

# THE GELATION OF MONTMORILLONITE

By M. B. MCEWEN.

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The combination of optical and elastic studies on sols of Wyoming bentonite containing the smallest particles sizes (15 to 20  $\mu$  equivalent spherical diameter) have led to the conclusion that the gelation of this system is due to the formation of a fibrillar network in which the plates are aggregated end-to-end in the form of flat, ribbon-like, filaments. The investigation of the effect of the addition of uni- and divalent electrolytes upon the rigidity is found to be consistent with the hypothesis that the particles are not in close contact, held by chemical bonds, but are situated at equilibrium distances which are determined by the combination of repulsive forces between their electrical double layers and attractive van der Waals forces.

The theory of the light scattering by a system of thin rectangular plates has been developed, and applied, to establish the existence of ribbon-like aggregates in undialysed sols (pH 8.9) at concentrations as low as 0.05 per cent.

When placed in cylindrical tubes less than 2 cm. in diameter sols at concentrations between 1.5 and 2 per cent show spontaneous birefringence due to a tendency for these aggregates to orientate perpendicular to the wall. This is confirmed by measurement of the effect of static shear upon the particle orientation in a cylindrical annulus, when it is found that at any given point in the annulus the change of particle orientation is equal to the theoretical angle of shear at that point. This tendency for the plates to orientate with their *c* axes parallel to the tube axis is confirmed by the X-ray measurements of Stokes. On electrodialysis the birefringence decreases and disappears at a pH of 4.5.

The irregularity in the particle size and shape necessitates the use of indirect methods to establish the long-range force (or electrical) theory of gelation in this system. An investigation of the elastic properties over a wide range of conditions is an obvious method of approach.

Taking as the elastic model a network of particles aggregated end-to-end in positions of minimum potential energy, an expression for the rigidity of the system in terms of the depth of the potential minimum, interparticle distance and double layer thickness can be derived. With the aid of potential energy curves, calculated from the recent theory of Verwey and Overbeek, the values of these quantities can be determined for different concentrations of uni- and divalent electrolytes up to the flocculating concentration. The variation of the rigidity with electrolyte concentration is found to be in accordance with this theory. This test is only valid after the addition of a certain amount of electrolyte (about 60 millimoles litre<sup>-1</sup> for NaOH), when the subsequent additions result predom-

antly in compression of the double layer and preferential adsorption of OH<sup>-</sup> virtually ceases, as shown by the constancy of the electrophoretic mobility. It is noteworthy that the rate of increase of rigidity with electrolyte concentration is higher in the latter than in the initial stages. According to the random-mesh (or contact) theory we would expect the reverse to be true.

The theory can also be used to show that for small thin plates end-to-end aggregation is a more stable configuration than parallel aggregation. On the other hand for larger and thicker particles the latter arrangement may be the state of minimum energy. This is of significance in the discussion of the effect of particle size upon the elastic properties of the system.

This work has been carried out in collaboration with Mr D. L. Mould.

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### Reference.

Verwey and Overbeek. Theory of the Stability of Lyophobic Colloids (Elsevier, 1948).

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## THE CRYSTAL CHEMISTRY OF MONTMORILLONITE—I\*

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Many analyses of montmorillonite indicate liberation of water above 300°C in excess of the amount required by the structure proposed by Hofmann, Endell and Wilm (1933). The structure of Edelman and Favejee (1940) will account for a larger quantity of water, but other inconsistencies with experimental results seem to arise.

Using as an analogy the hydrogarnets (Flint *et al.*; Pabst; McConnell), it is suggested that hydroxyl ions can occur as tetrahedral groups within the silica sheets in substitution for SiO<sub>4</sub> groups. Liberation of this "tetrahedral water" is believed to be associated with the second high-temperature endotherm which is occasionally a small deflection on the D.T.A. curve but is, nevertheless, characteristic of montmorillonite.

Although the ideal model would contain discrete tetrahedra of (OH)<sub>4</sub> replacing SiO<sub>4</sub>, real crystals of montmorillonite probably do not show such regularity. Statistically, however, 4 H ions or (Al + H) would proxy for Si within the silica sheets.

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