in the adsorbed water could tend either to increase or to decrease the diffusion coefficient and mobility of the ion, depending on the nature of the alteration. It is possible to determine whether or not the latter two factors have a significant effect on the diffusion coefficient and mobility of an ion. Such a determination involves the use of the activation energy concept. This concept will be discussed briefly in the next paragraph.

In the upper part of Fig. 2 an ion (cross-hatched circle) is shown surrounded by water molecules (open circles) in a close-packed arrangement. Undoubtedly, the arrangement of the ion and water molecules in a real system is different from that depicted but the diagram illustrates the principle involved. If the ion moves from position a to position b it must push back the water molecules in front of it to provide space for itself at b and break bonds with the neighboring water molecules and the surface charge site so that it can move into this space. The process of pushing back water molecules and the process of breaking bonds require different amounts of energy, the sum of which is E_a , the activation energy. The change in energy as the ion progresses from a to b in the absence of an electric field is shown in the lower part of Fig. 2. Thus, it may be said that for an

ion to hop from one equilibrium position to another it must pass over an energy barrier equal in height to the activation energy. Note that this energy is independent of the geometry of the migration path. If the ion is hydrated, more water molecules would be pushed back to form a larger space for the ion at *b* and water-water bonds would be broken instead of ion-dipole bonds. A different activation energy would result but the principle would remain the same. As one might expect, the rate of movement

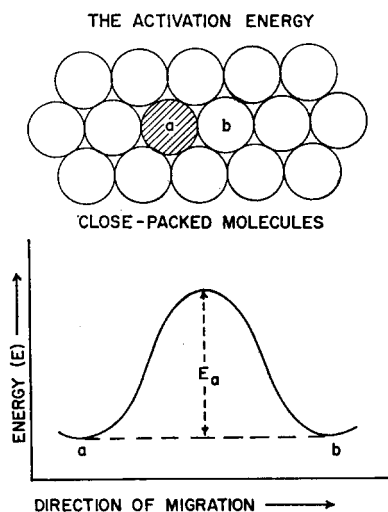


FIGURE 2.—Schematic representation of an ion surrounded by water molecules (top) and the energy barrier (bottom) it must surmount in moving between equilibrium positions.

of an ion decreases as the activation energy increases, and vice versa. This relationship is expressed by the equations,

$$D = A e^{-E_a/RT}, \quad (2)$$

$$u = B e^{-E_a/RT}, \quad (3)$$

which are based on the theory of Eyring (Glasstone, Laidler and Eyring, 1941). In these equations *A* and *B* are constants which include the hop distance and an exponential term involving the entropy of activation, *R* is the molar gas constant and *T* is the absolute temperature. When the equations are used for ion migration in a clay system, the constants *A* and *B* also include the geometry factor of the system. To obtain the activation energy for ion movement either by diffusion or electrical conductance the logarithm of *D* or *u*, whichever is appropriate, is plotted against $1/T$. In keeping with eq. (2) and (3), the slope of the resulting line equals E_a/R .

A direct-current method (Low, 1958) was used to determine the activation energies for exchangeable ion movement in three series of homoionic Wyoming bentonites. Each series included a Li-bentonite, a Na-bentonite and a K-bentonite. The same method of preparation (Low and Anderson, 1958) was used for every homoionic clay. The activation energy data are presented in Fig. 3.

Before discussing the results in Fig. 3 it is important to point out that, in these experiments, the electro-osmotic flow of water did not contribute

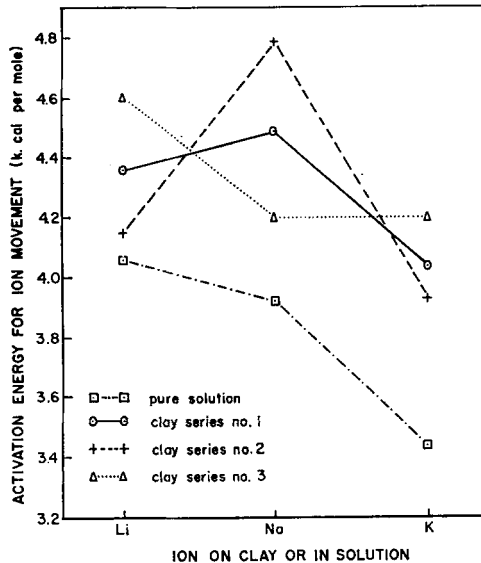


FIGURE 3.—Activation energies for the migration of Li, Na and K ions in solution and on clay surfaces.

to the ionic conductance, and hence to the activation energy. In series 3, water flow was detected by the movement of an air bubble in a solution-filled capillary which joined the electrode compartments. No electro-osmotic flow occurred in the Li- and K-clay and the flow in the Na-clay was so slight as to be considered negligible.

From Fig. 3 it is evident that the activation energies for the movement of the exchangeable ions were greater than those for the movement of the same ions in solution. We may conclude, therefore, that the energy expended by the ion in pushing back water molecules and breaking bonds with its neighbors, including the charge site on the clay, is greater in the clay system than in aqueous solution. No explanation is offered for the fact that the ionic activation energies are different in order and magnitude in the three clay series. Nevertheless, it will become clear that the differences are real and cannot be accounted for by experimental error.

In order to assess the relative contributions of ion-clay interaction and altered water structure to the increase in activation energies, the following analysis is made. The analysis is for movement of an ion along the planar surface of a clay particle and does not include edge effects. A plan of the charge distribution in this surface is shown in Fig. 4. A monovalent ion is represented immediately above a charge site by the closed circle at (a) and midway between charge sites by the dashed circle at (b). In both positions the ion is assumed to be 10 Å above the plane of the charge sites. When the

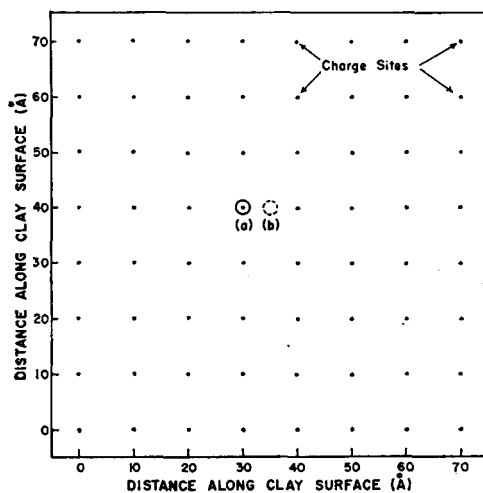


FIGURE 4.—Diagram showing two positions of an ion relative to the charges on a flat clay surface.

ion is at (a) its electrical potential energy is a minimum and when it is at (b) its electrical potential energy is a maximum. The difference in the electrical potential energy of the ion in the two positions should equal the maximum contribution of ion-clay interaction to the activation energy. Now, since potential energies are additive, the electrical potential energy of the ion in each position is the summation of the electrical potential energies of the ion with respect to the different charge sites; thus

$$\theta = \frac{z \varepsilon^2}{D} \sum_{i=1}^{i=n} 1/r_i,$$

where θ is the electrical potential energy of the ion, z is its valence, ε is the electronic charge in esu, D is the dielectric constant, r is the distance between the ion and any given charge site, designated by the subscript i , and n is the number of charge sites on the mineral surface. If the dielectric constant is assigned the value for normal water, the difference in electrical

potential energy per mole of ions at the two positions is 40 cal. This value is only about 1 percent of the observed activation energies and is a small fraction of the difference between the activation energies for ionic movement on the clay and ionic movement in solution. In fact, the magnitude of the experimental error in obtaining the activation energies exceeds 40 cal per mole. Consequently, if the water has its normal dielectric constant, the increased activation energy for exchangeable ion movement along the clay surface cannot be attributed to electrical interaction with the clay. If the water does not have its normal dielectric constant, but a much lower value, the electrical interaction may have a significant effect on the activation energy. But a lower dielectric constant would occur only if the water molecules had increased resistance to orientation in an imposed electric field, that is, if the adsorbed water had a more coherent structure than normal water. Hence, the water structure would also exert its effect. The necessary conclusion is that a more coherent water structure exists near the surface of a clay particle than in aqueous solution and that this structure is responsible, in part at least, for the increased activation energies.

From the standpoint of double layer theory, an ion in the diffuse part of the double layer does not interact with discrete surface charge sites. The charge sites are regarded as being so close together that any plane parallel to the clay surface is an equipotential plane. Therefore, an ion moving parallel to the clay surface in the diffuse part of the double layer should not have to surmount any electric barrier in moving from one equilibrium position to another. This is true regardless of the magnitude of the dielectric constant. Again we arrive at the conclusion that the adsorbed water structure is largely responsible for the enhanced activation energies for exchangeable ion movement. This conclusion is substantiated by the evidence presented in the following paragraphs.

The relationship between the specific volume of the adsorbed water and the activation energy for exchangeable ion movement is shown in Fig. 5 for clay series no. 1. The specific volume data are from Anderson and Low (1958) and the activation energy data are from Low (1958). Now the specific volume can be regarded as an index of structural change in the water. As the structure of the water departs from that of normal water, the specific volume should change. Since the specific volumes of the water were not the same in the different homoionic clay systems of series 1 and since they were greater than that of normal water, it may be said that the adsorbed water structure differs from that of normal water and is affected specifically by the nature of the exchangeable ion. Note that a good correlation exists between the specific volume of the adsorbed water and the activation energy for ionic movement in this water. As the specific volume of the water increases, suggesting a transition in the direction of a more ordered structure of greater viscosity, the activation energy increases, and

vice versa. This correlation indicates that it is the structure of the adsorbed water, rather than electrical interaction between ion and clay, that governs ionic movement within the pores of a clay-water system.

Both a dilatometric technique (Hemwall and Low, 1956) and a calorimetric technique (Kolaian, 1960) have been used in this laboratory to determine the unfrozen water in clay-water systems at -5°C . By both methods of measurement the unfrozen water exceeded that which could

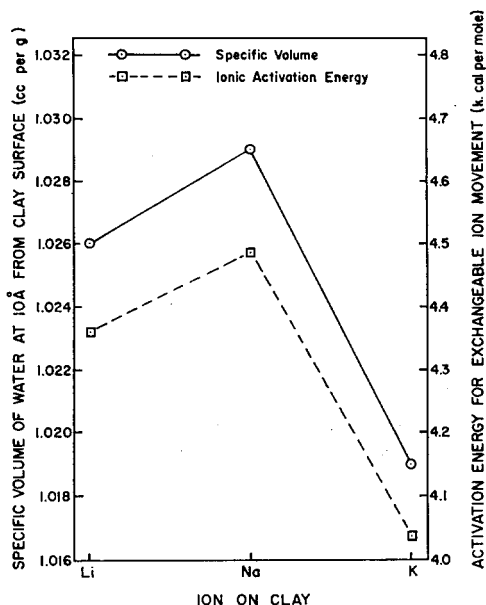


FIGURE 5.—Relationship between the activation energy for exchangeable ion movement and the specific volume of adsorbed water on Li-, Na- and K-clay.

be accounted for by the concentration of exchangeable ions. It might be inferred, therefore, that the transition from water to ice was precluded by the incorporation of the water molecules in an adsorbed water structure having a low energy or a high interfacial tension against ice, or both. In Fig. 6, Kolaian's (1960) data on unfrozen water and activation energies for exchangeable ion movement are presented for clay series no. 2. Again there is a good correlation between a structure-sensitive water property, namely, its resistance to freezing, and the activation energy for ion movement. Consequently, the results of this experiment support the conclusion that the structure of the adsorbed water governs ionic movement within the pores of a clay-water system.

A more direct approach to the influence of water structure on ion movement was taken by Dutt (1960) in this laboratory. He obtained the acti-

vation energies for exchangeable ion movement and deuterium oxide diffusion in clay-water pastes of clay series no. 3. His results are shown in Fig. 7.

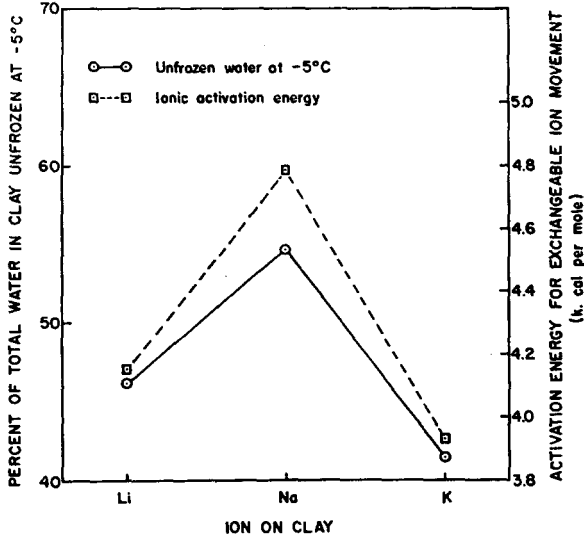


FIGURE 6.—Relationship between the activation energy for exchangeable ion movement and the unfrozen water at -5°C in Li-, Na- and K-clay.

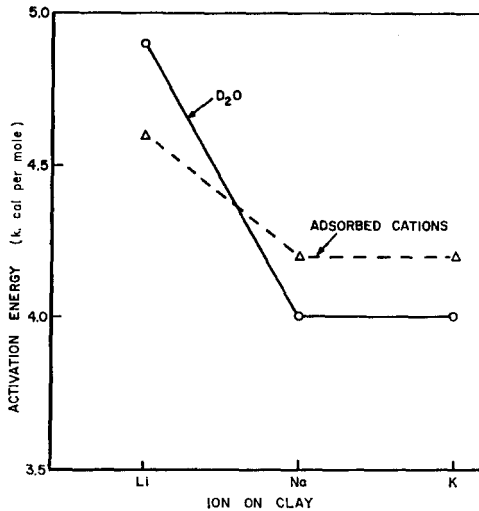


FIGURE 7.—Relationship between the activation energy for exchangeable ion movement and deuterium oxide diffusion in Li-, Na- and K-clay.

Now recall that deuterium oxide, although polar, is uncharged and should be attracted to the charge sites on the clay surface with far less intensity than the charged ion. We may regard the activation energy for deuterium oxide diffusion in any clay-water paste as being essentially the activation energy for the self-diffusion of water molecules in the water within the paste. Yet Fig. 7 shows that the activation energies for exchangeable ion movement are correlated with those for deuterium oxide diffusion and are of comparable magnitudes. Evidently, we can conclude that electrical interaction of the ions with the clay contributes very little to the magnitude of the activation energy. The greater part of this energy is that expended by the ion in forming a hole in the adsorbed water and in breaking bonds with neighboring water molecules. Further, the coherence of the adsorbed water depends on the nature of the exchangeable ion. The foregoing conclusions are consistent with the results of the previous experiments.

Before concluding this paper, attention is called to two criticisms by Martin (1960) relative to our activation energy data. One criticism is that the differences in activation energies might reflect differences in kind or amount or both, of hydrous aluminum oxide impurities in the clays. This criticism has merit because we know that our clays contain these impurities. It is conceivable that the presence of hydrous aluminum oxide, especially if it occurs as a surface film, may give rise to structural changes in the adjacent water. We intend to investigate the role of hydrous aluminum oxide impurities.

The second criticism is that, if the permeability (geometry factor) and/or entropy of activation have any temperature dependence, this temperature dependence is automatically included in the E_a term. This criticism is unjustified. Included in the constants A and B of eqs. (2) and (3) is the product $Ke^{\Delta S^\ddagger/R}$ where K is the permeability and ΔS^\ddagger is the entropy of activation. Hence if K and ΔS^\ddagger change significantly with temperature and are included in E_a , K must be an exponential function of $1/T$ and ΔS^\ddagger must be a linear function of $1/T$; otherwise, a straight line would not be obtained on plotting $\ln D$ or $\ln u$ against $1/T$. There is no evidence for these functional relationships. In addition, if such functional relationships did exist, the correlation between the experimental values of E_a and the water properties would remain to be explained. Therefore we contend that, although both K and ΔS^\ddagger may change slightly with temperature, they do not change sufficiently to invalidate the results.

In summary, a water structure, which is different from that of normal water, exists on bentonite surfaces. This water structure is affected specifically by the different exchangeable ion species. In turn, the activation energy for exchangeable ion movement is governed largely by the nature of the adsorbed water. Clay-ion interaction appears to have little effect on this energy.

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