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Water in clay-water systems ⁽¹⁾

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SUMMARY

Swelling,
Clay,
Water,
Montmorillonite,
Clay-water,
Hydration.

The swelling of clay-water systems and the thermodynamic, hydrodynamic and spectroscopic properties of water in these systems are discussed. The swelling pressure of the clay and the magnitudes of the various water properties are shown to be related to the same variable, namely, the mass ratio of clay to water, by exponential equations of the same form. Analysis of the data represented by these equations indicates that the hydrogen bonds between the water molecules in the clay-water system differ from those in pure bulk water in polarity, length and breakability or bendability and that this difference increases with decreasing water content. Consequently, it is hypothesized that the structure of the water is perturbed by the surfaces of the clay particles and that this perturbation affects swelling and the properties of the water.

RÉSUMÉ

Gonflement,
Argile,
Eau,
Montmorillonite,
Argile-eau,
Hydratation.

L'eau dans les systèmes argile-eau.

Cet article étudie le gonflement des systèmes argile-eau ainsi que les propriétés thermodynamiques, hydrodynamiques et spectroscopiques de l'eau dans ces systèmes. On montre que la pression de gonflement de l'argile et les grandeurs relatives aux diverses propriétés de l'eau sont reliées à une même variable, qui est le rapport massique argile-eau, et sont exprimées sous forme d'équations exponentielles. L'analyse des résultats représentés par ces équations montre que les liaisons hydrogène entre les molécules d'eau dans le système argile-eau diffèrent de celles de l'eau liquide par leur polarité, leur longueur et leur aptitude à être cassées ou déformées et que ces différences augmentent lorsque la teneur en eau diminue. En conséquence, l'auteur est conduit à faire l'hypothèse que la structure de l'eau est perturbée par les surfaces des particules d'argile et que cette perturbation affecte le gonflement de l'argile et les propriétés de l'eau.

The interstitial water in the earth's crust is in intimate contact with the surfaces of clay and other silicate minerals. If these surfaces perturb the structure of the water, its structure-sensitive properties will be altered and many naturally occurring reactions and processes will be affected accordingly. Therefore, the author has spent much time studying the structure-sensitive properties of water in clay-water systems. Some of his results are reviewed in the present paper.

The swelling pressure, π , of a clay-water system is related to the difference between \bar{g}_w , the partial specific free energy of the water in the system, and g_w^0 , the partial specific free energy of pure bulk water, by the following equation

$$\bar{g}_w - g_w^0 = -\bar{v}_w \pi \quad (1)$$

where \bar{v}_w is the partial specific volume of the water in the system. Thus, anything that affects \bar{g}_w will affect π . It has been supposed heretofore that exchangeable cations dissociate from the surfaces of the superimposed clay layers to form an interlayer solution and that π equals the osmotic

pressure of this solution at the mid-plane between the layers. Further, it has been supposed that π can be calculated by using electrical double-layer theory. However, experimental evidence does not support these concepts. For example, consider figures 1 and 2 which were taken from one of the author's recent papers (LOW, 1980). Figure 1 shows that

$$\ln [(\pi + 1)/B] = \alpha m_m/m_w \quad (2)$$

or, alternatively, that

$$(\pi + 1) = B \exp(\alpha m_m/m_w) \quad (3)$$

where m_m/m_w is the mass ratio of montmorillonite to water and α and B are constants that are characteristic of the clay. Now, we can write

$$m_w/m_m = \rho_w S d \quad (4)$$

where ρ_w is the density of the water, S is the specific surface area of the clay and d is the average thickness of the water on the particle surfaces (or the half-distance between adjacent clay layers if all of the water is in interlayer regions). Combination of Eqs. (3) and (4) yields

$$(\pi + 1) = B \exp(\alpha/\rho_w S d). \quad (5)$$

⁽¹⁾ Exposé présenté à la Journée « L'eau aux interfaces : relations entre les états de l'eau, l'organisation et les propriétés des systèmes argile-eau ». Versailles. 5-6 octobre 1981.

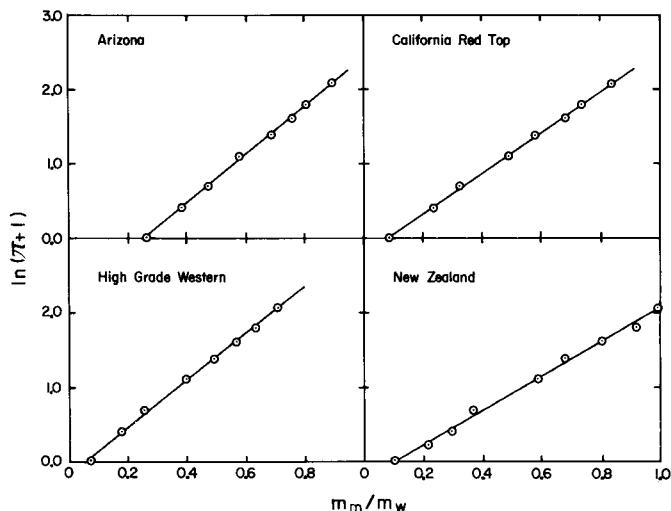


Figure 1
The relation between $\ln(\pi + 1)$ and m_m/m_w for the montmorillonites identified as Arizona, California Red Top, High Grade Western and New Zealand.

Relation entre $\ln(\pi + 1)$ et m_m/m_w pour les montmorillonites identifiées d'Arizona, de Red Top en Californie, de High Grade Western et de Nouvelle-Zélande.

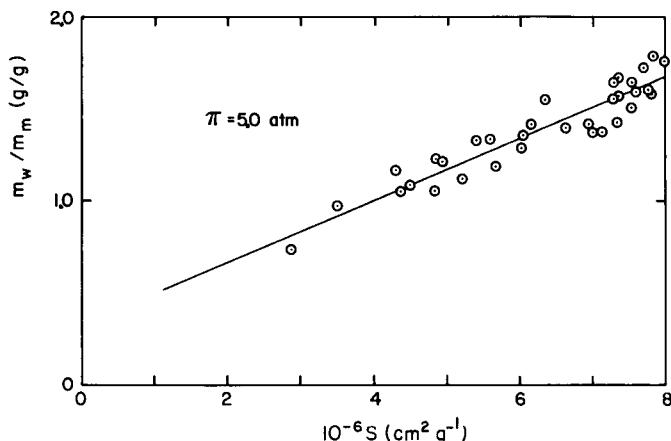


Figure 2
The relation between m_w/m_m and S when $\pi = 5.0$ atm.
Relation entre m_w/m_m et S pour $\pi = 5.0$ atm.

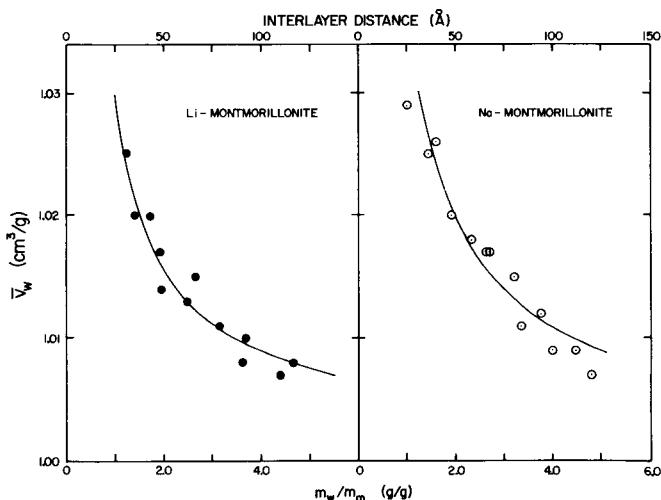


Figure 3
The dependence of \bar{v}_w on m_w/m_m at 25°C.
Variation de \bar{v}_w en fonction de m_w/m_m à 25°C.

It can be demonstrated (LOW & MARGHEIM, 1979) that Eq. (5) does not have the form expected from double-layer theory and, therefore, is not consistent with the osmotic concept of swelling.

Figure 2 shows that, when $\pi = 5.0$ atm, a linear relation exists between m_w/m_m and S for a series of montmorillonites having widely different values of σ , the surface charge density. The same kind of relation also exists at other values of π . By rearranging Eq. (2) we obtain

$$m_w/m_m = \alpha/\ln[(\pi + 1)/B]. \tag{6}$$

Hence we see that, if π is constant, m_w/m_m can be linearly related to S only if α is a linear function of S alone, and B is essentially the same for all montmorillonites. But if α is a linear function of S alone, it necessarily follows that swelling is independent of σ . Since σ regulates the osmotic pressure of the interlayer solution, the lack of dependence of π on σ reveals that swelling is not primarily osmotic in nature. Therefore, swelling must be attributed to the interaction of water with the surfaces of the montmorillonite layers.

It has been found experimentally (Low, 1981) that less than 2% of the exchangeable cations are dissociated from the surfaces of the montmorillonite particles. As a result, the effective value of σ , i.e., the value of σ at the outer limit of the Stern layer, is only a small fraction of that at the particle surface and the electrical double layer is weakly developed. Evidently, this is the reason why the osmotic contribution to π is so small.

Prior to discussing the nature of the water in clay-water systems, consider any extensive thermodynamic property, X , of the system. If we designate the masses of water and clay by m_w and m_m , respectively, then \bar{x}_w , the partial specific property of the water in the system, is defined by

$$\bar{x}_w = (\partial X/\partial m_w)_{P,T,m_m} \tag{7}$$

where P is the pressure and T is the temperature. Further, Φ_x , the apparent specific property of the water in the system, is defined by

$$\Phi_x = (X - m_m x_m^0)/m_w \tag{8}$$

where x_m^0 is the specific property (i.e., the value of the property per unit mass) of the pure montmorillonite. A few partial specific and apparent specific properties of the water in clay-water systems will now be discussed.

Presented as functions of m_w/m_m in figures 3, 4, 5 and 6 are the partial specific volume of the water, \bar{v}_w , the apparent specific expansibility or isobaric rate of change of the apparent specific volume of the water with temperature, $(\partial\Phi_v/\partial T)_P$, the isothermal rate of change of the apparent specific entropy of the water with pressure $(\partial\Phi_s/\partial P)_T$, and the apparent specific compressibility or isothermal rate of change of the apparent specific volume of the water with pressure, $(\partial\Phi_v/\partial P)_T$, respectively. It should be noted that, in all cases, the clay in the system was Li- or Na-saturated, $-2 \mu\text{m}$ Upton montmorillonite. Figures 3, 4 and 5 were taken from an earlier paper of the author (LOW, 1979) and figure 6 was taken from a paper which is being prepared for publication. In each of these figures, the solid curve is described by the empirical equation

$$J_i = J_i^0 \exp[\beta_i/(m_w/m_m)] = J_i^0 \exp[\beta_i(m_m/m_w)] \tag{9}$$

where J_i represents the value of any given water property, designated by the subscript i , for the clay-water system, J_i^0 is the value of the same property for pure bulk water and β_i is the appropriate constant.

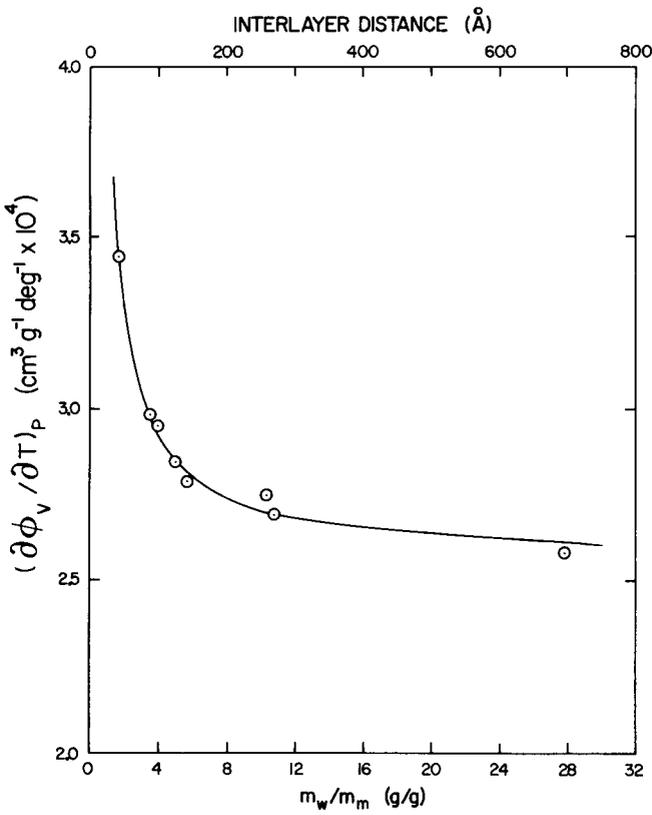


Figure 4
The dependence of $(\partial\Phi_v/\partial T)_P$ on m_w/m_m at 25 °C.
Variation de $(\partial\Phi_v/\partial T)_P$ en fonction de m_w/m_m à 25 °C.

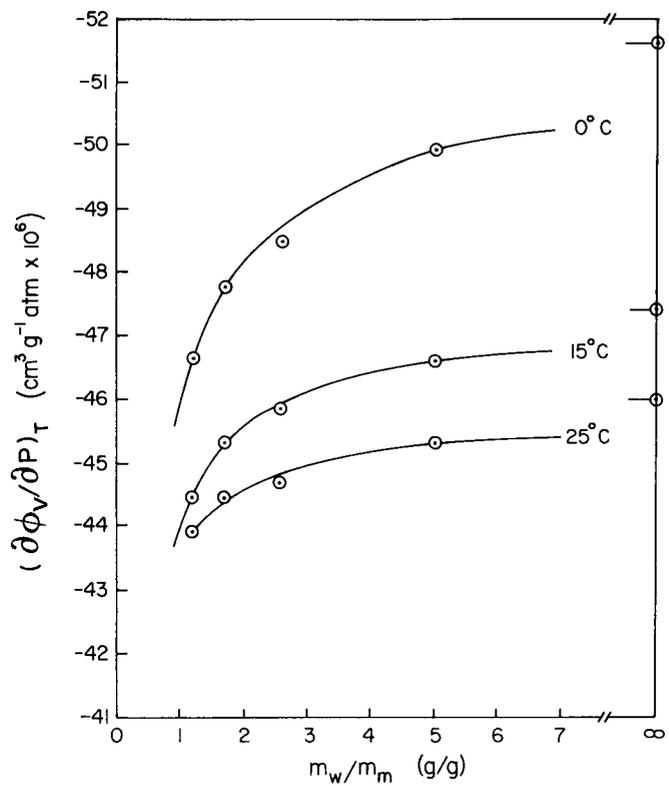


Figure 6
The dependence of $(\partial\Phi_v/\partial P)_T$ on m_w/m_m at three different temperatures.
Variation de $(\partial\Phi_v/\partial P)_T$ en fonction de m_w/m_m pour trois températures différentes.

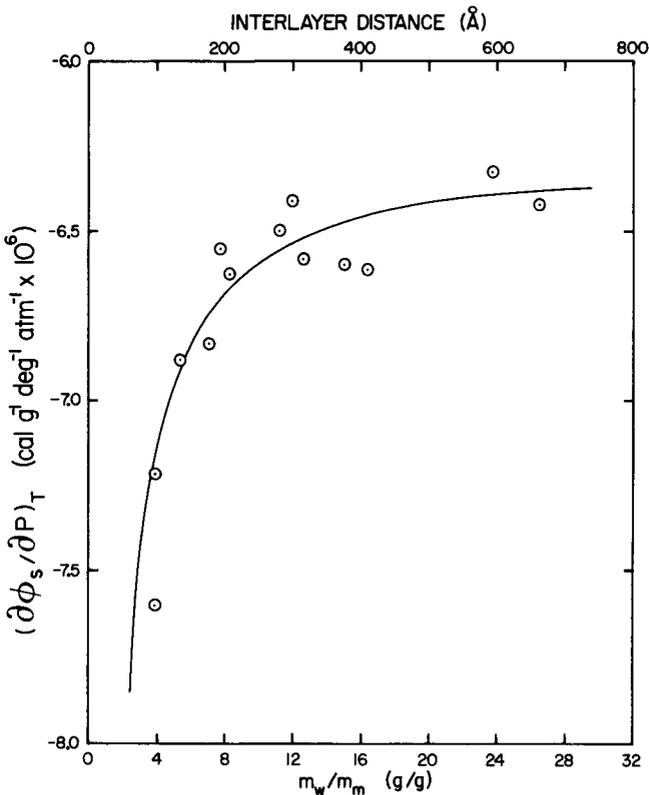


Figure 5
The dependence of $(\partial\Phi_s/\partial P)_T$ on m_w/m_m at 25 °C.
Variation de $(\partial\Phi_s/\partial P)_T$ en fonction de m_w/m_m à 25 °C.

Before interpreting the thermodynamic data just presented, it is advisable to recall that, over short distances, water is supposed to have an open hydrogen-bonded structure similar to that of ice. Hence, when the hydrogen bonds between any water molecule and its neighbors are broken, the water molecule can fall into interstitial sites. Or, alternatively, when these bonds are bent, it can move toward the same sites and pull its neighbors closer together. In either case, the net result is a decrease in volume and an increase in entropy, i.e., disorder.

From figure 3 we see that \bar{v}_w is greater than v_w^0 , the specific volume of pure bulk water, and increases as m_w/m_m decreases. We can conclude, therefore that the hydrogen bonds between the water molecules are longer and/or that fewer of them are broken or bent.

Figure 4 shows that $(\partial\Phi_v/\partial T)_P$ is greater in the clay-water system than in pure bulk water and increases as m_w/m_m decreases. The excess $(\partial\Phi_v/\partial T)_P$ in the clay-water system can be attributed to hydrogen bonds that are more easily extended or less easily broken or bent under the influence of the particle surfaces.

Figures 5 and 6 can be interpreted together. They show that $(\partial\Phi_s/\partial P)_T$ is more negative and $(\partial\Phi_v/\partial P)_T$ is less negative in the clay-water system than in pure bulk water and that the former becomes progressively more negative and the latter becomes progressively less negative as m_w/m_m decreases. Now

$$(\partial\Phi_s/\partial P)_T/(\partial\Phi_v/\partial P)_T = (\partial\Phi_s/\partial\Phi_v)_T$$

and so a relatively large negative value of $(\partial\Phi_s/\partial P)_T$ and a relatively small negative value of $(\partial\Phi_v/\partial P)_T$ indicates a relatively large decrease of entropy or disorder per unit

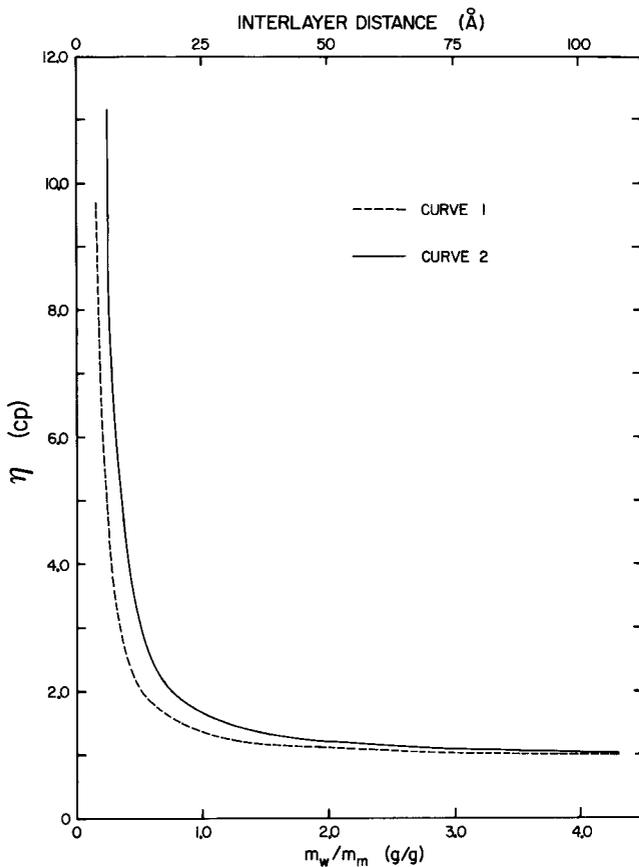


Figure 7
The dependence of η on m_w/m_m .
Variation de η en fonction de m_w/m_m .

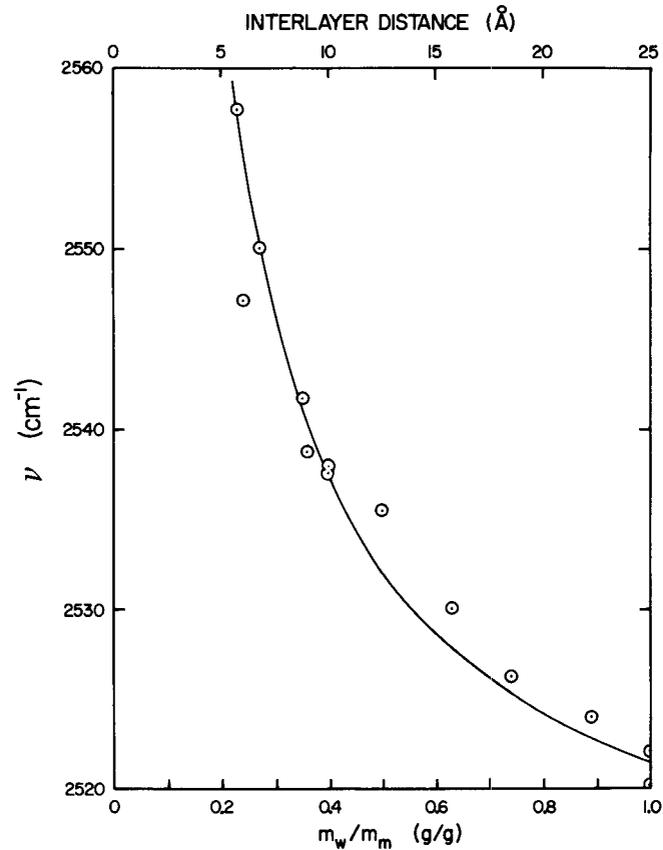


Figure 8
The dependence of ν on m_w/m_m at 25°C.
Variation de ν en fonction de m_w/m_m à 25°C.

decrease in volume. This can be true only if relatively few bonds are broken or bent in the interparticle water by the application of pressure.

Figure 7 was reproduced from an earlier paper (LOW, 1979). It shows curves, obtained by different methods, of the average viscosity, η , of the interparticle water versus m_w/m_m in an Upton montmorillonite-water system. Both curves are described by Eq. (9) with $i = \eta$ but the respective values of β_i are different. Since the laminar or viscous flow of water requires the breaking of hydrogen bonds between water molecules in adjacent laminae, the magnitude of η is supposed to depend on the strength and number of bonds involved. Assuming that the number of bonds per unit area is the same for interparticle water as for bulk water, we again conclude that the hydrogen bonds in the interparticle water are less easily broken than those in bulk water.

Figure 8 was taken from the same paper as figure 7 and applies to the same system. In the figure, ν , the frequency of O-D stretching in the interlayer water, is presented as a function of m_w/m_m . Note that the solid curve, which obeys Eq. (9) with $i = \nu$, adequately describes the data. Since ν has been observed to shift to higher frequencies as the length of the hydrogen bond increases (BELLAMY & PACE, 1969; NAKAMOTO *et al.*, 1955), it appears that the hydrogen bonds are longer in the interparticle water than in pure bulk water. The same conclusion was reached on the basis of the data in figure 3.

Figure 9 was taken from a paper which is being prepared for publication. It shows the molar absorptivity, ϵ , for O-D stretching in HDO mixed with Upton montmorillonite at different values of m_w/m_m . The solid line is described by Eq. (9) with $i = \epsilon$. Now, it can be shown (e.g., SESHADRI &

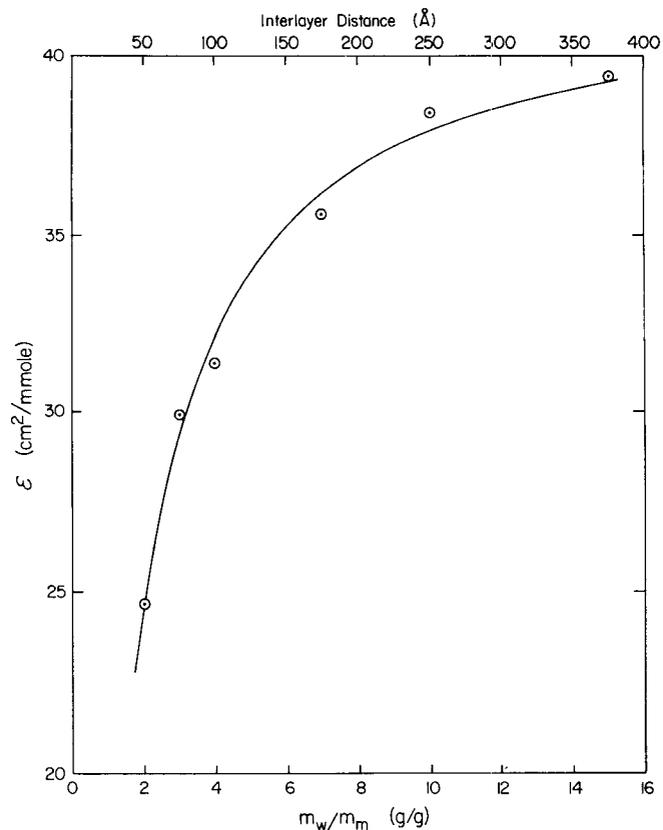


Figure 9
The dependence of ϵ for O-D stretching on m_w/m_m .
Variation de ϵ pour une vibration de valence O-D en fonction de m_w/m_m .

JONES, 1963 ; STEELE, 1971) that, for absorption bands of Gaussian shape,

$$B \propto \Delta\nu_{1/2} \varepsilon \propto (\partial u / \partial Q_1)^2 \quad (10)$$

where B is the integrated absorption intensity, $\Delta\nu_{1/2}$ is the width of the absorption band at half height, u is the dipole moment of the absorbing molecule and Q_1 is the normal coordinate describing the first fundamental vibration. Hence, the data in figure 9 in conjunction with Eq. (10) indicate that the distribution of molecular charge is different in the interparticle water than in pure bulk water and that the difference increases as m_w/m_m decreases.

In figure 10, the values of ε for the interparticle water in several montmorillonites are plotted against the corresponding values of σ at three values of d. Observe that ε is independent of σ at each value of d. This means that the particle surfaces, and not the interlayer cations that balance the charge on these surfaces, are responsible for the exponential change in ε with m_w/m_m .

This paper does not report all of the data that we have accumulated on the swelling of clay-water systems. Nor does it report all of the data that we have accumulated on the thermodynamic, hydrodynamic and spectroscopic properties of water in these systems. However, the reported data are sufficient to illustrate the fact that the swelling of such systems is described by Eq. (3) and that the properties of water within them are described by Eq. (9). Now, we can combine Eqs. (3) and (9) by eliminating the common variable, m_w/m_m . The result is

$$(\pi + 1)/B = (J_i/J_0)^{\alpha/\beta_i} \quad (11)$$

In a similar way, we can combine Eq. (9) for one property, designated by the subscript 1, with Eq. (9) for another property, designated by the subscript 2, and obtain

$$(J_1/J_1^0) = (J_2/J_2^0)^{\beta_1/\beta_2} \quad (12)$$

Thus, we see that the swelling pressure of a clay-water system is related to the properties of the water within it and that these properties are related to each other. This could be so only if the swelling pressure and water properties are mutually dependent on the same factor (or factors). In this regard, attention is called to the fact that this factor must influence the water to an appreciable distance from the particle surfaces because π does not fall to zero and J_i/J_i^0 does not become unity for the various properties until m_w/m_m reaches substantial values.

Before formulating any hypothesis on the nature of interparticle water, it is advisable to summarize the observations and interpretations that have been made. They are :

- 1) the value of π for a clay-water system is an exponential function of m_w/m_m or, alternatively, of $1/d$ and is essentially independent of σ ,
- 2) J_i/J_i^0 is also an exponential function of m_w/m_m ,
- 3) the hydrogen bonds in interparticle water are longer than those in pure bulk water,
- 4) the hydrogen bonds in the interparticle water are less breakable or bendable than those in pure bulk water,
- 5) the molecular charge distribution in the interparticle water differs from that in pure bulk water,
- 6) the molecular charge distribution in the interparticle water is not affected by σ ,
- 7) swelling and the properties of interparticle water are interrelated and, therefore, must depend on the same factor, and

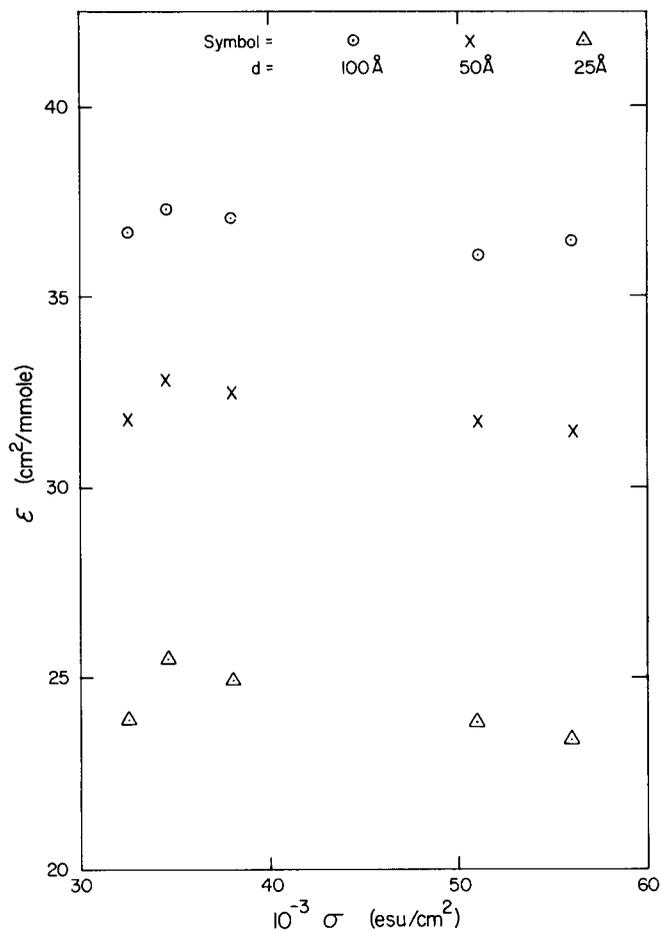


Figure 10
The effect of σ on ε at different values of d.
Influence de σ sur ε à différentes valeurs de d.

8) this factor must be effective to an appreciable distance from the particle surfaces.

On the basis of the foregoing observations and interpretations, and in view of the fact that hydrogen bonding in water is a cooperative phenomenon (i.e., the nature of any hydrogen bond influences the nature of other hydrogen bonds in the coordinated water structure, and vice versa) the following hypothesis is proposed. The motion, spatial arrangement and charge distribution of the oxygen atoms in the surface of a clay particle are different from those of the oxygen atoms in water. Consequently, the hydrogen bonds that form between the surface oxygens and the layer of water molecules next to them are different from those that normally form between water molecules. This difference affects the hydrogen bonds that form between subsequent layers of water molecules to a degree depending on their distance from the surface. Relative to the hydrogen bonds in pure bulk water, the hydrogen bonds in the water near the surface have a different polarity (they are probably more covalent) are longer and are less breakable or bendable. As a result, the properties of the interparticle water, including its \bar{g}_w which governs the magnitude of π , differ from those of pure bulk water. In other words, the structure of the water is perturbed to an appreciable depth by the particle surfaces and this perturbation affects swelling and the properties of the interparticle water.

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