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WAVE MODEL OF LIQUID STRUCTURE IN CLAY HYDRATION

Key Words—Hydration, Liquid structure, Swelling, Water, Wave pattern.

Numerous descriptions of the water of hydration of colloids can be found in the literature, in which terms such as adsorbed, crystalline, osmotic, capillary, swelling, and structural have been employed. This diversity of terms suggests that no unifying concept has been developed to cover the phenomenon in a general way. Indeed, in the well-known text by van Olphen (1977), the swelling of clays is described as having several causes which operate at two different stages of swelling. But whatever the causes, water is portrayed flowing against pressure, inward between the clay particles and pushing them apart. A corresponding picture at the molecular level, however, describing how water molecules achieve this feat is lacking. This situation is reminiscent of that faced by the physical chemists in their explanation of osmosis. Glasstone and Lewis (1963) gave an extensive account of five mechanisms of osmosis, none of which was deemed satisfactory by those authors. Considering the unmistakable similarity in the mechanics of both processes, the conclusion that they are based on the same underlying molecular mechanism can hardly be avoided.

In the present note, a much more active role is given to water than is usually found in the literature. For example, a commonly held view is that the water is an inert material filling the space between mutually repelling clay particles. In a new model of liquid structure (Watterson, 1987a, 1987b), molecular clusters were described as being much larger in size than heretofore proposed, even as large as individual clay particles. The clusters do not just flicker on and off at random, but travel as a wave through the liquid medium. Ordered aggregates are formed as the result of on-going polymerization and depolymerization reactions involving cooperative making and breaking of intermolecular bonds. These reactions have definite velocity and direction and therefore set up a wave pattern. Figure 1, from Eisenberg and Kauzmann (1969) depicts the to-and-fro oscillation of a cluster as a sinusoidal function of time. Using the arguments put forward here, it is an easy step to interpret the illustration as three neighboring regions within the liquid, resulting in a wave in distance as well. The size and shape of a cluster is determined by the boundary conditions, just as the more familiar types of wave motion seen in stretched strings and drum skins produce a variety of patterns depending on those conditions. Within the region of one wavelength the oscillation of the arrangement of intermolecular bonds produces a rhythmic rise and fall in the tension that holds the cluster together. The existence of such regular clusters can be shown to underlie the colligative nature of solutions, and an examination of their role in osmosis reveals that the volume of each unit, u, is given by the Gas Equation:

$$Pu = kT$$

where P, T, and k are pressure, temperature, and Boltzmann's constant. Thus, the size of each cluster is precisely the volume occupied by one molecule of a perfect gas; hence, a cubic unit would have an edge about 34 Å long at room temperature and pressure. For water, this unit contains about 1300 molecules corresponding to a molecular weight of more than 20,000 daltons.

The presence of a solute interface, be it mineral, organic, or biological material, imposes restrictions on the rotation of adjacent water molecules, thereby forming a boundary in the wave motion. Put another way, solutes force the positioning of nodes in the spatial arrangement of wave units in the liquid medium. Such a two-dimensional node may readily form at the clay-water interface, because the hexagonal array of oxygen atoms on the silica surface has a high degree of compatibility with the structure of ice. This does not mean that the adsorbed molecules become immobilized or removed from the influence of the exchangeable cations (Walker, 1949), but only that they take up position forming an extended plane within the liquid. A layer of solvent 30–40 Å thick would therefore spread itself across the surface, next and parallel to it, extending over macroscopic distances in two dimensions. The model thus predicts that clusters of various shapes and sizes can be formed depending on the geometry of the solute interface.

The model also offers an immediate explanation for the formation of tactoids, or stacks of particles in parallel formation, which occur even in dilute suspension (Fripiat, 1986). Between each pair of particles is sandwiched the layer-shaped hydration cluster. It occurs quite readily, without any special energetic mechanisms needed to give rise to its existence, because clusters form in the solvent alone. This idea, that hydration layers are naturally occurring water clusters, means that they are not produced by the clay; rather, it is their arrangement and final macroscopic form that is determined by the clay. Thus, the two participants, clay and water, together build the superstructure. The superstructure is energetically favorable because the dimensions of the building blocks are mutually compatible such that the blocks fit neatly together in the overall construction. Because the layer-shaped hydration clus-

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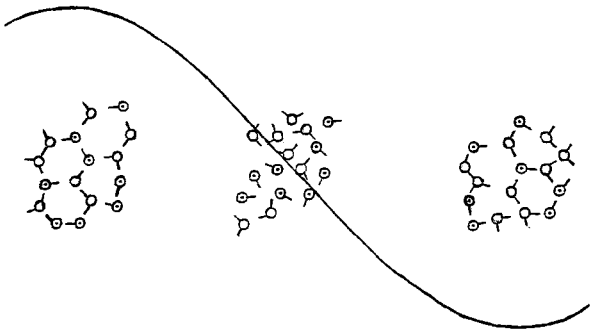


Figure 1. Illustration of a "flickering cluster" within bulk liquid water (from Eisenberg and Kauzmann, 1969). The three groupings of water molecules depict the order-disorder-order motion of a single cluster with time due to the rhythmic rearrangement of hydrogen bonds. Viewed as three neighboring regions within the liquid, they show structures that are periodic in distance as well, and coherent wave motion emerges.

ter is as large as a clay particle, the tension that extends through its interconnected bonds can be exerted over long distances on the molecular scale. This tension explains why hydrophilic clays retain water and how they can pull water laterally inwards against high applied pressures. This mechanism of strong lateral forces within the hydration layer is not considered in other models. The concept of water in the form of clusters has been presented to explain the packing of assemblies of components of biological systems, such as lamellar micelles and protein filaments, in which the dimension of 30 Å is also a recurring theme (Watterson, 1987c). From the point of view of the model, there is no difference in the way in which clay particles or protein molecules pack together to build larger entities. The mechanism that underlies both involves the active participation of the equally important hydration clusters.

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