EFFECT OF GELATION ON THE PROPERTIES OF WATER IN CLAY SYSTEMS*

by

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ABSTRACT

Particle size distributions in samples of Belle Fourche, Wyoming, Aberdeen, Utah, and Cheto bentonite were obtained by a centrifugation technique. From these distributions and the clay density the number of particles per gram was calculated for the different samples. Then the clays were mixed in different proportions with water and the clay concentrations required for thixotropy were determined. It was found that a smooth curve was obtained when the clay concentration required for thixotropy was plotted against the number of particles per gram of clay. A smooth curve was also obtained when the clay concentration at the upper plastic limit was plotted against the number of particles per gram of clay.

In each suspension the water tension at the upper plastic limit was measured at several temperatures. From the resulting data, the relative partial molar free energy, entropy and heat content of the water were calculated. In all cases the values were negative, suggesting that the water in the suspension had more order than pure bulk water.

When the water tension was measured in different suspensions of Aberdeen and Cheto bentonite it was found that the tension remained zero until the clay concentration was sufficient to allow gelation of the suspension. Thereafter, the tension increased rapidly with clay concentration. Consequently, it was concluded that the sol–gel transformation was accompanied by a change in the energy status of the included water. This conclusion was supported by reference to other investigations in which changes in water properties were noted on gelation.

INTRODUCTION

SEVERAL years ago Foster (1953, 1955) studied the swelling properties of several Na-montmorillonites that differed in chemical composition. She observed that swelling decreased with increasing octahedral substitution of Fe^{+3} and Mg^{+2} for Al^{+3}. But no relationship was obtained between swelling and cation exchange capacity. Since swelling is normally ascribed

311

to the osmotic activity of the exchangable cations, Foster proposed that the Fe^{+3} and Mg^{+2}, having a smaller polarizing power than Al^{+3}, altered the electronic atmospheres of the ions in the crystal and thereby reduced the dissociation of exchangeable cations. However, we felt that the observed decrease in swelling with increasing octahedral substitution could have been due partly to a reduction in clay–water attraction occasioned by the proposed alteration in ionic atmospheres. Therefore, we decided to study the thermodynamic properties of water in suspensions of montmorillonites having different degrees of octrahedral substitution.

MATERIALS AND METHODS

Four of the five montmorillonites investigated in this research were studied by Foster (1953, 1955). They were obtained from Upton, Wyoming; Belle Fourche, South Dakota; Rideout, Utah; and Aberdeen, Mississippi. The fifth was studied by Grim and Kulbicki (1961) and was from Cheto, Arizona.

The clays named above were prepared at different times by somewhat different procedures. In every case, however, the greater than 2 micron fraction was removed from the raw clay by sedimentation, in accordance with Stoke's law. Wyoming clay remaining in suspension was passed first through an OH-saturated exchange resin and then through a H-saturated exchange resin and a Na-saturated exchange resin, in that order. The resulting suspension was concentrated to a thick paste by centrifugation. The Belle Fourche, Utah and Aberdeen* clays remaining in suspension after sedimentation were mixed with NaCl in an amount sufficient to far exceed the exchange capacity of the suspended clay. Following this the clays were washed by centrifugation and decantation until the supernatant liquids gave a negative $AgNO_3$ test for Cl^-. The Cheto clay remaining in suspension after sedimentation was treated the same as the latter clays except that it received three treatments with NaCl solution. All the clays were spread in paste form in a thin layer around the inside surfaces of 2-liter freeze-drying flasks and quick-frozen by immersing the flasks in a dry ice–acetone mixture. After freezing, the water was sublimed from the clays under vacuum. Dried in this manner the clays were soft and friable. They were finally ball milled for 30 min to convert them to powder form.

The prepared clays were characterized by determining their cation exchange capacities, surface areas and particle size distributions. Exchange capacities were determined by a method described by Mackenzie (1951). During this determination, the ammonium acetate extracts containing the displaced Na^+ were saved. Later they were evaporated to dryness to remove ammonia, treated with hydrogen peroxide to remove any remaining acetate, redissolved in deionized water and analyzed for Na^+ by using a

* The Aberdeen clay received a pretreatment with H_2O_2 to remove organic matter.

Baird Atomic KY flame photometer. Internal and external surface areas were determined by the method of Diamond and Kinter (1956) and Kinter and Diamond (1956). Particle size distributions were determined by a centrifugation technique using an International No. 2 centrifuge. Stock suspensions of the clays were prepared to contain approximately 0.8 per cent clay. The exact clay concentrations were determined by removing duplicate 10-ml samples, drying them at 110°C and weighing them. One-hundred-ml portions of these suspensions were centrifuged at different speeds and for different times so that the particles remaining in suspension after centrifuging had equivalent spherical diameters of less than 2.0, 1.0, 0.5 and 0.2 microns, respectively. The appropriate speeds and times were obtained from monographs provided by Tanner and Jackson (1947). Then duplicate 10-ml samples were removed from the supernatant suspensions to determine the concentrations of clay remaining in suspension. This was done by drying and weighing as before. The concentrations of clay remaining in suspension were divided by the concentrations of clay originally present to obtain the per cents remaining in suspension.

Initially the plan was to compare the properties of water in suspensions of the different clays at the same clay concentration. However, it was soon found that this plan was not feasible. At any given concentration some of the suspensions had too much consistency to stir, whereas others were still highly fluid. Therefore, the decision was made to compare the properties of water in suspensions at the same consistency. Two different consistencies were regarded as being appropriate for this purpose. They were the consistency at the sol–gel transformation or thixotropic limit and the consistency at the upper plastic limit. The thixotropic limit is defined as the minimum concentration of clay required for the development of thixotropy. It was determined for each clay by mixing different amounts of the clay with a constant volume of water in beakers and, after allowing the resulting suspensions to stand for three days, noting whether or not flow occurred when the beakers were tipped. The upper plastic limit is defined as the minimum concentration of clay required to prevent flow when the suspension is jarred. It was determined for each clay by preparing suspensions of different clay concentration as before, but of greater consistency, and noting whether or not grooves drawn in their surfaces disappeared when the beakers were jarred.

The relative partial molar free energy, relative partial molar entropy and relative partial molar heat content of the water were determined in each suspension at its upper plastic limit by measuring the water tension at different temperatures and employing thermodynamic equations which are discussed later. In the case of the Aberdeen and Cheto clay, the water tension was also measured in suspensions of different clay concentration. All tensions were measured with the self-adjusting, null-point tensiometer described by Leonard and Low (1961). This tensiometer was calibrated over the tension range of interest at each temperature.

RESULTS AND DISCUSSION

Table 1 shows the cation exchange data for the five clays. Unfortunately, the clays were not saturated with Na+ to the same extent by the procedures employed. This fact, and the difficulty encountered in trying to prepare

TABLE 1.—CATION EXCHANGE CAPACITIES AND SODIUM SATURATION OF BENTONITES

Clay	Cation exchange capacity, (meq/g)	Exchangeable sodium, (meq/g)	Sodium saturation, (per cent)
Belle Fourche			
(1)	0.850	0.75	
(2)	0.858	0.64	
Average	0.85	0.70	82
Wyoming			
(1)	0.878	0.73	
(2)	0.867	0.74	
Average	0.87	0.74	85
Aberdeen			
(1)	0.834	0.43	
(2)	0.843	0.42	
Average	0.84	0.43	51
Utah			
(1)	1.10	0.44	
(2)	1.12	0.44	
Average	1.11	0.44	40
Cheto			
(1)	1.12	0.92	
(2)	1.11	0.99	
Average	1.12	0.96	86

suspensions of the proper consistency at the same clay concentration, precluded the attainment of our original objective, namely, to determine the effect of isomorphous substitution in the clay on the properties of the associated water. However, results of interest from another viewpoint were obtained in this study, as will be shown below.

The surface area data are shown in Table 2. If, as claimed by Diamond and Kinter (1956), the ratio of external to total surface provides an indication of the thickness of the particles, we would be forced to conclude that the different clays had widely different particle thicknesses. The

TABLE 2.—SURFACE AREAS COMPUTED FROM GLYCEROL RETENTION

Clay	Surface area			Ratio of external to total
	External (m^2/g)	Internal (m^2/g)	Total (m^2/g)	
Belle Fourche	175	289	464	0.377
Wyoming	166	316	482	0.344
Aberdeen	123	703	826	0.149
Utah	72	779	851	0.085
Cheto	70	789	859	0.081

particles of the Cheto clay were thickest, that is, had the greatest stacking of layers, and the particles of the Belle Fourche clay were thinnest.

Figure 1 shows cumulative plots of the particle size distributions of the clays used in this study. In constructing these plots it was necessary to extrapolate them to 0 and 100 per cent clay. The fact that significant
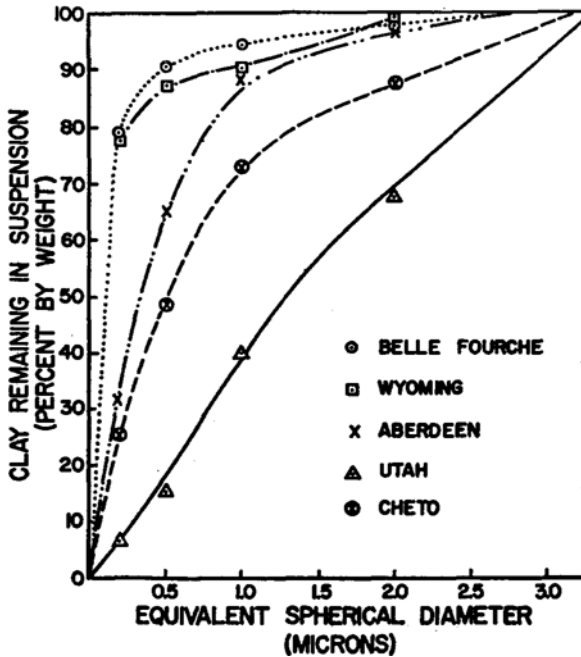

FIGURE 1.—Cumulative particle size distributions of different bentonites.

amounts of Cheto and Utah clays were found above 2 microns in size suggests that considerable aggregation of primary particles occurred during the initial drying process. The plots permit an approximate calculation of the number of particles per gram of clay if it is assumed that the particles are spherical in shape, that their average diameter in any size-class interval is the equivalent spherical diameter at the midpoint of the interval and that their density is 2.8 g per cm³. Then z, the number of particles in any size-class interval, designated by the subscript i, is given by

$$z_i = \frac{0.06\ \Delta W_i}{2.8\,\pi\,D_i{}^3} \tag{1}$$

where ΔW is the change over this interval in the clay remaining in suspension (expressed as a percentage of the total clay) and D is the equivalent spherical diameter at the midpoint of the interval. Further,

$$Z = \Sigma\ z_i \tag{2}$$

where Z is the number of particles per gram of clay. By using the particle
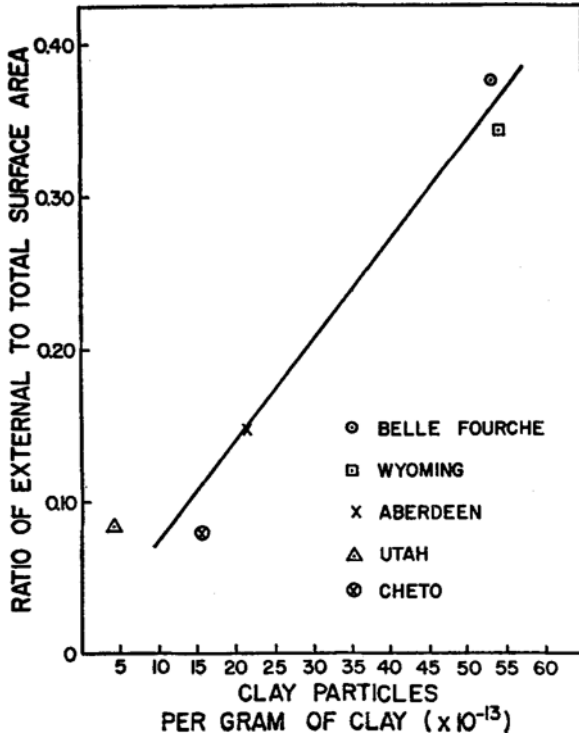

FIGURE 2.—The relationship between the ratio of external to total surface area and the number of clay particles per gram of clay.
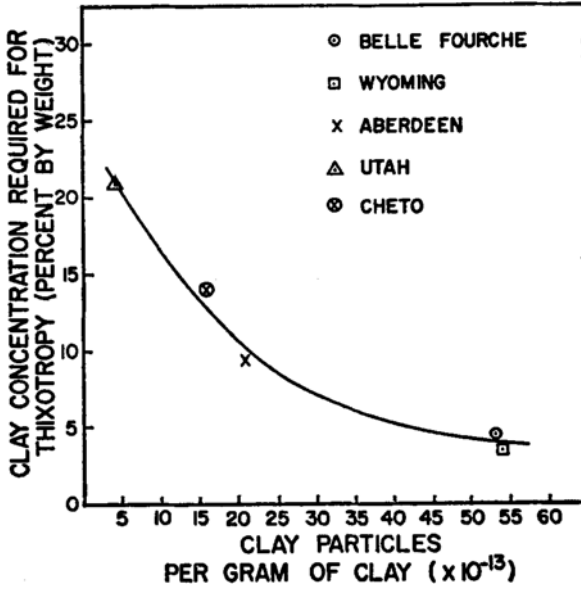
FIGURE 3.—The relationship between the concentration of clay required for thixotropy and the number of clay particles per gram of clay.
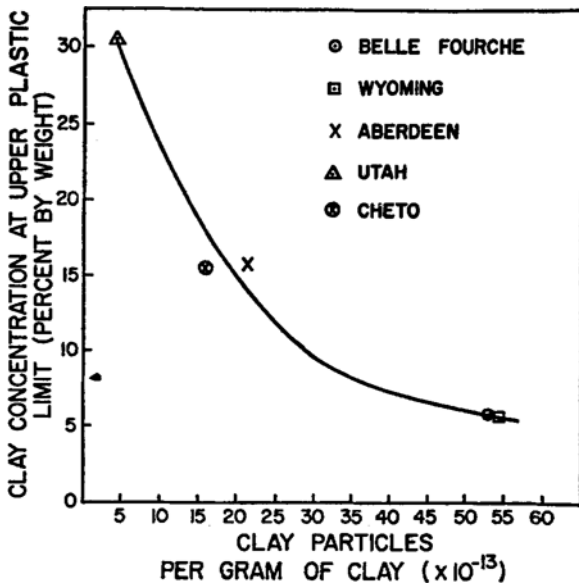

FIGURE 4.—The relationship between clay concentration at the upper plastic limit and the number of clay particles per gram of clay.

size distributions and these equations it was found that the number of particles per gram were: 53×10^{13} for Belle Fourche, 54×10^{13} for Wyoming, 21×10^{13} for Aberdeen, 4×10^{13} for Utah and 16×10^{13} for Cheto.

If the calculated values of the numbers of particles per gram of clay are valid approximations and if the ratios of external to total surface area give reliable estimates of the particle thicknesses, there should be a relationship between the two quantities. Such a relationship is shown in Fig. 2.

The number of interparticle contacts per unit volume should be a function of the number of particles per unit volume. The external surface area of the clay per unit volume should also be a function of the number of particles per unit volume. Therefore, if interparticle contacts result in interparticle bonds, or if external particle surfaces induce structural "rigidity" in the intervening water, the consistency of a clay suspension
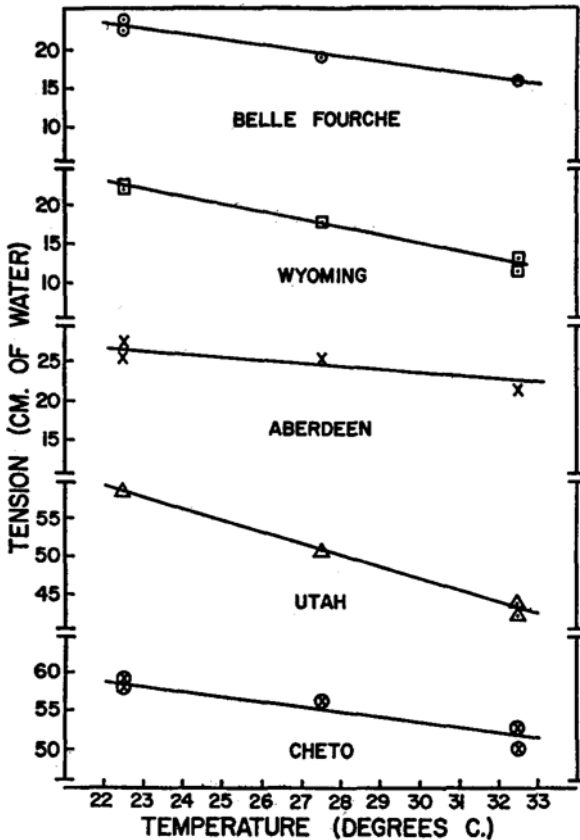

FIGURE 5.—The variation of water tension with temperature in suspensions of different bentonites.

or gel should be a function of the number of particles per unit volume. Expressed mathematically

$$\text{Gel consistency} = f\,(\rho_s c Z/100 \tag{3}$$

where f denotes the function, p_s is the suspension density in grams per cm³, c is the clay concentration in per cent by weight and Z, as before, is the number of particles per gram of clay. Since the density of a clay suspension changes very little over rather wide concentration limits we see that, at a given gel consistency, there should be an inverse relationship between the clay concentration and the number of particles per gram of clay. Figures 3 and 4 indicate that this is the case.

Figure 5 shows the variation of water tension with temperature in the different clays at the upper plastic limit. From the data in this figure the

TABLE 3.—Thermodynamic Properties of Water in Clay Suspensions
At the Upper Plastic Limit

Clay Suspension	$(\bar{F}-F^0)_{P_s}$	$(\bar{H}-H^0)_{P_s}$	$(\bar{S}-S^0)_{P_s}$
	Millicalories per mole	Millicalories per mole	Millicalories per mole per degree
Belle Fourche (5.8 per cent clay)	−8.01	−112	−0.346
Wyoming (5.7 cent clay)	−7.42	−134	−0.422
Aberdeen (15.8 per cent clay)	−10.7	−63	−0.177
Utah (30.5 per cent clay)	−21.3	−269	−0.822
Cheto (15.5 per cent clay)	−23.6	−114	−0.316

relative partial molar quantities in Table 3 were calculated by using the following equations:

$$(\bar{F} - F^0)_{P_s} = Mg\tau \tag{4}$$

$$(\bar{S} - S^0)_{P_s} = Mg\left(\frac{\delta\tau}{\delta T}\right) \tag{5}$$

$$(\bar{H} - H^0)_{P_s} = MgT\left(\frac{\delta\tau}{\delta T}\right) - Mg\tau \tag{6}$$

where $\bar{F}$, $\bar{S}$ and $\bar{H}$ are the partial molar free energy, partial molar entropy

and partial molar heat content, respectively, of the water in the suspension; F^0, S^0 and H^0 are the molar free energy, molar entropy and molar heat content, respectively, of pure bulk water at the same temperature; P is the pressure; M is the molecular weight of water; g is the acceleration of gravity; τ is the tension in cm of water; and T is the absolute temperature. The negative values for the relative partial molar quantities in the table suggest that the water in the clay suspensions is more strongly bonded and has a higher degree of order than pure bulk water.

Equations (4), (5) and (6) are slightly different from those used by Kolaian and Low (1960). They derived their equations by assuming that the water in a clay–water phase was brought into equilibrium with pure water in an adjoining phase by raising the pressure on the clay–water phase. Then they erroneously applied these equations to a system in which the pressure was reduced on the water in a pure water phase to bring it into equilibrium with the water in an adjoining clay–water phase. However, their calculated values for the relative partial molar quantities are not in error because they assumed that $\bar{v}$, the partial molar volume of the water in the clay–water phase, equalled v, the molar volume of pure water. If $\bar{v}$ in their equations is replaced by v, the resulting equations reduce to the ones we used, i.e., equations (4), (5) and (6). A simple derivation of the latter equations follows.

If the pressure on a pure water phase is reduced to bring the water therein into equilibrium with the water in an adjoining clay–water phase, we have

$$\bar{F}_{P_a} = F^0{}_{P_a} + \int_{P_a}^{P} \left(\frac{\delta F^0}{\delta P}\right)\, dP$$

$$= F^0{}_{P_a} + v(P - P_a) \tag{7}$$

in which $P_a > P$. This equation can be written

$$(\bar{F} - F^0)_{P_a} = -v\rho g\tau \tag{8}$$

where ρ is the density of pure water. But $v = M/\rho$ so that

$$(\bar{F} - F^0)_{P_a} = -Mg\tau$$

which is equation (4). Equation (5) can be obtained from it by differentiation with respect to T. And equation (6) can be obtained by combining equations (4) and (5) with the familiar equation

$$\Delta F = \Delta H - T\Delta S \tag{9}$$

Possibly the most interesting feature of our results was the correspondence between the clay concentration at the thixotropic limit and the clay concentration at which water tension developed. From Fig. 3 we see that the clay concentration at the thixotropic limit was about 9 per cent for
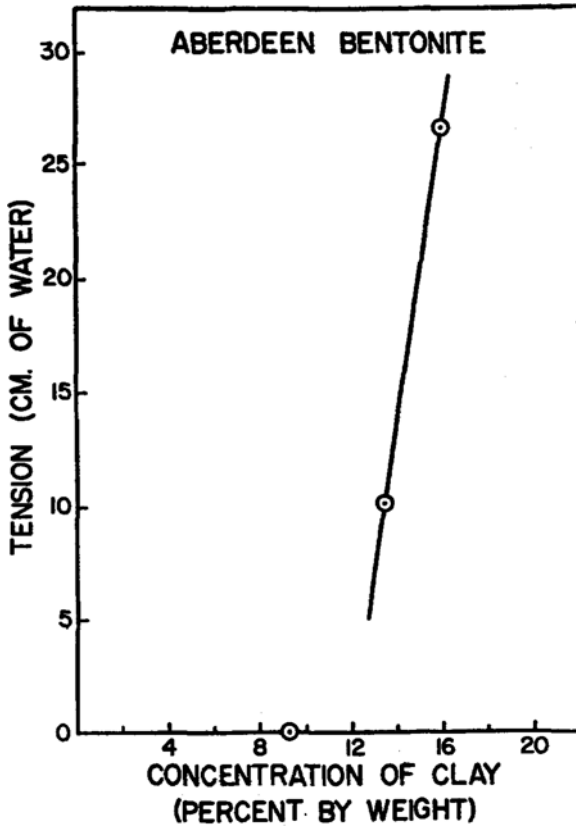
FIGURE 6.—Water tension versus clay concentration in Aberdeen bentonite
suspensions at 22.5°C.

the Aberdeen clay and about 14 per cent for the Cheto clay. From Figs. 6
and 7 we see that no water tension developed in these clays until the clay
concentrations were in the range of 9 to 14 per cent; then the water tension
increased quickly with concentration. It would appear, therefore, that the
development of water tension depends upon gelation, or vice versa.

The clay particles, acting as solute particles, would have an insignificant
effect on the water tension if it were not for their ionic atmospheres and/or
their interaction with the surrounding water. This fact is shown by
utilizing van't Hoff's law in the form

$$\tau \cong \frac{GkT}{\rho g} \tag{10}.$$

where G is the number of particles per cm^3 and k is the Boltzman constant.
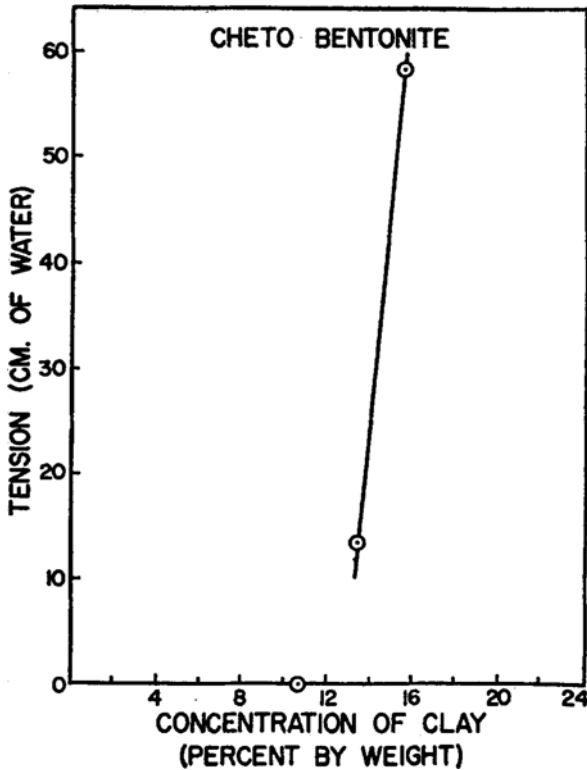
FIGURE 7.—Water tension versus clay concentration in Cheto bentonite suspensions at 22.5°C.

If it is assumed that the clay concentration is small, the volume of the suspension is almost the same as the volume of the contained water. Hence, assuming the water density to be essentially unity, we have

$$G \simeq \frac{x}{(1-x)} Z \tag{11}$$

where x is the gram fraction of clay in suspension. A combination of equations (10) and (11) yields

$$\tau \simeq \frac{x}{(1-x)} \frac{ZkT}{\rho g} \tag{12}$$

From the data already given we know x, Z and T. Consequently, we can calculate τ. For the Aberdeen and Cheto clays at the thixotropic limit τ is calculated to be 0.9×10^{-3} cm and 1.1×10^{-3} cm, respectively. These values are negligible compared to the observed values.

At the clay concentrations used in our experiments the observed water tensions cannot be ascribed to the osmotic activity of the exchangeable ions in the ionic atmospheres surrounding the particles. Note from Fig. 5 that, in all cases, the water tension decreased with increasing temperature. Had the osmotic activity of the exchangeable ions been responsible for the development of tension, the tension would have increased with increasing temperature. Theoretical justification for this conclusion has been presented by Kolaian and Low (1960). Therefore, the observed water tensions must have developed as a result of clay–water interaction.

Interaction between the particle surfaces and the water molecules probably causes these molecules to form a quasi-crystalline arrangement in which they have a low potential energy (Low, 1961). The interaction, and hence the degree of quasi-crystallinity, decreases as successive water layers are added. As a result, the tension of the water in a clay–water system decreases with increasing water content. However, the tension will not fall to the value given by equation (12) until the water films are so thick that the outermost layers are beyond the influence of the particle surfaces.

With the foregoing thoughts in mind, it is possible to provide a reasonable explanation for the observed relationship between the development of water tension and gelation. It may be supposed that, in those suspensions where the fields of influence of adjacent surfaces overlap, there is a coalescence of the quasi-crystalline water structures extending from these surfaces. Hence, there is no free water present in the system and tension develops. Simultaneously, the Brownian motion of the particles is reduced and the formation of interparticle bonds is facilitated. Both the coalescence of the water structures and the formation of interparticle bonds impart rigidity to the system. When such a system is disturbed by stirring or remoulding, the quasi-crystalline water is partly broken down and some of the interparticle bonds are ruptured. As a result, the system becomes a sol. But when the disturbance is removed the quasi-crystalline water and the interparticle bonds re-form and the system gels. On the other hand, if the fields of influence of adjacent surfaces do not overlap, the water midway between these surfaces remains the same as normal bulk water and no tension develops. Also, the free water molecules in this region transfer their momentum to the hydrated particles and thereby reduce the formation of interparticle bonds. Consequently, the system remains fluid.

The relationship between the development of water tension and gelation reported here is entirely consistent with the observations of Kolaian and Low (1960). They reported that the water tension in thixotropic clay suspensions was zero immediately after converting the suspensions to sols by stirring, but assumed progressively higher values as gelation occurred. In their experiments, as well as in ours, the sol to gel transformation was required for water tension to develop. They effected the sol–gel transforma-

tion by disrupting an existing gel and then allowing it to re-form, whereas, we effected this transformation by increasing the clay concentration to the thixotropic limit.

Now let us consider additional evidence indicating changes in the structure-sensitive properties of water during the gelation process. For this purpose we will define gelation as the time-dependent development of consistency in a particulate system. Hence, it will include all cases involving, not only the sol–gel transformation, but hardening or a gain in strength following some disturbance such as stirring or remolding.

The change in water tension with gelation appears to be a general phenomenon. Day* observed that an increase in water tension accompanied gelation in aqueous suspensions of different clay minerals. Mitchell (1960) noted that water tension was lower in freshly remolded clays than in the same clays that had been allowed to age after remolding. The aged clays had greater strength than the freshly remolded ones. And Bishop *et al.* (1960) reported a concomitant increase in water tension and gel strength with time after remolding a relatively dry London clay.

The susceptibility of water to freezing is affected by the sol–gel transformation. J. H. Kolaian, working in the junior author's laboratory, observed that a longer time was required to freeze water in montmorillonite gels than in the corresponding sols. His results have been reported by Low (1961). Further, Buehrer and Aldrich (1946) noted that very little water remained unfrozen at $-3°C$ in suspensions of Otay montmorillonite when the clay concentration was below 15 per cent by weight. However, when the clay concentration exceeded 15 per cent, most of the water remained unfrozen. The concentration of clay required for gelation, that is, the concentration at the thixotropic limit, was 15 per cent. Thus, it appears that the rate of freezing and the amount of water remaining unfrozen in clay–water systems are affected by the sol–gel transformation.

If the water structure in a clay–water suspension changes with gelation, it should be possible to detect a change in the volume of the suspension as this process occurs. Anderson *et al.* (1963) have detected such a change. They liquefied a suspension of montmorillonite by repeatedly dropping a steel ball through it. Then they kept the ball stationary and watched for any changes in volume. As gelation proceeded the suspension expanded.

In an interesting study of the sensitivity of clay Yamaguchi (1959) used a calorimetric technique to determine the heat capacity of a remolded moist Osaka clay. The clay was believed to be largely kaolinite. His results showed that the heat capacity increased with time. There was a simultaneous increase in gel strength. Since there was no reason for the specific heat of the clay to change, he concluded that the specific heat of the water increased. He also found that the electrical resistance of the clay increased as its gel strength increased. Presumably, the increase in electrical resistance was also due to the altered nature of the water.

* Unpublished Annual Report for 1956, California Agric. Exp. Sta. Project 1586.

Yamaguchi's work provides additional evidence for the idea that the properties of water in a clay suspension change with gelation.

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