Water on the Surfaces of Clay Minerals: Orientation, Diffusion and Proton Exchange

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I INTRODUCTION

The surface of clay minerals such as montmorillonite and vermiculite offers an unique environment for the study of water molecules arrangement and of their interaction with cations since

a) the negatively charged lattice framework may be considered as an anion with an infinite radius of curvature and

b) that there is no appreciable hydrogen bond interaction between the adsorbed species and the oxygen atoms of the basal planes.

Therefore, the H_2O-H_2O and H_2O cations interactions are essentially those effecting the water properties.

Oriented clay samples with high surface area (~ 800 m^2/g) are easily obtained by sedimenting slowly a clay suspension on a flat inert support. In these films, the microcrystals achieve an almost perfect orientation with respect to the "c" axis (normal to the surface of the film) but remain randomly distributed with respect to the "a" and "b" axis. Such films are suitable for X-ray diffraction or infrared spectroscopy investigations. When several of these films are stacked on top of each other thick pseudo monocrystals are obtained in which the proton or deuteron nuclear magnetic resonance

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signals are detectable. They may also be used for diffusion experiments using radioactive tracers or for neutron scattering measurements.

From these various experimental techniques information on the orientation, the motion and the chemical properties (dissociation) of the adsorbed water were obtained: this contribution aims to review critically these results in order to allow comparison to be made with observations made on other kinds of interfaces.

II THE STRUCTURAL ARRANGEMENT OF WATER MOLECULES

The uptake of water molecules from the vapour phase causes a swelling of the pseudo-monocrystals along the "c" axis and this expansion of the "c" parameter may be followed quite accurately by X-ray diffraction. Structural arrangements may therefore be proposed but it must be emphasized that these models only have a statistical significance as translational motions induce exchange of position of the adsorbed species at a rate which is high when refered for instance to the time scale of NMR.

The first obvious observations resulting from X-ray diffraction data is that it is the chemical characteristics of the cations balancing the lattice charge that rule the swelling phenomena. The higher the charge the lower the radius and the more pronounced is the expansion along the "c" axis. The structural arrangements for Na montmorillonite and Mg vermiculite have been especially refined by the purely crystallographic approach of Pererat and Mering[1] and Walker.[2]

For a Na montmorillonite (Wyoming) in the dehydrated state the exchangeable cations are slightly embedded into the hexagonal holes of the lattice oxygen planes. This same position is maintained when a water monolayer is adsorbed between the sheets. The electron density distribution across the interlamellar space reveals a double peak originating from the water oxygen. This suggests a tetrahedral distribution of water molecules as represented in Figure 1, Mamy.[3] Dielectric measurements performed on hydrated Na montmorillonite[4] show a close similarity with the dielectric properties of hexagonal ice. The difference may be interpreted by assuming that the charge-balancing cations behave as "lattice defects" in the structural arrangement shown in Figure 1.

In the fully hydrated Mg vermiculite[2] each water sheet is arranged in a regular hexagonal pattern and the interlayer cations are located midway between water sheets in octahedral coordination (Figure 2a). The H_2O-O distance in this case is 3.1 Å and the d(ool) spacing 14.81 Å.

On dehydration a contraction which lowers this spacing to 14.36 Å occurs and the H_2O-O distance decreases to 2.90 Å. The interlayer water

Medium plane of the octahedral layer

Medium plane of the octahedral layer
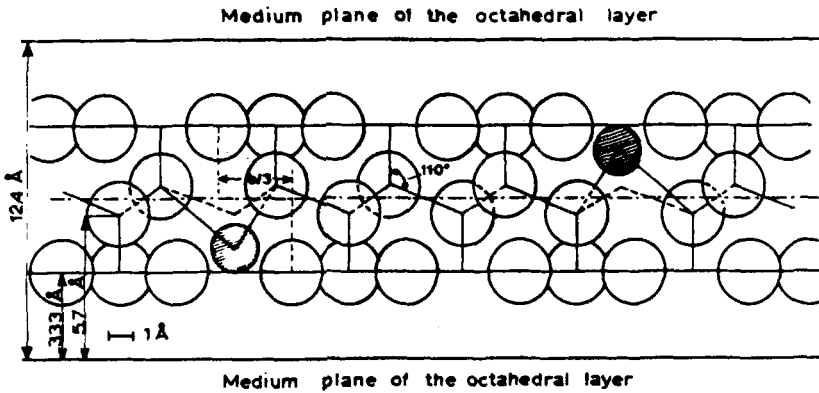
FIGURE 1 Tetrahedral distribution of a monolayer of water in montmoirllonite. ○ oxygen, ● exchangeable cation.

network consists of two sheets, arranged in a distorted hexagonal pattern as shown in Figure 2b. Upon further dehydration, the d(ool) spacing decreases to 11.59 Å. This phase corresponds to a structure in which monolayers of water molecules are interleaved with the silicate layers (Figure 2c).

The structure of this phase is asymmetric with the cations nearer to one of the silicate layer surfaces directly over triads of oxygen. The cation sites may in fact be associated with the hexagonal holes (see Figure 1).

It is interesting to point out that the 14.81 Å phase is less stable than the 14.36 Å phase. In the latter there are $12 H_2O$ molecules per exchangeable
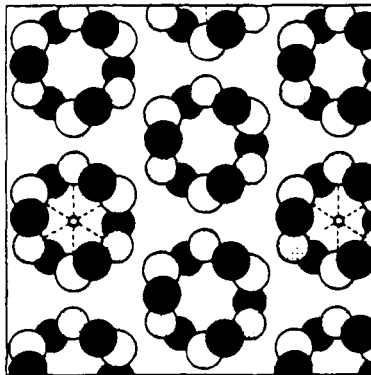
● Upper sheet oxygens ○ Upper sheet waters

● Lower sheet oxygens ○ Lower sheet waters

○ Mg^{2+} between water sheets

FIGURE 2a Mg-Vermiculite: interlayer water-cation network in the 14.81 Å phase.
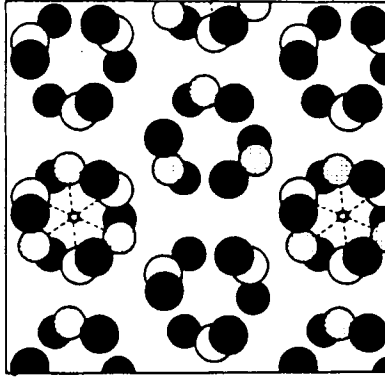
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○ Upper sheet oxygens   ○ Upper sheet waters

○ Lower sheet oxygens   ○ Lower sheet waters

○ Mg^{2+} between water sheets

FIGURE 2b   Mh-Vermiculite: interlayer water-cation network in the 14.36 Å phase.
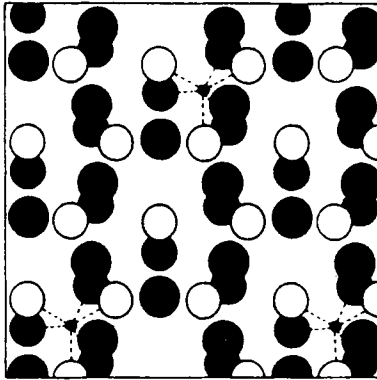
● Upper sheet oxygens   ○ Water molecules

● Lower sheet oxygens   ● Mg^{2+} between lower oxygens
                                           and waters

FIGURE 2c   Mg-Vermiculite: interlayer water-cation network in the 11.59 Å phase.

cation. When this number is reduced to 9, an abrupt change takes place and dehydration leads to the formation of an intermediate 13.82 Å phase and of a 11.59 Å phase. For the latter there are $8 H_2O$ per cation. The 11.59 Å phase subsists till only 3 water molecules per cation are left. On further removal the lattice collapses abruptly. There is a marked difference between the arrangement of H_2O molecules in the 11.59 Å phase and that shown for Na montmorillonite since in the former the tetrahedral medium is not maintained. Since the structure of the basal planes of montmorillonite and vermiculite are identical, the difference between the molecular ordering in the adsorbed phases originates obviously from the nature of the exchangeable cations. However the "structures" described in Figures 1 and 2 have one point in common namely that there are at least two kinds of water molecules on the surface, i.e., those in contact with the cations and forming what may be considered as their hydration shell and those which link the shells together.

These two categories of water have evidently different energies, as shown by Calvet.[5] For a tetrahedral organization such as the one reproduced in Figure 2 and for the alcalin-cation series the energy is of the order of 19 kcal mole^{-1} while for the molecules linking the shells this energy is of the order of magnitude of what is found in solution, i.e., $\leqslant 10.5$ kcal mole^{-1}. As it may be expected that during the hydration process of a dehydrated clay the first molecules to be adsorbed go into direct association with the cations the initial heat of adsorption should be of the order of the former value. This prediction is in good agreement with results obtained by Fripiat et al.[6] for a Na montmorillonite.

We have already insisted on the statistical significance of the structural ordering of adsorbed H_2O. With respect to this, there are two points which are of interest, i.e.:

a) what is the average life-time of a molecule in any of the position of the previously shown configurations and

b) what happens to these ordered configurations when more than just two sheets of water are introduced between the silicate layers.

An answer to these two questions can to some extent be given by a careful examination of the line shape of the proton magnetic resonance spectrum of adsorbed water as it was performed for instance by Woessner and his group.[7,8,9] The time dependence of a 90° pulse free induction NMR signal for a two-spin system is directly proportional to Re exp$(i\omega't)$ where t is the time after the pulse and where

$$\omega' = B(3 \cos^2 \theta - 1) \qquad (1)$$

B is the doublet splitting constant and θ is the angle between the H–H vector
and the direction of the steady magnetic field of the NMR spectrometer. In a
tetrahedral model as that of Figure 1, the H–H vector jumps randomly
among the four internal positions described by the four vectors joining the
center and each of the four vertices of the tetrahedron.[10] There are then two
cases of particular interest, namely equal population for all four positions in
the tetrahedron and unequal population.

For unequal populations (i.e., low water content) and assuming that the
rate at which a relaxation H–H vector leaves any of the four positions is
identical, $(3 \cos^2 \theta - 1)$ has a non-zero average value and the free induction
decay shows a residual doublet splitting. This splitting observed at low
hydration levels ($\sim$ a monolayer of water) is temperature dependent.
Hougardy et al.[11] have also observed this effect for a powdered sample of Na
vermiculite containing one layer of water in all the temperature range from
$-150°C$ while for the two layers hydrate of the same sample, the splitting
occurs at low temperature only (Figure 3). On oriented films the effects are
more spectacular, as shown in Figure 4, Hougardy et al.[12] When the sepa-
ration between clay platelets largely exceeds the size of a water molecule
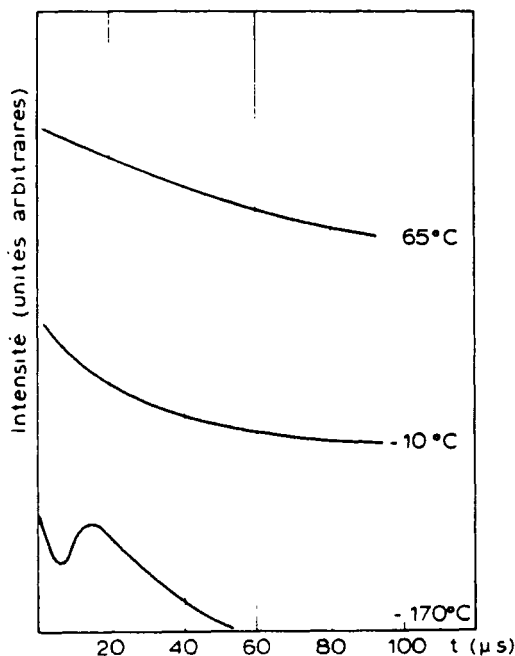

FIGURE 3   NMR free induction decay of a two water layer powdered sample of Na-Vermicu-
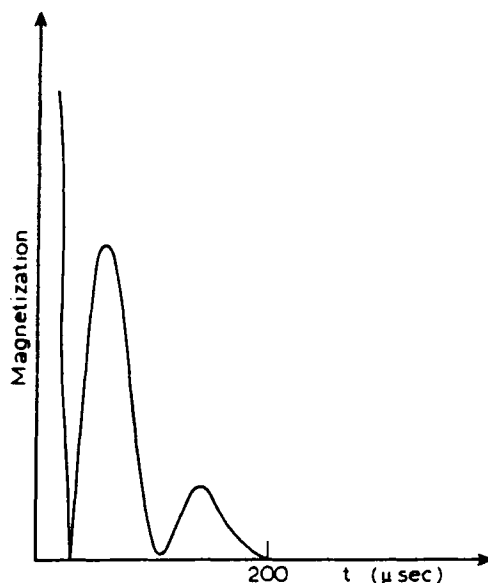lite at various temperatures.

FIGURE 4   NMR free induction decay of a two water layer oriented sample of Na-Vermiculite at room temperature.

(hydration of the order or larger than 1 gm H_2O/g clay, equal population), the adsorbed species exchange positions with those which are further removed from the surface. As this exchange of position occurs many times during a NMR measurement all the molecules are equally affected by the surface. The quantity $(3 \cos^2 \theta - 1)$ is then averaged over all positions of the molecules in the system, it also depends on the orientation of the parallel clay platelet in the magnetic field. For a probability distribution axially symmetric about the normal to the surface ω' becomes proportional to

$$(3 \cos^2 \theta' - 1) \qquad (2)$$

where θ' is either the angle between the H–H vector and the normal to the surface in the case of H_2O or the angle between this normal and the symmetry axis of the intramolecular electrostatic field gradient experienced by the deuteron for D_2O. θ' is of course time dependent because of the translational motions. The advantage of using D_2O arises from the fact that if proton exchange occurs with a rate $> \omega'$ the doublet splitting is washed out. This is not the case for D_2O because the coupling between the deuteron quadruple moment and the electrostatic field gradient does not depend on the spin state of the other deuteron in the molecule.

Woessner et al.[10] have observed doublet splittings on D_2O-clay systems with water contents as high as 8.4 g D_2O/g clay at room temperature.

Therefore even when the platelets are separated by more than 100 Å, does the surface exercise its influence on the orientation of the molecules. Moreover, for a Na hectorite (magnesian montmorillonite lattice) where doublet splittings were measured up to H_2O or D_2O contents of 2.3 g/g, it was suggested from the comparison of the average values of $(3 \cos^2 \theta' - 1)$ obtained for D_2O and H_2O that the molecules have a tendency to orient parallel to the surface. The life-time of such oriented configurations is of the order of 10^{-3} sec at room temperature.

In summary:

a) The exchangeable cations mainly through dipole-cation association (Calvet[5]) are responsible for an ordered arrangement of the water molecules on the first or two first layers in contact with the surface.

b) This ordering remains even in the presence of enhanced translational diffusion due to numerous water layers contained between the clay platelets.

c) The life-time of this configuration is of the order of 10^{-3} sec at room temperature.

III   THE DIFFUSION OF CATIONS AND H_2O ON THE SURFACE OF MONTMORILLONITE AND VERMICULITE

We have summarized in Figure 5 some recent values of self-diffusion co-efficients on clay surfaces. The data for water were obtained by Olejnik et al.[13] using neutron scattering. As the ratios of the diffusion coefficients obtained for water adsorbed on clay and on silicagel surfaces (Resing[14]) to that observed in the bulk liquid are very close, it may be concluded that the exchangeable cations present on the first type of surfaces but not on the second do not restrict appreciably the translational motions. This probably implies that the water molecules in the hydration shell of these cations exchange readily with those outside the hydration shells. What is more the cation diffusion shown in Figure 5 and obtained by Calvet[5] by a radioactive tracer technique are much smaller than those observed for water. They are also extremely sensitive to surface hydration.

This comparison between the two translational behaviors seems to imply that the water molecules exchange positions without breaking their statistical ordering while the translation of cations requires a redistribution of the water molecules. This is confirmed by results obtained for the hetero-diffusion of cations[5] on montmorillonite since it was observed that the diffusion coefficient for a cation M in presence of cations $N(D_M^N)$ is smaller when the affinity for water of M is less than the corresponding affinity of the other cations N: for instance $D_{Na}^{Na} > D_{Na}^{Li} > D_{Na}^{Ca}$.
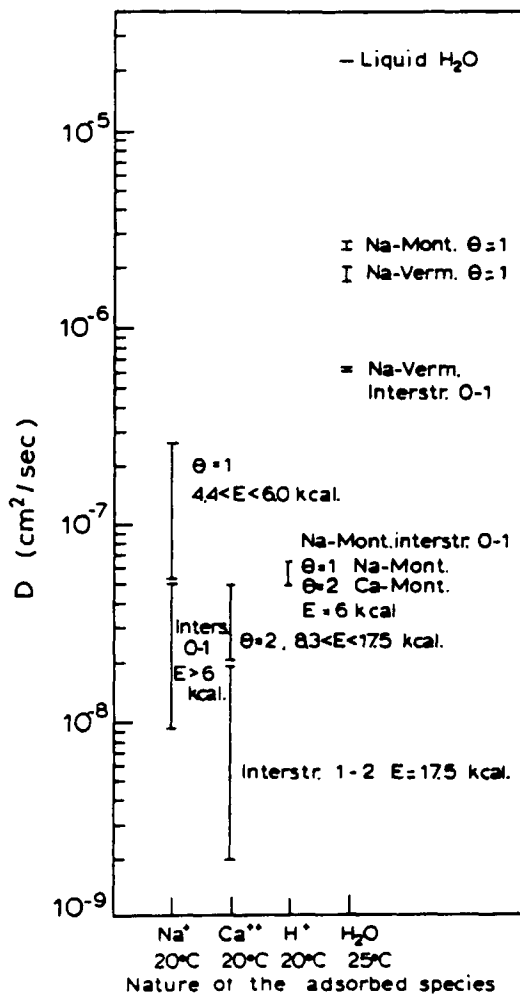
FIGURE 5 Self-diffusion coefficients of adsorbed species on Montmorillonite and Ver-miculite.

The diffusion coefficients of the water protons shown in Figure 5 have been obtained by Touillaux et al.[15] using pulse NMR and are much less sensitive to the state of hydration of the mineral. The time of association τ_A of a proton with a specified water molecule is found to be 0.6 10^{-10} sec at 20°C for a water monolayer situation on the Na sample. From the diffusion results by Olejnik et al.,[13] the residence time τ_R of the molecule in one among the surface

configuration may be deduced assuming that:

$$<\tau_R> = \frac{l^2}{6D} \tag{3}$$

where l^2 is the surface packing of physically adsorbed H_2O, namely $\sim 11\,\text{Å}^2$. At $20°$, $\tau_R = 10^{-10}$ sec for the monolayer Na sample. Consequently in this situation $\tau_R/\tau_A \simeq 2$. In the bulk liquid, the mean period of association of a proton with a specified molecule (τ_A) is approximately 10^{-12} sec whilst the diffusion coefficient at $25°C$ is $2.3\ 10^{-5}\ \text{cm}^2/\text{sec}$.

Assuming a molecular jump distance of 3 Å, τ_R is obtained for the liquid and it may be easily checked that $\tau_R/\tau_A \simeq 6$. Therefore, the number of times a molecule gets protonated during its residence time at a particular point in the liquid is approximately the same as that in the considered adsorbed state. A similar result has been observed for the protonation of CH_3OH by surface proton of a silicagel surface by Cruz et al.[16] We shall discuss later the occurrence of H_3O^+ in the adsorbed phase but it is already possible to sketch the complexity of a cation exchange process just by considering the various translational motions implied in the rather simple systems as those described in Figure 5.

Consider for instance an overall exchange reaction like:

$$\text{M surface} + \text{N} \longrightarrow \text{N surface} + \text{M}$$
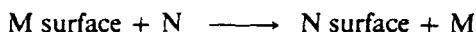
where M and N are different cationic species. The values of the hetero-diffusion coefficients will then depend on the building or breaking effect of these cations on the "structure" of the water layers immediately in contact with the clay surface and also probably on the ordering of the layers adjacent to these first ones, an additional effect due to proton diffusion being eventually superimposed! It would be highly desirable to obtain information on the correlation between these different motions but as far as we are aware this is not available.

IV   THE ABNORMAL DEGREE OF DISSOCIATION OF ADSORBED WATER

The idea that water adsorbed on montmorillonite surface has a degree of dissociation much higher than in the bulk liquid has been developed independently from infrared (Mortland et al.[17]) and NMR data (Ducros et al.[18]) ten years ago. It has received since then many confirmations from chemical as well as from physical determinations and a ratio (H^+/H_2O) of the order of 10^{-2} is now generally accepted.
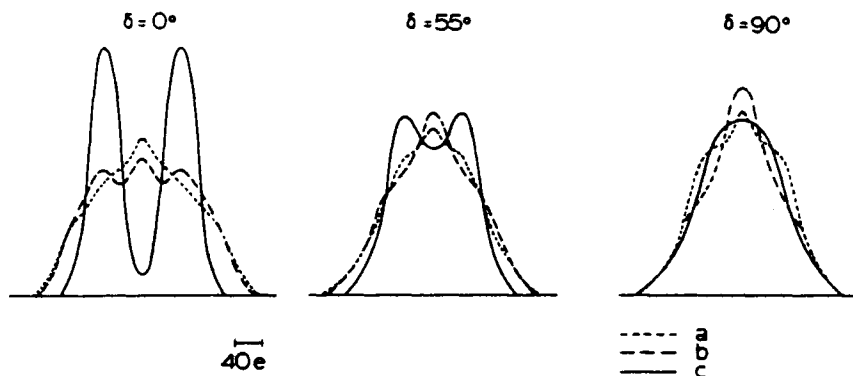
FIGURE 6   NMR lineshape of a monolayer of water adsorbed on a synthetic fluor-mont-morillonite at 4°K. a: Experimental, b: Simulated with 40% H_2O, 30% H_3O^+ and 30% OH^-, c: Theoretical line for a monolayer of ice.
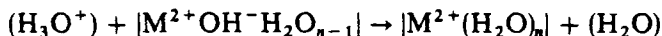
Recently, Hecht[19] has shown very clearly the difference between the NMR spectra of water and of hexagonal ice. Figure 6 reproduces the variation of the proton NMR band at 4°K when δ, the angle between H_0 and the normal to the oriented film is increased from 0° to 90°. At this temperature, the diffusion motions are of course negligible. The main difference between the spectra obtained for the one layer hydrate of the Na montmorillonite and that for a layer of hexagonal ice is the presence of the central component. Hecht was able to simulate theoretically a line shape similar to that observed for the adsorbed state by taking the following parameters:—a composition of the adsorbed layer of 40% H_2O, 30% H_3O^+ and 30% OH—an inter-protonic H–H vector in H_2O tilted by either 35° or 90° (in equal proportion) with respect to the normal to the film and an angle between the C_3 axis of H_3O^+ and this normal of 71°.

The two orientations are those found in hexagonal ice and are compatible with those shown in Figure 1. The (H^+/H_2O) ratio is noticeably higher than the one indicated above but the temperature and the degree of ordering is different also the fluor-montmorillonite used by Hecht is not actually comparable to a natural montmorillonite.

In the initial paper by Mortland et al.,[17] the increase in the degree of dissociation was assumed to be due to the polarization effect of exchangeable cations. It must be recalled that the screening effect of the negative lattice framework on the cationic charge is much less than the screening effect of anions in solution.

Taking into account the previous consideration on the ionization mechanisms, the proton diffusion and the molecular exchange between water molecules inside and outside the hydration shells, the following scheme

could be proposed:

$$(H_2O) + |M^{2+}(H_2O)_n| \rightarrow |M^{2+}OH^-H_2O_{n-1}| + (H_3O^+)$$

$$(H_3O^+) + (H_2O) \rightarrow (H_2O) + (H_3O^+)$$

$$(H_3O^+) + |M^{2+}OH^-H_2O_{n-1}| \rightarrow |M^{2+}(H_2O)_n| + (H_2O)$$
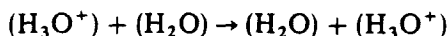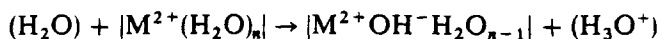
where M^{2+} is the exchangeable cation of valence Z, | | represents the hydration shell and ( ) the adsorbed species outside this shell.

To what extent does the ordering of the water network contribute to the increase in the degree of dissociation is not known. Most probably it influences the frequency of the proton jumps. (H_2O) is moving more rapidly than the molecules associated with the hydration shell (see Figure 5) but during the relatively long residence time of | | on the adsorption site, a first protonic exchange occurs between (H_2O) and the proton of a strongly polarized H_2O in | |. The proton injected in this way in the clusters of water connecting the hydration shells is transmitted from one molecule to another until it comes back for a short time in | |. Perhaps the exchange with the hydration shell does not involve H_3O^+ but H^+: only determination of surface self-diffusion of H_2O with labeled oxygen could clear this point.

An increase of the degree of dissociation of bulk water under the combined influence of high pressure and temperature has been reported by Holzoppel and Franck.[20] For instance at 1000°C and 98 kbars pK = 1.1 ± 0.7.

According to their experimental results $pK_w = 4$ (corresponding to an approximate degree of dissociation of 10^{-2}) would require a density of approximately 2.2 g/cm^3 at 25°C. It is clearly evident that the compression work necessary to achieve such a density is far beyond that which may be computed from the free energy variation of a molecule leaving the gas for the adsorbed phase. Therefore, the influence of a strong polarizing electrical field seems more compatible with the observed data since density in the surface phase is only slightly superior to that in the liquid phase (Deeds et al.[21]).

CONCLUSIONS

It has been shown in this paper that:

1) a short range order exists in the first and two first layers of water adsorbed on montmorillonite or vermiculite surfaces. This organization is comparable to that in hexagonal ice,

2) this short range order is not disturbed by additional layers of water and may possibly influence the properties of that water.

3) the life-time of these structural arrangements is of the order of 10^{-3} sec

4) the H_2O surface diffusion coefficient in the monolayer is reduced by a factor of 10 with respect to that in the liquid phase. This implies an increase of the viscosity by the same factor. The translational mobility of cations is reduced by almost two orders of magnitude. The values of the cation diffusion coefficients are mainly ruled by the organization of the adsorbed water layers.

5) there is a fast exchange between water in the cation hydration shells and the water outside these shells.

6) the degree of dissociation of adsorbed water is at least 10^6 times higher than that of bulk water.

Several of these characteristics are similar to those shown by the so-called anomalous water. It is not our intention to reopen here a discussion on its controversial nature but the ordering (also observed from birefringence measurements carried out on montmorillonite by Green-Kelly and Deryagin[22]), the enhancement of the degree of dissociation and a marked increase in viscosity are among the main characteristics that apply to its description. M. Prigogine et al.[23] have recently proposed an hypothesis to explain its formation on silica surfaces. Again on the surface of clay minerals such an anomalous water film seems to be present but it is also clearly evident that these films cannot exist independently of the presence of the support.

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Discussion of the Report of J. J. Fripiat and W. Stone

R. Parsons

a) It seems that the measurement of water dissociation in montmorillonite was made at 4°K. If one extrapolates the normal dissociation constant of water down to this temperature, one gets a value of about 10^{-700} mol^{2}l^{-2}. Perhaps the dissociation is frozen from its value at higher temperatures? The comparison with water seems rather surprizing.

b) Salts do not affect water dissociation very much but perhaps one should look at the behavior of small amounts of water in molten salts.

W. Stone   The free energy of water in the sphere of influence of cations at the surface of clays is actually not known. Moreover, a comparison with the behavior of electrolyte solutions or small amounts of water in molten salts would not take account of the fact that in the water-clay system the radius of curvature of the "anion," i.e., the clay lattice, is infinite. Therefore, the charge exposed by a cation on the surface is not screened as it would be in an electrolyte solution.

J. E. Mayer   I question whether the conductivity measurement gives, even within several orders of magnitude, a reliable value of the proton concentration. The conductivity measures the product of concentration times mobility. I wonder if the mobility is within orders of magnitude the same as in normal water. I too am uncertain of the values, but if I do remember correctly the mobility of protons in ice is many order of magnitude greater than that in water. May it not be so in this ordered structure of the bound water layer? Actually you seem to have several different quantities combinations which enter in the different measurements and I have difficulty in understanding which are measured unambiguously. There is an average time that a proton remains bound, which, if I understood correctly was long, order of 10^{-3} sec. There is also a concentration of free positive charges,

and it is not clear to me whether stress are assumed to be free protons or H_3O^+. A third quantity is somewhat equivalent to a mean free path, although presumably not one that is entirely free, but described better by a mobility. It is the distance the charged entity can travel before again being bound.

H. G. Hertz   How are the diffusion coefficients of protons measured? One must not forget that the diffusion coefficient of a proton in an acidic solution is mostly the diffusion coefficient of a proton sitting on a water molecule, or H_3O^+ ion. Only a vanishingly small fraction of the protons are "free," i.e., in a state of jumping from one molecule to the other.

But this small fraction suffices to cause the high electric conductivity; e.g., the proton self-diffusion coefficient in an aqueous solution of HCl decreases steadily with increasing concentration.

W. Stone

a   About degree of dissociation and life-time.   Consider the following second-order reaction

$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+ \tag{1}$$
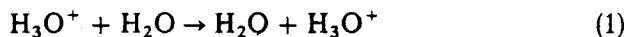
The rate of disappearance of H_3O^+ is

$$\frac{d|H_3O^+|}{dt} = k|H_3O^+|\,|H_2O| \tag{2}$$

the relative rate:

$$\frac{1}{|H_3O^+|}\frac{d|H_3O^+|}{dt} = k|H_2O|$$

isobviously the inverse of the life-time of H_3O^+, i.e., $\tau_{H_3O^+}^{-1}$.

In Meiboom's paper,[1] the time of association of a proton with some undefinite protonated form of oxygen is obtained from the broadening of the H^+ NMR resonance line. This broadening is provoked by the jump of a proton from a O^{16} towards a O^{17} bearing entities. This time τ is given by

$$\tau^{-1} = \tfrac{1}{3}k_1|H^+|\cdot + \tfrac{1}{2}k_2\left(\frac{K_w}{|H^+|}\right) \tag{3}$$

where $k_1 = (10.6 \pm 4)\,10^9$ mole^{-1} liter sec^{-1} at $25 \pm 1°C$

$k_2 = (3.8 \pm 1.5)\,10^9$ mole^{-1} liter sec^{-1} at $25 \pm 1°C$.

Chemistry teaches us that at low pH, the main form of association of oxygen with proton is H_3O^+ while at high pH the dominant form is OH^-. At pH 7, H_2O is the most probable species. Therefore, by superimposing

this chemical concept onto Eq. (3), which has a purely operational meaning, at pH 7, τ being 10^{-3} sec, this value may be considered as the life-time of H_2O. In the acid range, for instance, at pH = O, $|H^+| = 1$, τ according to (3) is of the order of 10^{-10} sec. Eigen et al.[2] have obtained $k = 1.26 \; 10^{11}$ liter mole^{-1} sec^{-1} at $25°C$ by their procedure of electric pulse from which a life-time for H_3O^+ of $0.143 \; 10^{-12}$ sec is derived.

Such a short life-time could be obtained also from (3) for very high, and probably unrealistic H^+ concentrations. On the surface of montmorillonite and under the hydration conditions which have been discussed, the life-time of the adsorbed species (without further specification) is of the order of 10^{-10} sec. If this life-time (measured in this case by analyzing the results of spin relaxation times as function of temperature) is introduced into the operational Eq. (3), it corresponds to a degree of dissociation $|H_3O^+|/|H_2O|$ of approximately 10^{-2}, i.e., to a very high acidity. This is not surprising since the observed life-time of the adsorbed species is much closer to the one measured for H_3O^+ than for H_2O, i.e., at pH 7.

b   About conductivity and life-time   Meiboom[1] has pointed out that the excess protonic mobility in water leads to a $H_3O^+\tau$ value of approximately $1.6 \; 10^{-12}$ sec. Therefore k in Eq. (2) is $1.1 \; 10^{10}$ mole^{-1} sec^{-1} liter. This is very close to k_1 but approximately 10 times lower than the value obtained by Eigen et al.[2]

Undoubtedly, conduction processes imply more than "straight" proton jumps but also reorientation and so on, . . . as outlined by Professor Mayer in his question.

However, as shown here above conductivity measurements may give at least a rough approximation about the life-time. It is a matter of fact that if both the H^+ surface concentration and the proton jump rate obtained for the hydrated montmorillonite are introduced into the Einstein equation, the predicted conductivity is within less than one order of magnitude that observed by Mamy[3] or by Fripiat et al.[4]

This agreement brings about a confirmation of the order of magnitude observed for the life-time of adsorbed water. This life-time is thus close to that observed for H_3O^+ in the normal liquid phase.

We have suggested an explanation for that by assuming that a water molecule, inside the cation hydration sphere, transfers a proton to a water molecule outside the hydration sphere and that, from there, the proton is transfered as shown in Eq. (1).

Moreover, one should again point out that the situation in the adsorbed state is very different from that in bulk since on the one hand variation of conductivity may be measured as a function of the degree of coverage (which allows one to extract by taking a reasonable model for conduction, a value

for the degree of dissociation) and on the other hand the anion coming from the dissociation of H_2O remains in the coordination shell of the cation.

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H. G. Hertz   Your finding that the hydration water is more strongly dissociated is also found for highly charged small ions in aqueous solutions, but it is not known for larger ions like Na^+, Rb^+. But we know that in aqueous solutions of NaI, $NaClO_4$, the proton exchange of the water molecule is slower than in pure water. This may be mostly due to the anions, but at any rate Na^+ in aqueous solution does not represent a force center which causes a speeding up of proton exchange.

W. Stone H^+ or H_3O^+ in concentration of 1/100 with respect to H_2O does not influence appreciably the molecular diffusion coefficient but it influences strongly the proton exchange from one molecule onto another and thus the proton diffusion coefficient.

H. A. Resing   Dr. Stone has a check been made to determine whether all of these different material parameters are self consistent? For example, the exchange rate for protons in water molecules, which should be related to protonic conductivity, certainly limits the lifetime of the orientation of the intramolecular proton-proton vector, which you have given as 10^{-3} sec. The high value of the diffusion coefficient would seem to also limit this lifetime, unless the molecules skated with final orientation over the surface. Would you comment?

W. Stone   The 10^{-3} sec lifetime given by Woessner[1] has been observed in the case of certain clay samples with large amounts of water between the platelets. This lifetime can certainly be thought of as depending strongly on the exchange rate of protons between vicinal molecules. Such a process implies suitably oriented orbitals between the exchanging water molecules.

With respect to diffusion, it has been found,[2] using an isotropic rotational diffusion equation that the picture of a molecule migrating along a corrugated surface but keeping a constant orientation with respect to each point of the surface could be applied with success in some cases. Such a model has been already suggested from entropy measurements.[3]

It is perhaps also appropriate to stress at this point that since for adsorbed water, $\tau_R/\tau_A \simeq 2$, and that this ratio seems to be of the same order in bulk

water, NMR measurements could not distinguish between proton or molecular diffusion, unless the jump distance is adequately known. The proton transfer implies a shorter distance than the molecular diffusion.

Finally, it appears that this is a place to emphasize that in a choice of a suitable model more than one single technique should always be involved.

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H. G. Hertz   Assume the water molecule fluctuates between two environments, A and B. Then the translational diffusion coefficient is given by

$$D = p_A D_A + p_B D_B$$

p_A is the probability to find the molecule in environment A.

$$p_A + p_B = 1$$

For the lifetimes in A and B, τ_A and τ_B, we have

$$p_A = \frac{\tau_A}{\tau_A + \tau_B}$$

Now, if B is the "bound" state, i.e., $D_B \simeq 0$, then

$$D = \frac{\tau_A}{\tau_A + \tau_B} D_A$$

While $D_A \simeq 10^{-5}$ cm^2 sec^{-1}, $\tau_A = 1/g \, \tau_B$, it follows $D = 10^{-6}$ cm^2 sec^{-1}. Thus, if $\tau_B \simeq 10^{-3}$ sec, τ_A may be $\simeq 10^{-4}$ sec.

W. Stone   We suppose that the equation proposed by Professor Hertz, namely

$$D = p_A D_A + p_B D_B$$

should be applicable to the case where A stands, for instance, for the gas phase and B for the adsorbed phase.

The problem is then to evaluate p_A and p_B and we are sorry to say that we do not understand the equation suggested for this purpose.

G. Careri   I wish to add the point of view of an experimental physicist to the problem of bound water. In my opinion, just following by some modern techniques the stepwise increase of the amount of water on a surface, one can learn something on this complex situation. For instance, we have seen both

the water and the globular protein to change their IR spectrum when the initial water is allowed to be adsorbed (see *Biopolymers* **11**, 519, (1972). Similar experiments by N.M.R. have been carried out by Fuller and Brey (see *J. Biol. Chem.* **25**, 274 (1968), with results consistent with those reported here by Dr. Resing.

We have also investigated by the laser Raman technique, the state of water adsorbed on proteins and other inorganic catalyzers (like γ–AlO_3), (see *Phys. Lett.*, **32A**; 495 (1970), and J. of Calalysis, in the press).

S. Claesson   I would like to mention one interesting thing in connection with your laser experiments, when you did find the structure of polypeptide chain. Somebody in Berkeley was studying how living things can survive when they have been dried out. The proteines inside the cell were studied when they were gradually adding small amounts of water in the same way as you did, and then, at one particular level, this inside became active again. The interesting thing is that you needed just about the same very small amount of water to get the effect.

H. A. Resing   The "structure" of water at interfaces is presently uncertain, as our deliberations here clearly show. Structure is a detailed statement of the geometrical disposition of the atoms of a body with respect to one another; a *complete* statement should also involve the time. NMR relaxation measurements tell us about the temporal correlation of atomic (nuclear) position, as William Stone has intimated; we express our knowledge in terms of the correlation time τ, which for liquid water is essentially the time between rotational and diffusional jumps. In the Figure VIII.1 we compare correlation times at 0°C for liquid water, ice, and water adsorbed on or in various substrates, to wit, in zeolite 13-X, in the 30 Å diameter pores of a charcoal, and
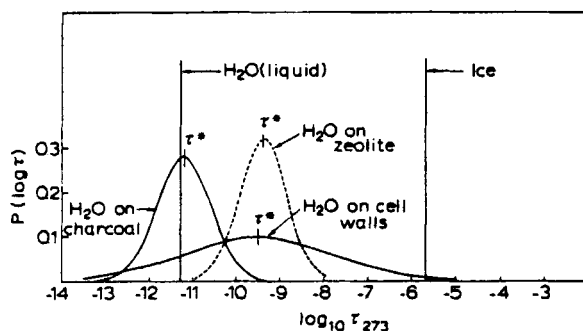

FIGURE VIII.1   Distribution functions of the jump time for water, ice, and for adsorbed water on various substrates at 0°C.

adsorbed on the cell walls of bacillus megatherium. For these latter three systems the NMR relaxation data could be fitted to theory under the assumption of a log-normal distribution of correlation times. Water and ice on the other hand are well represented by a single correlation time. The figure shows that at 0°C the median correlation times in the adsorption systems are much closer to that of liquid water than to that of ice. Thus, it can be stated with confidence for these systems that any hypothetical "ice-like" arrangements *do not* persist for "ice-like" times at or above 0°C. The geometrical question must be answered by other means.

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General discussion

D. H. Everett   I have been in some doubt as to the most appropriate point in this discussion at which to make these remarks. Solvay meetings have traditionally developed two main objectives: to review the current situation in the chosen field of study, and to set the course for future developments. In the present meeting it seems to me that we have tended not to be sufficiently self-critical and, consequently, although we have been shown the way in which water "structure" affects a wide range of physico-chemical and biological phenomena, we have not evolved a clear view of the way in which the subject should evolve.

On the first day, I was drawn into a discussion about the thermodynamics of ionic hydration in which some calculations done over thirty years ago appeared relevant. As one who has not been closely associated with detailed work in this field in recent years, I had gained the impression from abstracts and reviews that more sophisticated theoretical ideas had been carried forward to such an extent that the older work was now largely irrelevant. However, it is clear that this is only partly true. Many of the qualitative ideas which were introduced around 1945 still lack a satisfactory quantitative formulation, even though in the intervening period they have been valuable in stimulating a very impressive amount of experimental work. We should perhaps not be too surprised at this—for the complex nature of water and its physical properties will provide a challenge to science for a long time. But what is dangerous is the too ready acceptance of the idea that we understand much more than we are justified in claiming. This danger has been realised by some, and I would particularly draw your attention to a paper by Holtzer

and Emerson,[1] which, although expressed in places in somewhat extreme terms, nevertheless presents views with which I have considerable sympathy. They say, for example, "It is our contention that, in fact, the position has been little advanced since the work of Frank and Evans and Kauzmann and that the widespread practice of invoking changes in water structure to rationalize experimental data can only serve to perpetuate the illusion that some real understanding exists." After quoting a number of examples they conclude with the observation that "It would seem then, that aqueous solutions are too complex to be interpreted molecularly in the facile manner that has become rather common. It is noteworthy, however, that we have raised no fundamental difficulties that were not envisioned by Frank and Evans, who stated the following in their comments about icebergs: 'It is not implied that the structure is exactly icelike, nor is it necessarily the same in every case when the word iceberg is used.' With this to fall back on, however, it is clear that a qualitative explanation can readily be supplied for *any* experimental results simply by postulating a suitable kind of iceberg. Unfortunately, since no experimental methods, except, possibly definitive X-ray or neutron diffraction, can give such specific structural information, the 'explanation' cannot be tested by experiment, can lead to no unique prediction, and therefore can convey no more information than was obtained by doing the experiment in the first place. Water is structural, all right, but knowing that doesn't seem to help. The situation would appear to be bad enough without the curiously assured, yet essentially sterile, invocations of water structure that seem to be proliferating so boundlessly in the literature."

As pointed out by Magat in his introductory paper, there is still, as far as pure water is concerned, no clear way of distinguishing between "association complex" and "continuous network" theories; it is equally clear that in relation to ionic and molecular hydration the concept of "icebergs" still lacks a precise quantitative formulation, and indeed a recent paper by Levine and Perram[2] suggests that the idea of a "defective network" may prove to be a better starting point for a more valid theory. We should not, however, be too pessimistic. We must realize on the one hand that in the past there has been over-optimism (not altogether a bad trait) and lack of self-criticism (to be guarded against). On the other hand, modern computer methods are putting into our hands the ability to follow through in increasing detail the consequences of our theoretical models. It may be just too soon to expect a major breakthrough, for present-day computers have only recently had the power to solve problems associated with simple liquids of spherical molecules: we may hope that the next generation of computers will be able to do the same for aqueous systems. Meanwhile we need to sharpen up our ideas and to formulate them in terms which can be most efficiently developed by computer.

References

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J. E. Mayer   I heartily agree with Mr. Everett's remarks. Science advances by asking the right questions, and the difficulty of finding the correct question is often greater than the difficulty of finding the correct answer. I remember vividly a question posed to me by G. N. Lewis after I, as a graduate student forty-five years ago, had presented a seminar report. After long hesitation, watching Lewis' increasing scowl, and increasing rate of chewing his cigar, I answered that I was sorry, but I did not understand the question. There followed more scowling and more cigar chewing. Finally Lewis smiled and said "Of course you don't, Mayer, if I understood the question I would know the answer." I think that in much of the present discussion, we have not yet found the correct questions.

For instance I do not believe that if, given an interview with a benign and all knowledgeable archangel, we could ask an intelligible question of the nature of the structure of water for which his answer would be enlightening. We can understand the result of a successful X-ray analysis of the periodic structure of any of the crystalline forms of ice, although only with considerable effort and time. For a liquid like argon, we believe that we can ask an intelligible question, and that we even have a moderately satisfactory beginning of the answer. We fix our attention on the sequence of probability density functions $\rho_n(r_1, \ldots, r_n)$ for $n \geq 1$ and particularly on their logarithms. For $n = 1$, ρ_1 is a constant equal to N/V_s, the number density. For $\rho_2(r_1 - r_2)$ we have a function of $\pi_{12} = |r_1 - r_2|$ only, and

$$\ln \pi_{12} = 2\rho_1 - (kT)^{-1} W_2(r_{12})$$

where W_2 is a potential of average force. For $n = 3$ we can write

$$\ln \rho_3 = 3\rho_1 - \frac{1}{kT}\left[W_2(\pi_{23}) + W_2(\pi_{31}) + W_2(\pi_{12}) + W_3(\pi_{23}, \pi_{31}, \pi_{12}) \right]$$

which defines W_3 and hope that it is relatively of less importance than W_2 in some ill defined sense. Similarly $\ln \rho_4$ requires a new function, W_4, of six distances. We have at least some reason to believe that in some sense the proceedure converges. We thus can feel that we have some real understanding of the liquid structure.

For water, even if we concerned ourselves only with the positions of the centers of gravity, and left out the all-important orientation terms, we could have little hope that the description would even "converge" and almost surely not before $n = 13$ for which the function $W_{13}(\vec{r}_1, \ldots, \vec{r}_{13})$ would require description in a 30 dimensional space!

Similar difficulties seem to dog much of our discussion, although in most of the other cases I have the feeling that we would have less difficulty in posing questions which are, at least in principle, answerable, and with an understandable answer. Much of the difficulty appears to be that most of our quantitative interpretation of experimental data has been in terms of the macroscopic parameters suitable to the description of a continuum: density, dielectric constant, electrical potential, etc. and then have the task of fitting this on to a picture of molecular structure. It was asked whether the dielectric constant is definable when it changes greatly in the distance between change centers in a molecule. No one volunteered an answer. The concept of electrical potential at a point within a molecule is defined in terms of a non-existent infinitesimal charge probe of infinite mass.

A constant, or very low gradient perturbing electrical potential offers no conceptual difficulties, nor difficulties in handling, but a potential perturbation with a gradient that is large in a molecular diameter seems to me to be an animal that requires a little care in its use. Its effect on different charges entities such as ions and electrons must be rather complicated. I have no doubt that precise concepts are available, and perhaps it is my ignorance of recent work in this field that leads to my momentary view that more attention to fundamental concepts may be desirable.

Finally I would like to suggest that more attention to entropy density as a quantitative measure of "structure," that is of "structure making" and "structure breaking," might be useful. With the ensemble concept it is quantitatively definable as a point quantity in a classical system. I should think that with the density matrix formulation it would be definable for a quantum system.

M. Mandel. I want to raise a question which has been bothering me since Prof. Randles talk. Prof. Randles has introduced oriented molecules in the surface layers of water in order to account for the surface potential. I wonder however if such oriented dipoles near the surface should not produce, by their electric field, some bulk effects, which are of course not known. If the oriented dipoles are symmetrically disposed as, e.g., on a spherical surface, these effects could cancel out, but this need not be the case for a system with an arbitrary surface. In fact I am thinking here of an effect which would be somewhat connected to the reverse situation where the fixed orientation of a dipole in the bulk may produce a polarization also near a surface in a system. If this were true however, the surface potential should be strongly shape dependent.

J. E. B. Randles The surface potential is due to a surface layer containing preferentially oriented dipoles (and possibly an ionic double layer) of the

order of 10 Å thickness. Provided that the size of the liquid phase is large compared with this thickness the average potential in the bulk phase is uniform and independant of the overall shape.

The important thing is that the radius of curvature of the surface shall be large compared with the thickness of inhomogeneous layer (order of 10 Å) at the interface. If this is the case then the layer may be regarded as planar and the potential distribution corresponds to that of a flat layer.

D. H. Everett   Even though the effects mentioned by Prof. Mandel may not be significant for the problems we have been discussing, we would all I expect agree that they may be of major importance in problems of nucleation of water droplets.

C. Dejak   Using the Debye-Hückel theory and its subsequent extent, like the ionic cluster-theory and the hypernetted chain equation, applied on the electrolytes, to obtain information on the short range forces between ions, it is convenient to note that to the higher concentrations one has two kinds of contributions. First of all, the superior terms of D. H. theory, that were calculated by Gronwall, La Mer *et al.*, and that you obtain in a more simple way as contributions of the more complex graphs in the clusters theory, calculated by Poirier. Secondly, the proper short range interactions, that generally in these theories are given through approximation of the rigid spheres, or of the dielectric saturation.

Separating the two contributions, we have been able to show that the first effect disappear at high concentrations, both in the theory of Gronwall–La Mer and in the one of Mayer–Poirier. Instead, the second remains very low at medium concentrations in order to become well-known even prevailing at the high ones. When applying the HNC-equation, it is more difficult to separate these contributions, whereas this fact seems to be quite simple in the ionic cluster-theory, as you take an interionic coulomb potential between rigid spheres and you keep separated only the pure rigid repulsions.

The trend of the first part, according to the experimental data too, is rather complex, and made insecure an extrapolation at concentration zero for quantities correlated to the activity coefficients: fortunately, its area of influence is limited to the medium concentrations. Therefore, for the higher ones remain only the second contributions, which as physical significance are much more interesting. Therefore, it could be useful to consider exclusion of the zone of medium concentrations, and to join together high concentration directly with the DHLL, in order to obtain more reliable informations of the short range forces in electrolytes with extrapolation at zero concentration.

J. E. Mayer   Mr. Dejak has made these impressive calculations on what is frequently called the "primitive model," namely a model in which the water is structureless and characterized only by a continuous medium with a dielectric constant. In so far as such calculations are completely and rigorously correct, I would be inclined to *define* structure effects as anything that causes a deviation of observed experimental behavior from the results of the calculations. Of course, however, a good part of the deviation depends on the difference between the "structure" of the solute ion and the assumed hard sphere of fixed radius. Not all is due to changes in water structure around the ion.

C. Dejak   In the mono-monovalent electrolytes this effect is generally negligible, whereas it becomes very important in the plurivalent electrolytes, above all if asymmetrical.

A. Bellemans   Computer experiments on water by Rahman and Stillinger have led to very interesting results for the bulk properties. It would therefore look promising to apply the same technique to surface properties; however the difficulties to realize such a program are two-fold:

a) the required number of molecules necessary to simulate an interface is quite large to handle on a computer;

b) the results will be more sensitive to the detailed form of the inter-molecular potential than for the bulk phase.

To illustrate this last point, notice that the potential of Ben-Naïm–Stillinger assumes a symmetrical tetrehedron centered on the oxygen atom, with two positive and two negative charges at the corners. The central part of the potential itself is a Lennard-Jones one, also centered on the O atom. This means, on account of symmetry, that the surface potential of water is zero for this model.