THERMODYNAMIC PROPERTIES OF WATER IN SUSPENSIONS OF MONTMORILLONITE[1]

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ABSTRACT

The partial molar free energies, entropies and heat contents of the water in suspensions of Li-, Na-, and K-clay were measured relative to pure water by means of a tensiometer. This method of obtaining these thermodynamic properties is far more sensitive than the more common method utilizing adsorption isotherms and a form of the Clausius–Clapeyron equation. The partial molar free energy of the water decreased with time after stirring and increased rapidly upon stirring. This was taken as evidence that a gradual increase in the degree of orientation of water molecules associated with the clay particles occurred as the particles fell into the more random edge-to-surface thixotropic structure. The partial molar entropies and heat contents of the water in the suspensions were found to be less than those for pure water. Hence, this evidence also supported the postulate that an ordered water structure exists in the thixotropic suspensions.

INTRODUCTION

The thermodynamic properties of water in clay suspensions or gels of high water content have not been studied extensively. Probably the lack of interest in these properties can be attributed to the prevalent belief that water in such systems is, with the exception of that in a very thin layer at the clay surface, the same as normal water. However, evidence obtained in this laboratory (Low, 1960, 1961) suggested to the authors that even in dilute suspensions the bulk of the water might have properties which are measurably different from those of normal water. In the light of this evidence the present study was undertaken.

THEORY

Low and Anderson (1958b) derived equations for the partial molar free energy, partial molar entropy and partial molar heat content of water in a clay–water system involving variables which are measurable with great

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71

sensitivity. Taylor and Stewart (1960) derived essentially the same equations. However, these equations did not take into account the possible effects of curved air–water menisci which might exist at the surface of a clay–water gel or suspension. The following derivation is similar to that reported earlier (Low and Anderson, 1958b), but takes the effects of the air–water menisci into account.

Let us consider a two-phase system consisting of a clay gel or suspension separated from pure water by a membrane which is impermeable to the clay particles but permeable to water. If F^0 is the partial molar free energy of the pure water and $\bar{F}$ is the partial molar free energy of the water in the clay gel or suspension, for the equilibrium condition we can write

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

where P_a is atmospheric pressure and P is the pressure on the water within the suspension. Now

$$\left(\frac{\partial \bar{F}}{\partial P}\right) = \bar{V},$$

in which $\bar{V}$ is the partial molar volume of water in the suspension. Since water is nearly incompressible we shall assume $\bar{V}$ to be constant. Hence,

$$(\bar{F} - F^0)_{P_a} = -\bar{V} \int_{P_a}^{P} dP = -\bar{V}(P - P_a).$$

It should be observed that P is not the external pressure, P_e, applied to the suspension phase but, if curved air–water menisci are present at the surface of the suspension, is related to P_e by the equation

$$P_e - P = \frac{2\gamma}{r}. \tag{1}$$

In this equation γ is the air–water interfacial tension (surface free energy per unit area) and r is the curvature of the menisci, assumed to be spherical. In consequence

$$(\bar{F} - F^0)_{P_a} = -\bar{V}\left[(P_e - P_a) - \frac{2\gamma}{r}\right] \tag{2}$$

Letting $(P_e - P_a)$ equal π, the "osmotic pressure," we have

$$(\bar{F} - F^0)_{P_a} = -\bar{V}\pi + \frac{2\gamma\bar{V}}{r}.$$

If we assume that temperature changes do not alter the distribution of ions in the electric double layers of the particles enough to change significantly the ionic composition of the suspension, we can take the partial

derivative of equation (2) with respect to the temperature, T, and obtain

$$\left[\frac{\partial (\bar{F} - F^0)}{\partial T}\right]_{P_a} = -\bar{V}\left[\left(\frac{\partial \pi}{\partial T}\right) - \frac{2}{r}\left(\frac{\partial \gamma}{\partial T}\right)\right] - \left[\pi - \frac{2\gamma}{r}\right]\left(\frac{\partial \bar{V}}{\partial T}\right).$$

But recall that

$$\left(\frac{\partial \bar{F}}{\partial T}\right) = -\bar{S},$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right) = \beta \bar{V},$$

$$\left(\frac{\partial \gamma}{\partial T}\right) = -S_\gamma,$$

in which $\bar{S}$ is the partial molar entropy of the water in the suspension phase, β is the temperature coefficient of expansion of this water and S_γ is the surface entropy per unit of air–water interfacial area. Therefore,

$$(\bar{S} - S^0)_{P_a} = \bar{V}\left(\frac{\partial \pi}{\partial T}\right) + \beta \bar{V} \pi + \frac{2\bar{V}}{r}(S_\gamma - \beta \gamma), \tag{3}$$

and since

$$\Delta F = \Delta H - T \Delta S, \tag{4}$$

we can combine eqs. (2), (3), and (4) to obtain

$$(\bar{H} - H^0)_{P_a} = \bar{V} T\left(\frac{\partial \pi}{\partial T}\right) + \bar{V} \pi (\beta T - 1) + \frac{2\bar{V}}{r}(\gamma + S_\gamma T - \beta \gamma T). \tag{5}$$

Equations (2), (3) and (5) are identical to those published by Low and Anderson (1958b) with the exception of the last term on the right-hand side in every case. These terms include any capillary effects which were neglected earlier.

The above equations were derived using the concept that P_e, a positive pressure in excess of atmospheric, was applied to the suspension phase to keep the water therein in equilibrium with pure water at a pressure P_a, the atmospheric pressure. In keeping with custom, the pressure differential was referred to as the osmotic pressure. However, if a tensiometer (Fig. 1) is used to measure the variables in these equations, water equilibrium is maintained by suspending a column of water from the suspension such that it counterbalances the osmotic attraction of the suspension. Then the osmotic pressure equals the difference between P_a acting on the surface of the suspension at F in Fig. 1 and P_0, the pressure at the same level in the pure water within the membrane device (D). But

$$P_0 = P_a - \varrho g \tau$$

where ϱ is the density of the pure water in the manometer, g is the acceleration of gravity and τ is the tension, *i.e.* the difference in level at equilibrium

CCM 6

between the suspension surface at F and the meniscus in the manometer arm at G. Consequently,

$$\pi = P_a - P_0 = \varrho g \tau$$

and eq. (2) can be written

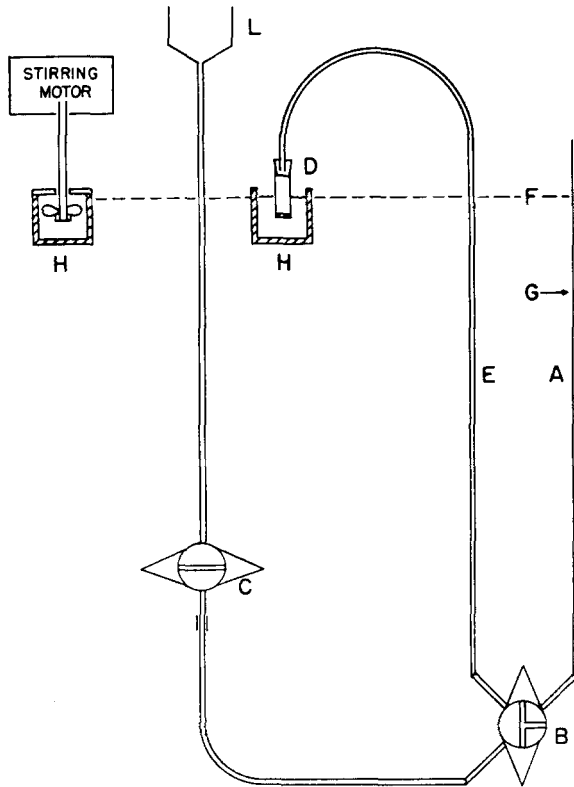$$(\bar{F} - F^0)_{P_a} = -\varrho g \bar{V} \tau + \frac{2\gamma \bar{V}}{r} \tag{6}$$

FIGURE 1.—Schematic representation of the tensiometer.

Further, if it is recalled that, for pure water,

$$\varrho = \frac{M}{V}$$

where M is the molecular weight of water and V is its molar volume, then it can be shown that

$$\left(\frac{\partial \varrho}{\partial T}\right) = -\varrho \beta$$

and, on taking the partial derivative of eq. (6) with respect to T or making the appropriate substitutions in eq. (3), we have

$$(\bar{S} - S^0)_{P_a} = \varrho\, g\, \bar{V}\left(\frac{\partial \tau}{\partial T}\right) + \frac{2\,\bar{V}}{r}\,(S_\gamma - \beta\gamma). \tag{7}$$

Finally, combining (4), (6) and (7)

$$(\bar{H} - H^0)_{P_a} = \varrho\, g\, \bar{V}\, T\left(\frac{\partial \tau}{\partial T}\right) - \varrho\, g\, \bar{V}\, \tau + \frac{2\,\bar{V}}{r}\,(\gamma + S_\gamma\, T - \beta\,\gamma\, T). \tag{8}$$

The terms on the left in eqs. (6), (7), and (8) shall be referred to as relative partial molar quantities.

EXPERIMENTAL METHODS

The homoionic montmorillonites employed in this study were prepared from Wyoming bentonite in the same manner as reported earlier (Low and Anderson, 1958a). To prepare the suspensions, the dry powdered clays were mixed with deionized water. The clay:water ratio was determined by the consistency of the resulting suspension. In general, water was added until the suspension could be stirred readily by the electric stirrer. Some of the suspensions were diluted further for comparative purposes.

The tensiometer[1] shown in Fig.1 was constructed by connecting two perpendicular arms of the three-way stopcock (B) to glass tubing with an inside diameter of 2 mm. The left-hand length of the glass tubing (E) was attached to the membrane device (D) by a rubber stopper. The remaining arm of the three-way stopcock was connected by Tygon tubing to the leveling bulb (L), through the single stopcock (C). The membrane device, obtained from the E. H. Sargent Company, was a fritted glass filter disc of fine porosity, sealed into a glass tube with an inside diameter of 10 mm. One side of the glass tube was cut off at the disc, allowing it to come into direct contact with the clay suspension upon immersion.

The three-way stopcock with the attached manometer arms, leveling bulb, Tygon tubing and single stopcock (C) were well secured to a rigid frame. The 50 ml plastic container (H) for the clay suspensions and the stirring motor were also secured to the rigid frame. The entire assembly was placed in a constant temperature air bath which was controlled to 25.0 ± 0.1 °C by a Philadelphia Microset thermoregulator. Cooling coils with tap water passing through them were used in conjunction with a 150 W incandescent bulb as a heater.

The procedure employed in obtaining the values of tension throughout a time period was as follows. A clay suspension of known concentration was

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[1] Appreciation is extended to Dr. Dale Swartzendruber for helpful suggestions regarding the design of the tensiometer.

6*

made up and stirred thoroughly in container (H). Throughout the stirring process a cap was fastened over the container. Slightly prior to the end of the stirring, the membrane device was mounted so that a continuous column of deionized water extended from the leveling bulb to the bottom of the filter disc. Stopcock (C) was then closed and the three-way stopcock adjusted so that manometer arm (E) was blocked off but arm (A) was open to the leveling bulb. The level of the water in the arm (A) was then adjusted to the expected equilibrium position by opening (C) again. After this adjustment, (C) was closed and a cathetometer was focused on the meniscus in arm (A). An appropriate time was allowed to elapse to ensure that the level of the water in arm (A) did not move because of leaks or temperature change. The excess water clinging to the filter disc was removed and then the disc was inserted into the clay gel.

The three-way stopcock was positioned so that a continuous column of water extended from the clay gel through the filter disc to the meniscus in the right-hand arm of the manometer. A movement of the meniscus downward, indicating movement of water into the clay suspension in response to the osmotic forces, would be corrected for by changing the position of the three-way stopcock and lowering the level of the water in arm (A) with the leveling bulb. The cathetometer would then be focused on the new level of the meniscus and the three-way stopcock positioned as before to allow the continuous column of water from the clay gel to the meniscus. If the meniscus again dended downward the above process was repeated. If the meniscus rose, the procedure was the same except that the level of the water in arm (A) was raised. This adjustment of the meniscus was continued until a level was obtained which did not tend to move either up or down. This level would then correspond to the tension of the water in the clay gel at that time. For example, in Fig. 1, the distance FG would correspond to the tension in centimeters of water when the meniscus was equilibrated at (G). After the value of tension had been obtained, the container was moved downward and recapped. The membrane device was removed from arm (E), washed, and placed into deionized water to preclude the possibility of air entering the fine pores of the filter disc and reducing its permeability.

The entire process of obtaining a value of tension, at any time, never required more than five minutes. This efficient experimental procedure was due to the rapid passage of water through the filter disc, together with the strong magnification of the meniscus by the cathetometer. Movement of the meniscus on the order of 0.50 mm, corresponding to a volume increment of 0.00039 ml, was readily discernible.

The procedure followed for a complete determination was to stir the suspension and measure the increase of tension with time until no further increase was observed. After this equilibrium was obtained, the clay sus-

pension was re-stirred and a second tension–time curve was obtained on the same sample. It should be emphasized that the membrane device was inserted into the suspension only during the period of measurement.

To obtain partial molar entropy data, curves were obtained of tension vs. time at different temperatures, the entire measuring apparatus being at the temperature of the air bath for each determination. Then a plot of the final equilibrium tension vs. the temperature was constructed.

RESULTS AND DISCUSSION

Figs. 2, 3 and 4 illustrate tension vs. time curves for Li-clay, Na-clay and K-clay suspensions. On the right-hand ordinates of the graphs, negative values of the relative partial molar free energy of the water are given. These values were obtained by using eq. (6) with the capillary term omitted. The reason for omitting this term will be apparent later. For the present we will consider only the tension values.
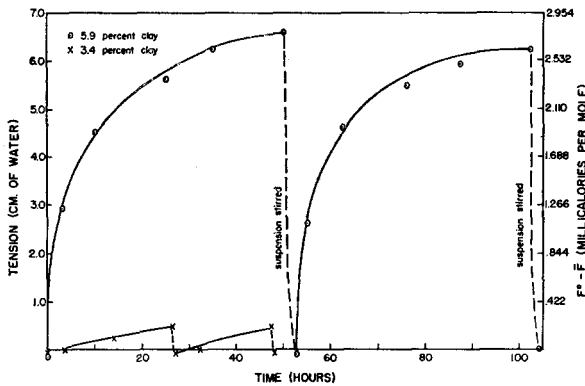

FIGURE 2.—The time-dependent development of tension in Li-bentonite suspensions.
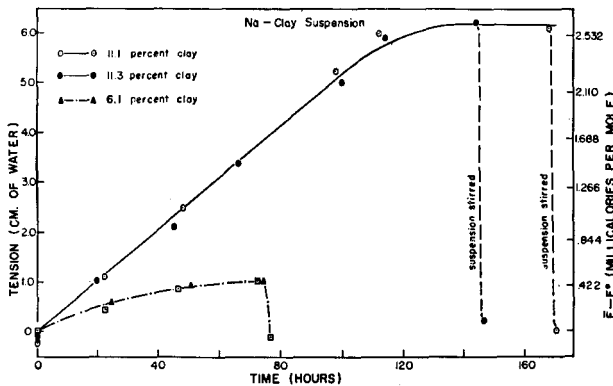

FIGURE 3.—The time-dependent development of tension in Na-bentonite suspensions.

Evidently in every case, the tension increased with time after stirring and then dropped suddenly when the suspension was stirred again. This phenomenon was first observed by Day (1956). Referring to eq. (6), it is evident that the increase in tension can be accounted for by either a decrease in the radius of curvature of the air–water menisci or a decrease in the partial molar free energy of the water in suspension. It should be recalled that no water interchange occurred between the tensiometer and the clay suspension during measurement. Therefore, all air–water menisci remained at the same level, namely, the level of the suspension surface. Hence, if the term on the left-hand side of eq. (6) was zero, i.e. only capillary forces were present, the radius of curvature of every meniscus,
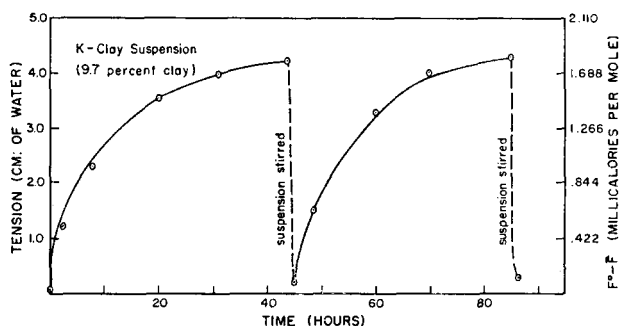

FIGURE 4.—The time-dependent development of tension in a K-bentonite suspension.

regardless of its radius in the equatorial plane, was the same. Now immediately after stirring the clay particles should have been oriented parallel to the streamlines (Marshall, 1949) whether they existed as individual laminae or as packets of laminae produced by compression during the stirring process[1]. As time passed and thixotropy developed, the particles should have assumed a more random arrangement, presumably that described by van Olphen (1956). These arrangements are illustrated in Fig. 5. If the transition with time after stirring was from (a) to (b), r for the menisci should have increased and the component of the tension due to capillary forces should have decreased. Further, the clay particles, being dispersed to a lesser extent, should have had less influence on the water so that $\bar{F}$ should have increased with an accompanying decrease in the tension. The available evidence (Buehrer and Rose, 1943; Campbell, 1952; Croney and Coleman, 1954) indicates that, in a clay–water system at equilibrium, the water tension is higher when the particles are in a highly dispersed state.

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[1] The possibility that associated clay laminae might be reversibly compressed into more compact packets or domains by stirring has been proposed independently in private communications by A. S. Michaels and J. P. Quirk.

Therefore, one might conclude that the transition was not from (a) to (b). But it is quite possible that, whereas the particle rearrangement with time tended to reduce the tension, the falling of water molecules into positions of minimum energy in a gradually developing water structure tended to increase the tension, and that the latter tendency predominated. If the clay particles induce changes in the structure of the water, one would expect
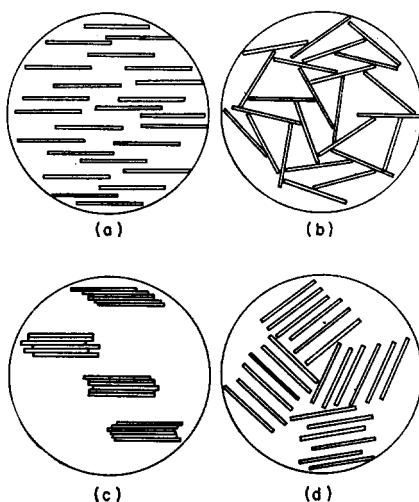

FIGURE 5.—Schematic representation of the arrangement of (*a*) individual clay particles immediately after stirring, (*b*) individual clay particles after development of thixotropy, (*c*) compressed clay packets immediately after stirring, and (*d*) expanded clay packets after development of thixotropy.

this structure to increase in coherence and extent as the agitation of the particles decreased. And, at equilibrium, the structural development in the water should be directly correlated with the degree of dispersion of the particles.

If the transition in particle arrangement with time after stirring was from (c) to (d), r for the menisci should have decreased. Also $\bar{F}$ should have decreased as the water became more intimately associated with the clay. Consequently, the tension should have increased, as observed. On the basis of the data available thus far it is not possible to discriminate between the two modes of particle rearrangement.

In Fig. 6 are shown the tension *vs.* time curves for an 8.34 percent Li-clay suspension at different temperatures. Similar curves were obtained at different temperatures for the Na-clay and K-clay. The plots of equilibrium tension *vs.* temperature for the three clays are shown in Fig. 7. In every case the equilibrium tension decreased linearly with an increase in tempera-

ture, the rates of decrease being 0.71, 0.29, and 0.33 cm per °C for the Li-clay, Na-clay and K-clay, respectively. According to eq. (7), the tension decrease with temperature can be attributed either to capillary effects or to the fact that the partial molar entropy of water is less in the suspension than in pure water. We will examine first the effect of temperature on capillarity.

If the measured tension is due to capillary action only, eq. (6) reduces to

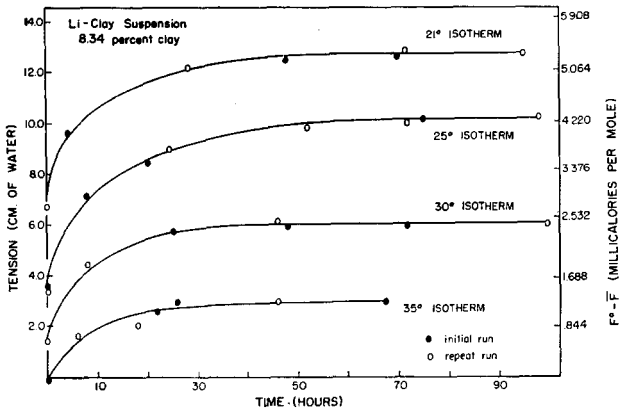$$\tau = \frac{2\gamma}{\varrho\, g\, r}.$$

FIGURE 6.—Curves of tension *vs.* time at several temperatures for an 8.34 percent Li-bentonite suspension.
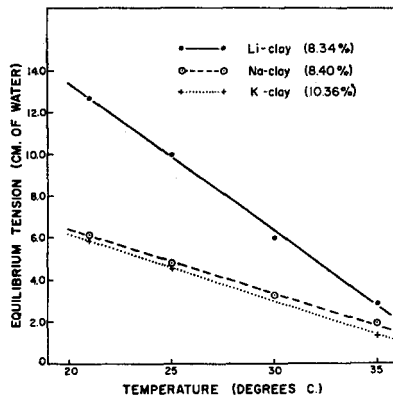

FIGURE 7.—Equilibrium tension *vs.* temperature for suspensions of Li-bentonite, Na-bentonite and K-bentonite.

From the observed value of τ and assuming that normal water is present in the suspension so that ϱ and γ are known, it is possible to calculate the appropriate value for r. In the 8.34 percent Li-clay at 25 °C this value is 0.015 cm. Now $\beta\gamma$ in eq. (7) has a negligibly small magnitude and since, under the specified conditions, the relative partial molar entropy is zero, the equation can be written:

$$\left(\frac{\partial \tau}{\partial T}\right) = -\frac{2 S_\gamma}{\varrho\, g r}.$$

When the value of S_γ, i.e. $-(\partial\gamma/\partial T)$ for normal water and the calculated value for r are substituted into this equation, the partial derivative of τ with respect to T is -0.021 cm per °C. This value is less than 3 percent of the observed value. Similar calculations could be made for the other two suspensions. Therefore, capillary action cannot account for the observed results and the capillary term in each thermodynamic equation can be neglected. An additional reason for neglecting the capillary term is that, for the measured tension to be zero immediately after stirring, the value of r in the preceding equations would have to equal the radius of the manometer tube. This is highly implausible.

A consideration of the data in Fig. 7 and eq. (7), with the last term omitted, leads to the conclusion that the partial molar entropies of the water in the clay suspensions were less than that of pure water. The relative partial molar entropies were -2.99×10^{-4}, -1.22×10^{-4} and -1.39×10^{-4} cal per °C per mole for the 8.34 percent Li-clay, the 8.40 percent Na-clay and the 10.36 percent K-clay suspensions, respectively. Since the partial molar entropy is a measure of the degree of disorder or randomness of the water, it may be said that the water in the suspensions was slightly less disordered or random in its molecular organization than pure water. The question now arises as to whether the exchangeable cations or the clay surfaces were responsible for the increased ordering of the water molecules.

If exchangeable cations were responsible for the observed tension, then, by virtue of van't Hoff's law, we can write

$$\varrho g \tau = R T m.$$

Here R is the molar gas constant and m is the effective molar concentration of exchangeable cations in the suspension. This effective concentration is not necessarily the concentration which would be calculated by dividing the total milliequivalents of cations on the clay by the volume of suspension because a portion of these cations would be undissociated and between laminae in packets. Taking again as an example the 8.34 percent Li-clay suspension at 25 °C, the value for m can be calculated from the equation, using the known values for the other variables. This calculated value is 3.9×10^{-7} moles per cm³. If we ignore the small change in the water

density with temperature, take the derivative of the equation with respect to temperature and rearrange, the result is

$$\left(\frac{\partial \tau}{\partial T}\right) = \frac{Rm}{\varrho g}.$$

Values for all the variables on the right hand side of this equation are known so $(\partial \tau / \partial T)$ can be calculated. The calculated value is $+0.033$ cm per °C. Note that the calculated value is less than 5 percent of the observed value and has the opposite sign.

It may be argued that this result is inapplicable because the exchangeable cations are not uniformly distributed and their distribution changes with temperature. Since this argument has some validity we shall examine it in the light of double-layer theory. First we shall specify the conditions of the experiment. The clays were prepared by a method (Low and Anderson, 1958a) which was intended to render then homoionic and salt-free. To test their purity, the dry powdered clays were mixed with deionized water to produce suspensions containing 1 percent clay by weight. These suspensions were centrifuged and the resulting supernatant liquids were tested for conductance and for the presence of SO_4 and Cl ions with solutions of $BaCl_2$ and $AgNO_3$, respectively. The specific conductances of the supernatant liquids at 25 °C were less than 2.5×10^{-5} mhos per cm and both ion tests were negative in all cases. These results indicate that the clays were essentially salt-free; therefore it may be said that, in the tensiometer experiments, salt-free clay suspensions were separated by a membrane[1] from pure water with which they were in osmotic equilibrium. The double-layer equation applicable here can be obtained by integrating the Poisson–Boltzmann equation for the condition that there are no interlaminar ions of the same sign of charge as the laminae themselves. The result, obtained independently by Langmuir (1938), Schofield (1946) and Eriksson (1950), is

$$d = \frac{kT}{\varepsilon z} \bigg/ \left(\frac{3.1416 D}{2\pi_m}\right),$$

where d is the distance between the clay laminae, k is the Boltzmann constant, T is the absolute temperature, ε is the protonic charge, z is the valence of the exchangeable ion, D is the dielectric constant and π_m is the osmotic pressure mid-way between the laminae. According to the theory, π_m is the equivalent of π, the observed osmotic pressure. Hence, we obtain

$$d = \frac{kT}{\varepsilon z} \bigg/ \left(\frac{3.1416 E}{2\varrho g \tau}\right).$$

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[1] Note that, since the membrane was permeable to ions, the presence of free salt in the suspension would not affect the magnitude of the observed tension.

Applying this equation to our system, the calculated value of d for the 8.34 percent suspension of Li-clay at 25 °C is 960×10^{-8} cm. This is a larger value than would be calculated from the concentration of clay in suspension assuming every particle to be a single lamina. After solving for τ and differentiating with respect to temperature, the result is

$$\left(\frac{\partial \tau}{\partial T}\right) = \frac{3.1416 D}{2 \varrho g} \left[\frac{kT}{\varepsilon z d}\right]^2 \left[\frac{1}{D}\left(\frac{\partial D}{\partial T}\right) + \frac{2}{T}\right],$$

ignoring again the change in water density with temperature. When the first term in the square brackets is given the handbook value of -0.0045 (Conway, 1952) and d is given the calculated value, $(\partial \tau / \partial T)$ is $+0.022$ cm per °C. Here again the calculated value is much less than the observed value and of opposite sign.

From the foregoing discussion it appears that exchangeable cations, like capillary forces, cannot account for the experimental observations. Therefore, the negative relative partial molar entropies of the water in the suspensions are ascribed to the influence of the clay surfaces. In view of the fact that the partial molar entropy of the water is not constant throughout the suspension and is the entropy increment per mole for the last addition of water, it appears that the water is ordered to the mid-plane between clay particles even in relatively dilute suspensions. This order should increase as the particle surfaces are approached.

Values for the relative partial molar heat content of the water in suspension were calculated from the data in Fig. 7 and eq. (8). They were -0.093, -0.038, and -0.043 cal per mole in the Li-clay, Na-clay and K-clay suspensions, respectively. The observed tension values employed in these calculations were 10 cm, 4.7 cm and 4.5 cm in the order quoted above. Recall that, in an ideal solution, which the solution mid-way between the clay laminae would approximate if the water had its normal properties, the relative partial molar heat content is zero. In other words, the first and second terms on the right-hand side of eq. (8) would cancel each other. But, in these experiments, the magnitude of the second term is only about 5 percent of that of the first. In addition, both terms have the same sign. We have shown that the magnitude of the first term depends on the degree of order in the water structure. Therefore, it is reasonable to conclude that the implication of water molecules in the structure is responsible for the low relative partial molar heat content of the water.

In summary, the partial molar free energy of water in a clay suspension decreases gradually with time after stirring. On the basis of the available evidence, this decrease is attributed to the development of a water structure which is induced by the particle surfaces. Apparently, the water in this structure has a lower partial molar entropy and partial molar heat content than pure water at the same temperature.

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