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Structure of Water Adsorbed on Smectites

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I. Introduction

A. Adsorbed Water Structure as an Experimental Concept

The continued appearance of reviews over the past 20 years concerning one or more aspects of the molecular structure of water adsorbed by smectites[1-9] attests to the enduring importance of this subject to colloid chemistry and clay technology. During the last few years, there has been a significant increase in the number of studies of smectite-water systems that employ relatively sophisticated chemical methods, with the result that the structure of adsorbed water has begun to leave the domain of speculative hypotheses to become an experimental concept. This transition is complete enough at present to warrant an initial attempt, not yet made in the literature, to synthesize the available empirical information obtained by diverse laboratory methods. The question that can be posed at this time thus is simply: Does enough of a consensus exist among the available experimental data to make it possible to draw a *minimal* set of nonconflicting conclusions, i.e., to state what the structure of water adsorbed by smectites *must* be like?

In this paper, a review will be made of the results of recent experiments concerning the structure of water in smectite-water systems. The review will be organized according to the kind of experimental method employed, including within its perspective infrared, incoherent neutron scattering, magnetic resonance, and dielectric relaxation spectroscopy, neutron and X-ray diffraction, and thermodynamic measurements. Emphasis will be given to data obtained by these techniques during the past 10 years. This kind of organization recommends itself because each of the experimental methods listed is characterized by a particular *time scale* during which it probes the structure of a molecular environment (Figure 1). As will become evident during the course of this review, information about the structure of adsorbed water provided by a given experimental method pertains, in principle, only to the properties of the structure as they exist during the time scale appropriate to that method. This point of view is essential to any attempt at making a coherent picture from the data on smectite-water systems obtained by the techniques indicated in Figure 1.

B. Structural Concepts for Bulk Liquid Water

For reasons of economy of space, no discussion will be given in this review concerning the basic physical properties of the water molecule, liquid water, or ice, nor will there be a detailed accounting of smectite nomenclature, methods of clay preparation, and the instrumentation that has been employed in the studies reviewed. The chemistry of smectites and the modern methods for studying it have been described recently in comprehensive reviews.[10-13] Thus, it will be noted here only that the smectites form a subgroup of the 2:1 phyllosilicates, characterized by (1) a negative charge per unit cell, from isomorphous substitutions, that ranges between 0.50 and 1.3 electron charges and is compensated by exchangeable cations, and (2) a specific surface area near 750 $m^2\ g^{-1}$ on the oxygen cleavage planes. The crystal chemistry of the smectites is summarized in a clear fashion by Swartzen-Allen and Matijevič.[6] The properties of water also have been documented exhaustively in widely available publications.[14-18] On the other hand, there is a useful concept regarding the molecular structure of bulk liquid water that should be mentioned explicitly, since it is closely related to the idea of characteristic time scales probed by different experimental techniques. This concept is the definition of "liquid water structure" given by Eisenberg and Kauzmann.[14] On a time scale which is long relative to the period of vibration of a hydrogen bond in liquid water (about 10^{-13} s) but short relative to the time required for a water molecule to diffuse a distance equal to its own diameter (about 10^{-11} s), a typical molecule in liquid water "sees" a spatial arrangement of its neighbors that is called the *vibrationally averaged structure* (V structure). This structure will include only the effects of vibrational motions of the water molecules and, according to Figure 1, it can be probed by infrared, neutron scattering, and magnetic resonance spectroscopy. At the other extreme, on a time scale that is long compared with that during which a molecule diffuses a nominal distance in liquid water, a typical molecule "sees" a surrounding spatial arrangement that is called the *diffusionally averaged structure* (D structure). This structure includes the effects of vibrational, ro-

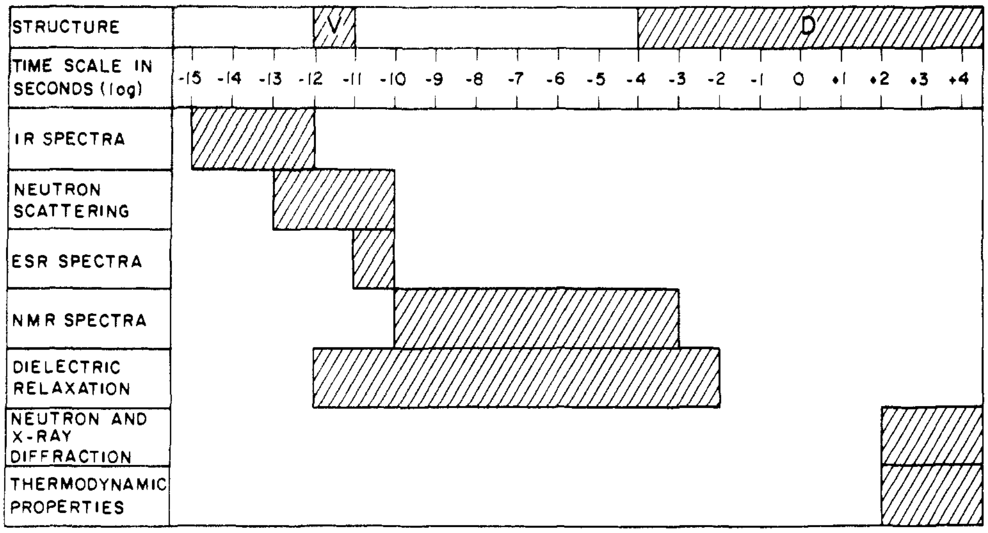

Figure 1. Time scales for adsorbed water structures and the experimental methods used to measure the properties of adsorbed water.

tational, and translational motions of the water molecules and will be more ordered than the V structure because it comprises only the most probable molecular configurations. The D structure can be probed by neutron and X-ray diffraction experiments, and it provides a basis in molecular structure for thermodynamic properties, as suggested in Figure 1.

Between the time domains of the V and D structures, there is a transition region that can be investigated by neutron scattering, magnetic resonance, and dielectric relaxation spectroscopy. These techniques are expected to give information about the rotational and translational motions of water molecules that lead from the V structure to the D structure. Thus, it is clear that the concept of "structure" in liquid water is a *dynamic* one, and the same should be true for the water adsorbed by smectites. In the case of adsorbed water, an additional complexity is provided by the exchangeable cations, whose vibrational and translational motions take place in the transition region between the V and D structures.[10] Nonetheless, it is expected that the conceptual framework summarized in Figure 1 will be useful as a guide to understanding the molecular structural significance of experiments on smectite–water systems.

II. Infrared Spectroscopy

A. Method of Progressive Deuteration

The infrared (IR) spectrometers available for studies on adsorbed water cover the range of wavenumbers between 30 and 3×10^4 cm^{-1} corresponding to periods of molecular vibration between 10^{-12} and 10^{-15} s. Thus, IR spectroscopy permits the study of molecular structure on a time scale that is very short compared to those characteristic of other available techniques (e.g., incoherent neutron scattering or magnetic resonance spectroscopy). Because of the complex nature of the structure of water adsorbed by smectites, the normal mode analysis of this system cannot yet be carried out. Instead, the vibrational spectrum must be simplified by suppressing the coupling between adsorbed water molecules and between the hydroxyl groups in a single water molecule. This can be accomplished through a progressive deuteration of the adsorbed water in a manner so as to obtain levels of deuteration for which the water molecules or hydroxyl groups can be regarded, from the point of view of IR spectroscopy, as individual units. This technique, employed by Falk and Knop[19] to study water in crystalline hydrates, has been developed and utilized by Prost[20] to study adsorbed water structures on clay minerals.

The absorption spectrum between 250 and 10 000 cm^{-1} (50 to 1 μm wavelength) of air-dried smectites comprises a series of bands attributable either to adsorbed water or to the clay mineral itself. The spectrum of the valence vibrations in adsorbed water on smectites (Figure 2) differs from that of bulk liquid water or ice by the presence of a band whose wavenumber varies between 3620 and 3640 cm^{-1}.[20–22] The position of this band depends both on the nature of the exchangeable cations on the clay surface and on the location within the clay structure of the deficits of positive charge produced by isomorphous substitutions. Moreover, the intensity of this band increases when an oriented deposit of an air-dry smectite is rotated away from normal incidence of the infrared beam; this result implies that the adsorbed water molecules have a preferred orientation on the smectite surface.[20]

The interaction between water and smectite does not produce changes only in the IR spectrum of the water. Significant modifications of the spectrum of the clay mineral also are observed, as illustrated in Figure 2 for Na–montmorillonite. It can be seen in Figure 2a that there is a significant increase in the intensity of the lattice vibrational band at 1118 cm^{-1} as the water content of the clay increases. Changes in the spectrum of the structural hydroxyl groups in hectorite[20] and in saponite[23] have been noted as well. These changes depend on whether the smectite is di- or trioctahedral.

The study of these kinds of perturbations in the IR spectrum has provided information about the relationship among the adsorbed water molecules, the exchangeable cations, and the mineral structure of smectites. In particular, the available data permit conclusions to be drawn concerning the spatial organization of adsorbed water molecules, the mechanism of hydration of smectites, and, tentatively, the thickness of the layer of adsorbed water whose IR spectrum is modified significantly by the surface of the clay mineral.

B. Spatial Organization of Adsorbed Water Molecules

At a given water content, the water adsorbed by smectites can be found in two different states: the water solvating the exchangeable cations in the interlamellar space and the water in external regions (e.g., external surfaces and micropores).[20] The study of the changes in the IR spectrum of adsorbed water during the course of isothermal dehydration of a smectite allows one to define the ranges of water content in which one of the two states predominates. For example, in the case of Li–hectorite, dehydration under 0.01 torr produces a state corresponding to three molecules of water, on the average, for each exchangeable cation. The IR spectra of progressively deuterated adsorbed water in this system[20] indicate that the water molecules hydrating the Li ions are located on sites with C_{2v} symmetry. A band at 3610 cm^{-1} is observed for the OH groups in HOD, showing that the water molecules form very weak hydrogen bonds, and the dichroism of the high-wavenumber member of the doublet at 3580–3640 cm^{-1} (symmetric and antisymmetric vibrations of the water molecule) demonstrates that the transition dipole moment of the antisymmetric mode points nearly along a normal to the hectorite surface. Figure 3 illustrates a spatial arrangement of the water molecules that is consistent with these results. On this model, the lone-pair orbitals of the oxygen atom in each water molecule are directed toward the Li$^+$ cation and one of the protons in each molecule lies along an axis normal to the clay surface. This proton can be expected to perturb the structural OH groups significantly in *trioctahedral* smectites because it will reside in the center of a ditrigonal cavity in the tetrahedral sheet adjacent to the one onto which it is adsorbed (Figure 4). This effect has been observed in the IR spectrum of the structural hydroxyl groups in Li–hectorite, where shifts of the stretching mode wavenumber from 3680 to 3690 cm^{-1} and of the bending mode wavenumber

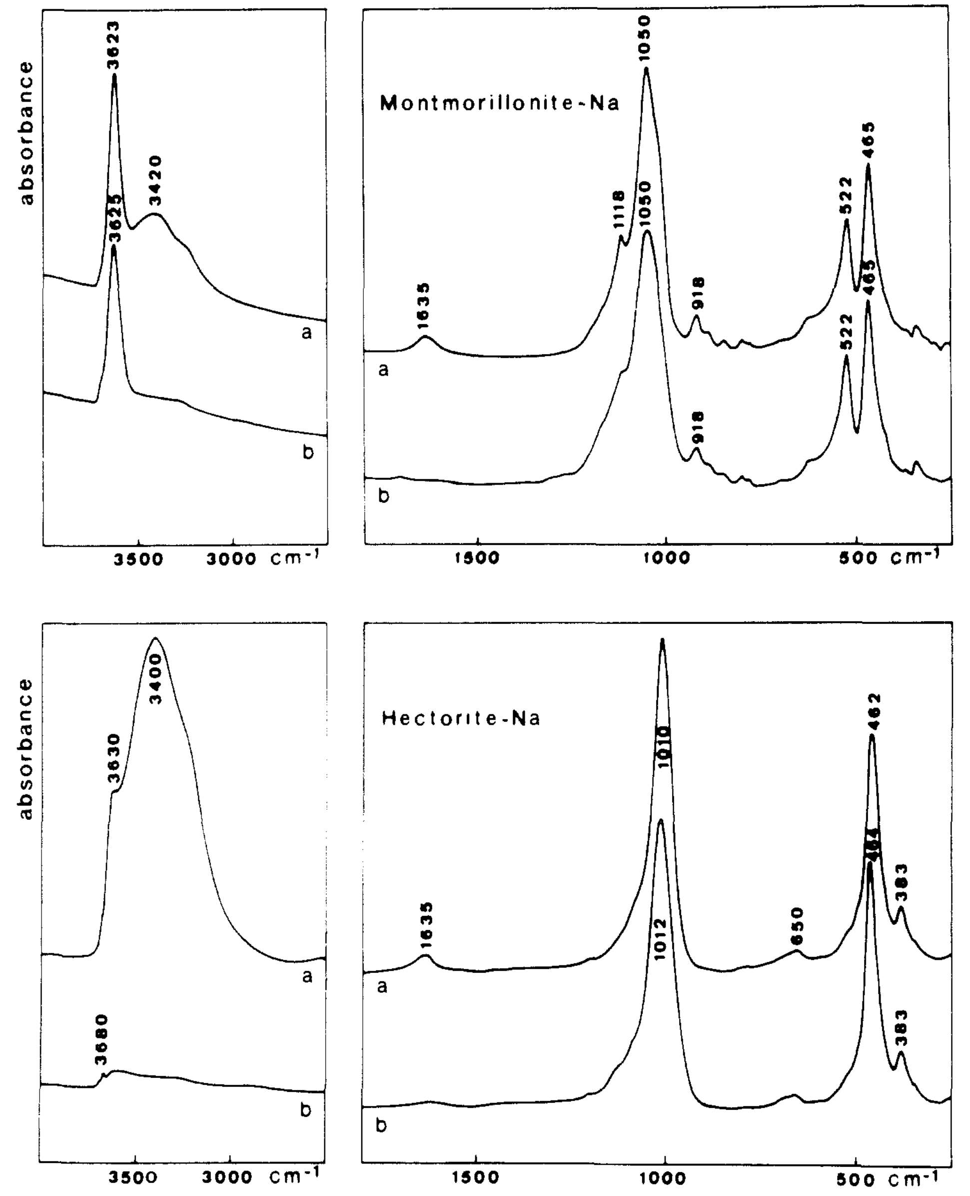

Figure 2. (a) IR spectrum of the skeletal vibrations of Na–montmorillonite dehydrated under vacuum and air-dried at ambient temperature. (b) The same as in (a) for Na–hectorite.

from 655 to 645 cm^{-1} have been noted as the clay mineral is hydrated.[20] The directions of these wavenumber shifts are consistent with the perturbation of the clay mineral OH groups by a neighboring *positive* charge. This arrangement of the proton, which has been confirmed also for Li–montmorillonite, is possible, despite the repulsive interaction with the structural OH group, because the proton is situated in the center of a cluster of lone pair orbitals, each inclined at 20° relative to the clay surface, that emanate from the oxygen atoms surrounding a ditrigonal cavity.

Progressive deuteration experiments carried out at ambient temperature and at 148 K on Na– and Ca–hectorite[20] lead to the conclusion that similar arrangements of the water molecules around exchangeable Na$^+$ and Ca^{2+} cations exist at low water contents. Therefore, it is reasonable to suppose that the structures illustrated in Figure 3 and 4 apply generally to alkali-metal and alkaline-earth cations. However, this conclusion is no longer tenable when there is a significant deficit of positive charge in the tetrahedral sheet of a smectite. In this case, the adsorbed water molecules will form hydrogen bonds with the clay surface oxygen atoms at sites where Si^{4+} has been replaced by Al^{3+}. Models for the arrangement of water molecules around exchangeable Mg^{2+}, Ca^{2+}, and Li$^+$ on saponite have been proposed on the basis of X-ray diffraction and IR spectroscopic studies.[21-23] Figure 5 illustrates the structure proposed for Ca–saponite.[22]

It is clear on the basis of IR spectroscopic experiments that the location of the deficit of positive charge in the structure of a smectite plays an important role in determining the spatial arrangement of the water molecules solvating the exchangeable cations. If this charge deficit occurs in the octahedral sheet, the negative charge on the surface oxygen atoms is delocalized and the adsorbed water molecules form only weak hydrogen bonds with these surface atoms. On the other hand, if the charge deficit occurs in the tetrahedral sheet, there is a greater localization of the negative charge, and the formation of relatively strong hydrogen bonds between the adsorbed water molecules and surface oxygen atoms near sites of isomorphous substitution is favored.[21] Another important effect of the

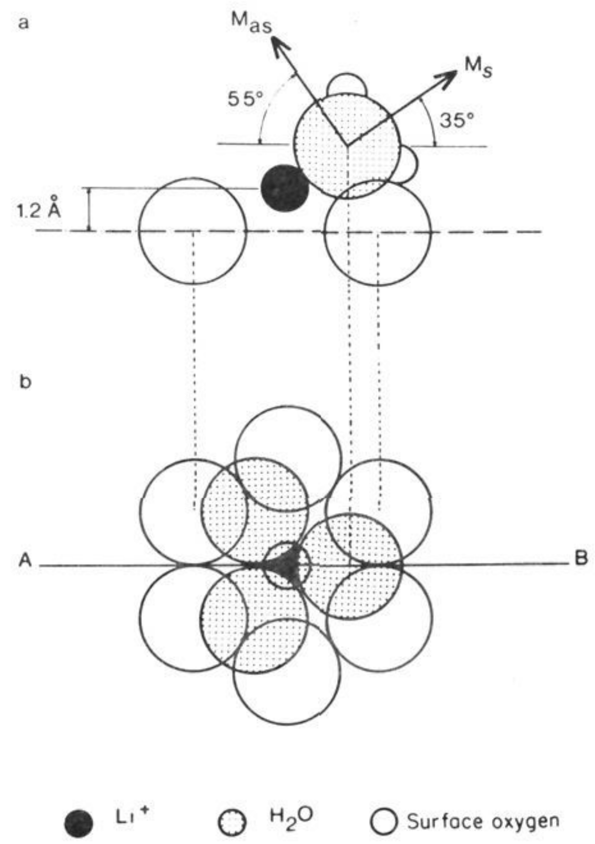

Figure 3. Spatial arrangement of water molecules solvating exchangeable Li^+ cations on hectorite as determined by IR spectroscopy:[20] (a) section view in the plane AB; (b) plan view. *M* denotes the transition dipole moment for the symmetric (s) and asymmetric (as) stretching modes.

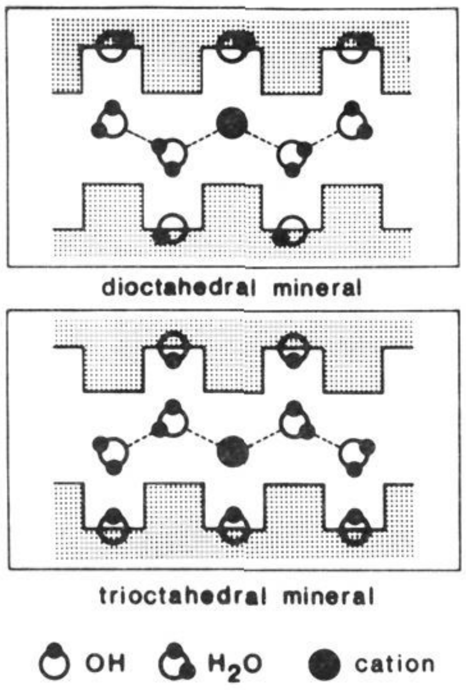

Figure 4. Spatial arrangement of water molecules adsorbed in the interlamellar spaces of smectites without isomorphous substitution in the tetrahedral sheet.[25]

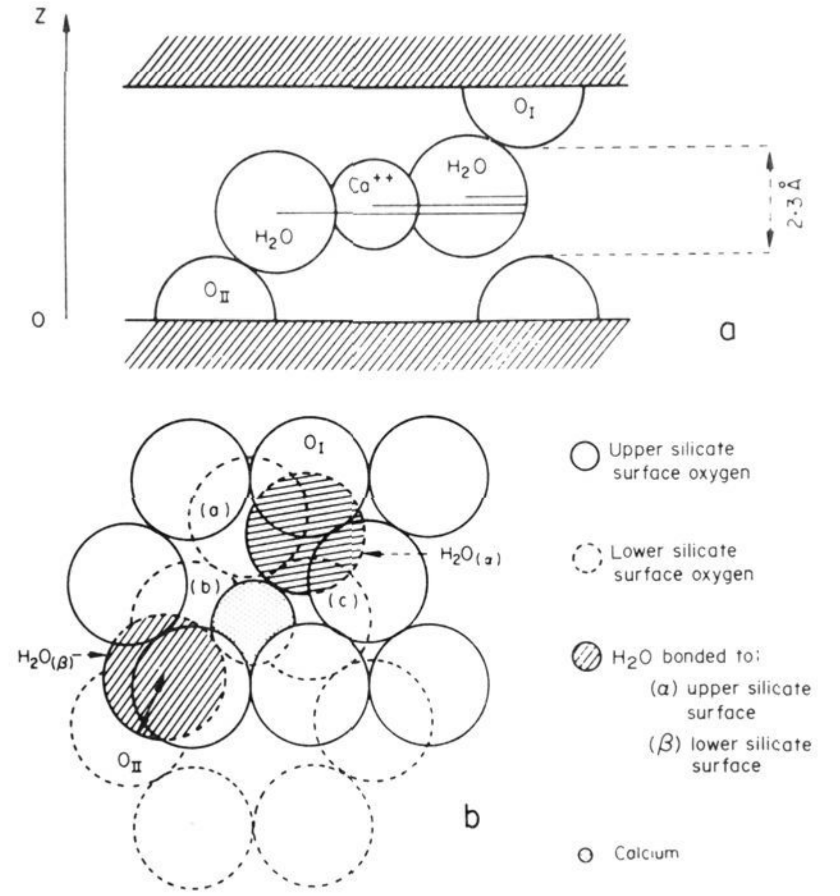

Figure 5. Spatial arrangement of water molecules solvating exchangeable Ca^{2+} cations on saponite as determined by X-ray diffraction and IR spectroscopy:[22] (a) section view; (b) plan view showing water molecules hydrogen bonded to oxygen atoms in an upper silicate surface (O_I) and to oxygen atoms in alower silicate surface (O_{II}) bounding the interlamellar space.

smectite structure on the water–clay interaction was illustrated in Figure 2, where it can be seen that changing the water content perturbs the structural vibrational bands in Na–montmorillonite (Figure 2a) but does not seem to perturb those in Na–hectorite (Figure 2b). This difference in behavior may be related to the changes in the crystallographic *b* dimension observed when Na–montmorillonites adsorb water.[24] Evidently this characteristic pertains only to dioctahedral minerals.

C. Mechanisms of Hydration

Infrared spectroscopic studies of smectite hydration[20,25,26] have led to the suggestion that the first stage of water adsorption by these clays is the solvation of the exchangeable cations by either three (monovalent ions) or more (bivalent cations) water molecules. These hydration states correspond to interlamellar *c* axis spacings large enough to accommodate either one or two layers of adsorbed water molecules. The second stage of hydration is the formation of either an octahedral solvation complex for the monovalent exchangeable cations or a second solvation sheath for the bivalent exchangeable cations.[20] Since this stage of hydration depends only on the ability of the exchangeable cations to solvate themselves, it is not necessarily accompanied by the formation of complete monolayers of water molecules in the interlamellar space.

Beyond the solvation of the exchangeable cations, the water adsorbed by smectites can condense in micropores and on external surfaces. Prost[25] has employed the shift in wavenumber of the absorption band of the structural OH group produced by water adsorption on hectorite to show that the fraction of interlamellar surface covered by water molecules at a given water content depends strongly on the nature of the exchangeable cation (Figure 6). The greater is the solvation energy of the cation, the greater is the amount of internal surface hydrated.

D. Estimation of the Extent of the Smectite–Water Interaction

Although it is clear that the IR spectrum of a smectite–water system differs from a simple, linear combination of the IR spectra of bulk liquid water and the fully dehydrated clay, it remains to specify the extent of the interfacial region whose spectroscopic properties are perturbed significantly by the clay–water interaction. This difficult problem has been approached in two distinct ways. One approach is through the study of strictly macroscopic properties of the smectite–water system as a function of water content.[27] The other is through an investigation of the intrinsic molecular

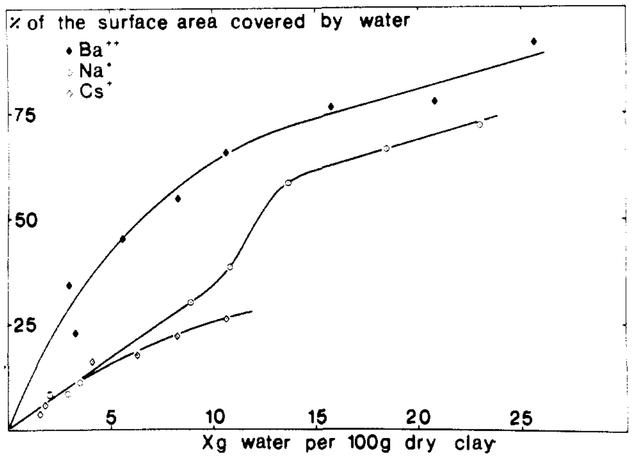

Figure 6. Percentage of the silicate surface area covered by water molecules as a function of water content in homoionic hectorites.[20]

properties of adsorbed water molecules as revealed by spectroscopic techniques.[28,29] These investigations have led to the conclusion that the stretching mode wavenumber of water adsorbed by Na–montmorillonite decreases as the water content increases and has not yet become equal to the value for bulk liquid water even at water contents above 1.0 kg of H_2O/kg of clay.

Prost[30] has studied the absorption bands at 1.45 and 1.93 μm in the near-IR spectrum of Na–hectorite–water systems as a function of water content in the range 0.5 to 10 kg of H_2O/kg of clay. A comparison among the different spectra was made by subtracting them consecutively after normalization to the same total quantity of clay. In this way, one could estimate the water content at which the last added increment of water has the same spectroscopic characteristics (band position, intensity, and profile) as bulk liquid water. It was found that this water content, in the case of Na–hectorite, is less than 0.5 kg of H_2O/kg of clay. Since a water content of 0.2 kg of H_2O/kg of clay corresponds to one monolayer of water molecules on the Na–hectorite surface,[25] it can be concluded that the near-IR spectroscopic properties of the adsorbed water are not perturbed significantly beyond about two monolayers.

III. Incoherent Neutron Scattering

A. The Incoherent Scattering Law

The translational, rotational, and vibrational motions of the protons in adsorbed water molecules can be studied through experiments in which well-collimated beams of monoenergetic, thermal neutrons are scattered elastically or inelastically by the protons. Neutron scattering probes the structure of a liquid on a time scale between 10^{-13} and 10^{-10} s. Therefore, protons whose residence times in a particular configuration of water molecules are longer than about 10^{-8} s will act as stationary targets for the neutrons. On the other hand, only low frequency vibrational modes, corresponding to hindered translations and rotations (i.e., wavenumbers up to about 10^3 cm^{-1}), can be studied conveniently by inelastic neutron scattering. Thus neutron scattering explores a time domain that is intermediate between those characteristic of infrared spectroscopy and magnetic resonance spectroscopy, respectively.

The fundamental theoretical and experimental aspects of neutron scattering along with representative applications are discussed in standard monographs.[31,32] Ross and Hall[33] have given an excellent discussion of the principles and applications in relation to clay–water systems. The pioneering studies of adsorbed water by the Oxford group have been summarized by White,[34] whereas Hall[35] has given an overview of the recent investigations carried out by the Birmingham group and others. Reference to these review chapters and books should be made for details of the equations and data that follow.

Neutron scattering by protons produces very few interference effects and usually can be described by the scattering function, $S_{\text{inc}}(\mathbf{Q},\omega)$, known as the *incoherent scattering law*. The probability that the scattered neutron has exchanged momentum $\hbar\mathbf{Q}$ and energy $\hbar\omega$ with the target proton is proportional to $S_{\text{inc}}(\mathbf{Q},\omega)$. Experimentally, this probability also is proportional to the intensity of a scattered beam of neutrons in an appropriate geometric configuration.[32] The experimental scattering law must be corrected empirically for undesired contributions from the clay mineral structure (e.g., structural protons) and the sample apparatus. The corrected scattering law will contain both the quasielastic and inelastic peaks, as was shown clearly for water adsorbed on Li–montmorillonite by Olejnik and White.[36] The inelastic peaks for adsorbed water on smectites have not yet been the subject of detailed investigation and, therefore, their contributions to the scattering law invariably are subtracted to obtain the quasielastic peak alone. This subtraction process always must involve an element of subjectivity that, in principle, makes the interpretation of the quasielastic peak ambiguous. Despite this problem, the consensus view is that experiments on the Q dependence of the quasielastic peak deconvoluted from the observed neutron scattering spectrum can provide useful information about the structure of adsorbed water.[35]

The quasielastic portion of $S_{\text{inc}}(\mathbf{Q},\omega)$ can be described theroetically by[33]

$$S_{\text{inc}}(\mathbf{Q},\omega) = \exp(-\langle u^2\rangle Q^2) S_{\text{tr}}(\mathbf{Q},\omega) * S_{\text{rot}}(\mathbf{Q},\omega) \quad (1)$$

where $\langle u^2\rangle$ is the mean square vibrational displacement of a proton from its equilibrium position and

$$f(\omega)*g(\omega) \equiv \int f(\omega - \omega')g(\omega')\, d\omega' \quad (2)$$

The interpretation of experimental quasielastic neutron spectra involves choosing model expressions for the contributions from translational $[S_{\text{tr}}(\mathbf{Q},\omega)]$ and rotational $[S_{\text{rot}}(\mathbf{Q},\omega)]$ proton motions, then convoluting the resultant $S_{\text{inc}}(\mathbf{Q},\omega)$ with the spectrometer resolution function to obtain an estimate of the observed neutron intensity data.[33,37] A number of models for $S_{\text{tr}}(\mathbf{Q},\omega)$ and $S_{\text{rot}}(\mathbf{Q},\omega)$ has been described by Ross and Hall.[33] Hall and Ross[38,39] have worked out the mathematical properties of model expressions for $S_{\text{tr}}(\mathbf{Q},\omega)$ appropriate to translational proton diffusion in the interlamellar space of a smectite. Hall et al.[40] have shown in detail how these expressions may be utilized to fit quasielastic scattering data directly.

B. Smectites Saturated with Monovalent Exchangeable Cations

Following the early studies of Olejnik and White,[36] Cebula et al.[37,41] have made extensive measurements of

TABLE I. Model Parameters Characterizing the Quasielastic Scattering of Neutrons by Water Protons on Li-montmorillonite[37]

no. of water layers	D, 10^{-9} $m^2\ s^{-1}$	τ_1, ps	$\langle l^2 \rangle$, nm^2	$\langle u^2 \rangle$, $nm^2 \times 10^3$	τ_R, ps
1	0.4 ± 0.1	15 ± 5	0.10 ± 0.04	1.7 ± 0.5	43 ± 5
2	0.7 ± 0.1	15 ± 5	0.15 ± 0.04	1.6 ± 0.5	33 ± 5
3	1.0 ± 0.1	15 ± 5	0.14 ± 0.04	2.2 ± 0.5	23 ± 5

the quasielastic spectrum of neutrons scattered by oriented Li–montmorillonite containing either one, two, or three layers of water in the interlamellar space. Several model forms for $S_{tr}(\mathbf{Q},\omega)$ and $S_{rot}(\mathbf{Q},\omega)$ were introduced into eq 1 and convoluted with the spectrometer resolution function to obtain a best least-squares fit to the quasielastic peaks measured at Q values between 0.6 and 4 $Å^{-1}$. It was found that model expressions corresponding to either isotropic translational or rotational diffusion alone could not describe the neutron spectra. But a model incorporating either two-dimensional translational diffusion (with due allowance for deviations from a perfectly parallel arrangement of the clay platelets) or isotropic translational diffusion *simultaneously* with isotropic rotational diffusion could describe the data very well. The model equation employed to represent the translational diffusion was based on the hypothesis that the adsorbed water molecules oscillate with a mean square amplitude $\langle u^2 \rangle$ about an equilibrium position for a mean time τ_R and then quickly jump to another equilibrium position at a mean square distance $\langle l^2 \rangle$ away during the time τ_J. For isotropic translational diffusion, the explicit forms of $S_{tr}(\mathbf{Q},\omega)$ and $S_{rot}(\mathbf{Q},\omega)$ used in eq 1 were (cf. Hall and Ross[39])

$$S_{tr}(\mathbf{Q},\omega) = \frac{1}{\pi} \frac{\Gamma[1 - F(\mathbf{Q})]}{\{\Gamma[1 - F(\mathbf{Q})]\}^2 + \omega^2} \tag{3}$$

$$\Gamma = 6D/\langle l^2 \rangle \equiv 1/\tau_R \qquad F(\mathbf{Q}) = \exp(-Q^2\langle l^2 \rangle/6) \tag{4}$$

$$S_{rot}(\mathbf{Q},\omega) = [j_0(Qa)]^2\delta(\omega) + [j_1(Qa)]^2[1 + (\omega\tau_1)^2]^{-1} \tag{5}$$

where D is the translational diffusion coefficient, $j_n(Qa)$ (n = 0, 1) is a spherical Bessel function, a is a radius of gyration (0.123 nm for a water molecule), and τ_1 is a rotational diffusion time constant. The derivation of eq 3 assumes that $\tau_J << \tau_R$.[37] Table I lists the values of the parameters D, τ_1, $\langle l^2 \rangle$, $\langle u^2 \rangle$, and τ_R determined by Cebula et al.[37] for adsorbed water on Li–montmorillonite. These parameters and eq 1, 3, and 5 were used to calculate the full width at half maximum (broadening) of the quasielastic peak as a function of Q^2.

The values of D and τ_1 in Table I may be compared with $D = 2.02 \times 10^{-9}$ $m^2\ s^{-1}$ and $\tau_1 = 9.3$ ps at 293 K for bulk liquid water.[18] Cebula et al.[37] concluded from this kind of comparison that the water molecules adsorbed by Li–montmorillonite were diffusing much more slowly than those in bulk water. It is apparent also that they are rotating somewhat more slowly. That the quasielastic spectra did not reflect significant anisotropy in the molecular motions was thought to be the result of the small spatial domain sampled by the neutrons (about the thickness of a water layer), the existence of water in micropores (isotropic environments), and the lack of perfect parallel alignment of the clay platelets. The values of $\langle l^2 \rangle$ in Table I are consistent with jump lengths of 0.33 to 0.37 nm—about the same as one molecular diameter—and the residence times are somewhat larger than the diffusion time for molecules in liquid water (12 ps at 293 K). The overall conclusion drawn by Cebula et al.[37] was that the motions of the water molecules on Li–montmorillonite are associated with correlation times less than 50 ps, a property shared by the molecules in bulk water.[18] The conclusion that none of the water molecules was stationary on the neutron time scale was deduced from the absence of an elastic peak surmounting the quasielastic spectrum. This result, in turn, means that none of the adsorbed water molecules is rigidly bound to the exchangeable Li^+ cations, since the self-diffusion coefficient of a Li^+ cation is only about 10^{-12} $m^2\ s^{-1}$ at 293 K on dry montmorillonite[42] and, therefore, it will be stationary on the neutron scattering time scale.

Estrade-Szwarckopf et al.[43] have come to rather different conclusions on the basis of their preliminary neutron scattering investigation of the water molecules remaining on Li–hectorite after pumping the clay at 10^{-3} torr at about 300 K. These investigators stated that the experimental quasielastic peak broadenings they observed could be fit well by a model that assumed that all of the water molecules were bound strongly to the (stationary) exchangeable Li^+ cations. Each solvating water molecule was allowed to rotate about its own symmetry (C_2) axis and about an axis perpendicular to the clay platelet through the exchangeable cation. These motions alone were considered to produce the observed broadenings. The resulting values of τ_2 (for the rotation about the C_2 axis of the water molecule) and τ_c (for the rotation about the cation center) were 2.7 ps and 148 ps, respectively, at 300 K. As the temperature was reduced, these two parameters were found to increase in value; at 200 K, no evidence for rotational motion was detected. Since the water content of the Li–hectorite studied by Estrade-Szwarckopf et al.[43] was much lower than that of the Li–montmorillonite studied by Cebula et al.,[37] no conflict would exist between the two sets of results, if cation solvation is the initial step in the adsorption of water by Li–smectite and either (a) the exchange of protons between the cation solvation shell and other adsorbed water molecules is very rapid when at least one layer of interlamellar water is present or (b) the rotational motion of the cation solvation shell and the jump diffusion of the adsorbed water molecules give similar contributions to the quasielastic peak after one layer of water is adsorbed. Neither of these two latter conditions is unreasonable physically. In particular, condition a is known to exist for the water molecules solvating monovalent cations in aqueous solutions.[44]

C. Smectites Saturated with Bivalent Exchangeable Cations

Hall et al.[45,46] have obtained quasielastic neutron scattering spectra for water adsorbed by Ca– and Mg–montmorillonite. Oriented clays containing up to three layers of water in the interlamellar space were investigated. The data were analyzed with the model of Hall

TABLE II. Characteristics of Water Protons on Ca- and Mg-montmorillonite As Determined by Neutron Scattering[33,35]

exchangeable cation	no. of water layers	X_{obsd}[a]	X_{theor}	D, 10^{-9} $m^2\ s^{-1}$
Ca	2	0.55	0.62	0.34 ± 0.02
Ca	3	0.65	0.69	
Mg	2	0.60	0.62	0.34 ± 0.02
Mg	3	0.68	0.69	

[a] X_{obsd} = ratio of quasielastic to (elastic + quasielastic) neutron scattering = fraction of protons in motion on the neutron scattering time scale. [b] X_{theor} = fraction of protons *not* in the clay structure or coordinated in solvation shells of the exchangeable cations = water protons not in solvation shells/(clay structure protons + all water protons).

et al.,[40] which permits the direct simulation of uncorrected intensity–energy (time-of-flight) measurements. The results of this analysis have been summarized by Hall.[35]

The physical characteristics of the model employed to describe the quasielastic spectra are as follows: (a) A fraction of the adsorbed water protons are stationary on the neutron scattering time scale (Table II, columns 3 and 4). These are associated with the first solvation layers of the bivalent exchangeable cations, whose self-diffusion coefficients are around $10^{-12}\ m^2\ s^{-1}$, making them also immobile on the neutron time scale.[42] (b) Some of the remaining adsorbed water protons diffuse by jumps within a region bounded by the opposing silicate surfaces and the solvated exchangeable cations, while others undergo isotropic, translational jump diffusion between adjacent bounded regions of this type. For example, in the two-layer hydrate of Ca–montmorillonite, the two sets of $\langle l^2 \rangle$ and τ_R values are 0.029 nm² and 10 ps, and 0.25 nm² and 100 ps, respectively. The second value of $\langle l^2 \rangle$ corresponds to a jump length of about 0.5 nm, which agrees well with the mean distance between Ca^{2+} solvation shells, calculated with the help of the specific surface area and cation exchange capacity of the clay under the assumption of octahedral coordination of the solvation shell water molecules.[35]

Table II lists the values of the self-diffusion coefficient for translational jump motion of the water molecules on each of the homoionic clays studied by Hall et al.[45,46] There is general comparability with the D values calculated by Cebula et al.[37] for water on Li^+–montmorillonite (Table I), suggesting that the water molecules that are not rigidly bound to an exchangeable cation diffuse similarly on any smectite. It should be emphasized that the motions of water molecules in both the interlamellar spaces and the micropores contribute to the parameter D in Tables I and II.

IV. Magnetic Resonance Spectroscopy

A. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance (NMR) spectroscopy can probe a molecular environment on the time scale between 10^{-3} and 10^{-10} s. The principles and experimental methodologies of NMR spectroscopy as applied to clay minerals have been discussed recently by Fripiat.[47] Glasel[48,49] has reviewed NMR studies on bulk liquid water and ice I_h, and Fripiat[47,50] has summarized the extensive contributions of his laboratory to the study of NMR spectra of adsorbed water protons and exchangeable cations on silicate surfaces. A general theoretical framework for the interpretation of NMR spectra of water in heterogeneous systems has been described by Halle and Wennerström.[51]

1. Measurements of Line Shape

Hecht et al.,[52] Hecht and Geissler,[53,54] and Woessner and Snowden[55,56] obtained perhaps the first well-resolved proton NMR spectra of water adsorbed by montmorillonite, beidellite, saponite, and hectorite saturated with Ca^{2+} and with monovalent exchangeable cations (usually Na^+). The characteristic features of the spectra were a doublet and a central line whose appearance depended on the temperature, the water content, and the orientation of the clay sample.[57a] Woessner and Snowden[55] studied the proton doublet for Na–hectorite at water contents between 0.21 and 2.3 dm³/kg clay and at 283 and 298 K. At the lower temperature, a doublet was observed whose splitting was inversely proportional to the water content. The doublet splitting when the applied magnetic field was normal to the oriented clay sample was twice that observed when the field was parallel to the plane of the sample. At room temperature, a doublet was seen only at the lowest water content; otherwise, the NMR spectrum consisted of a singlet. Hecht and Geissler[53] investigated the doublet splitting for a single layer of water adsorbed by a synthetic fluoromontmorillonite in the sodium form. Below 200 K, they found only a broad singlet, but at 298 K, a doublet was observed whose splitting followed the same orientation dependence reported by Woessner and Snowden.[55] This behavior was interpreted by both sets of authors to be evidence for a doublet separation proportional to the quantity $|3\cos^2\delta - 1|$, where δ is the angle between the applied magnetic field and a normal to the plane of the clay sample. According to standard theory,[47] a doublet whose splitting is proportional to $|3\cos^2\delta - 1|$ is expected for a pair of isolated protons located on a vector of fixed length that rotates very rapidly about a bisecting axis fixed in space. Thus, it was concluded that adsorbed water molecules on smectite surfaces are oriented preferentially in space at low water contents and at temperatures near 298 K. This behavior contrasts with that of the molecules in bulk liquid water, where no preferred orientation is expected on the NMR time scale and the spectrum consists of a broad singlet. In adsorbed water, translational diffusion is rapid on the NMR time scale, so the molecules sample all of the sites in the structure and, therfore, experience the same average preferred orientation. The fact that this average preferred orientation is diminished readily by increasing the water content or temperature[55,57a] suggests that the forces causing it are not very strong, perhaps being limited to the region within about 1.0 nm away from the clay mineral surface.[57b] Precisely the same general trend has been noted in NMR studies of water adsorbed by proteins.[58]

The early proton NMR studies have been refined and extended considerably by Conard[59,60] and by Fripiat et al.,[61] who have obtained both the proton and the $^7Li^+$

NMR spectra of an oriented film of Li–hectorite with a (001) spacing of 1.26 nm, corresponding to a single layer of water molecules in the interlamellar space. The proton NMR spectra for this smectite comprised the characteristic doublet, which decreased in separation as δ increased from 0° to 60°, then increased again as δ was varied from 60° to 90°. This variation was found to follow $|3 \cos^2 \delta - 1|$ very closely, with due allowance for small differences produced by slight deviations from parallel alignment of the clay platelets in the sample.[61] The doublet structure was found by Conard[59] to persist without change as the temperature was lowered from 300 to 208 K. However, by 193 K, the spectrum had become a broad singlet, in agreement with the data of Hecht and Geissler.[53] An examination of the first derivative of the spectrum of a powder sample of Li–hectorite[59,60] showed the presence of a narrow central line in addition to the doublet. This central line also disappeared below 200 K.[59] The amplitudes of the central line and the doublet peaks showed a smooth decrease with inverse temperature after the effect of Curie's law was taken into account.[60]

The proton doublet splitting for the one-layer hydrate of Li–hectorite was interpreted by Fripiat et al.[61] with the model expression:

$$h = (2.7 \times 10^{-4})(3 \cos^2 \gamma - 1)(3 \cos^2 \psi - 1)(3 \cos^2 \delta - 1) \tag{6}$$

where h is the doublet separation in tesla, γ is the angle between the axis of rotation of a water molecule and the vector between its two protons, and ψ is the angle between the axis and a normal to the hectorite surface. The derivation of eq 6, which assumes that the axis of rotation of the water molecule reorients very rapidly around the normal to the clay surface on the NMR time scale, has been described by Fripiat.[47] If it is assumed that the axis of rotation is the symmetry axis of the water molecule, then $\gamma = 90°$, and $\psi = 70 \pm 2°$ is required in order to fit the experimental values of $h(\delta)$. Thus the doublet splitting is consistent with oriented water molecules whose symmetry axes make an average angle of about 20° with the hectorite surface. Since the 1.26-nm hydrate studied by Fripiat et al.[61] contained about six water molecules per exchangeable Li^+, it is reasonable to suppose that some of the oriented water molecules surrounded the cation in the arrangement illustrated in Figure 7, while the others were either between the first cation solvation layers in the interlamellar space or outside this space itself. In a powder sample, there is a finite probability that the symmetry axis of a hydration shell will make an angle of 54° with the applied magnetic field in an NMR experiment, thereby making $3 \cos^2 \delta = 1$ and producing a central line instead of a doublet.[60]

The ^7Li NMR spectra obtained by Conard[59,60] confirmed the structure shown in Figure 7, in that they were consistent with a well-defined axial electric field gradient produced by water dipoles placed symmetryically about the $^7Li^+$ ion and engaged in rapid rotation around their dipolar axes. At temperatures below 200 K, the ^7Li NMR spectrum collapsed from a doublet plus central line to a broad singlet, indicating, in agreement with the proton NMR data, that the average electric field gradient had dropped to zero because the water dipoles were no longer rotating on the NMR time scale.

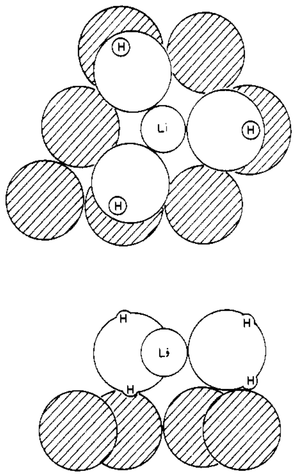

Figure 7. Spatial arrangement of water molecules solvating exchangeable Li^+ cations on hectorite as determined by NMR spectroscopy.[59,60] The shaded circles denote clay surface oxygen atoms.

2. Measurements of the Spin–Lattice Relaxation Time

Further insight into the structure proposed in Figure 7 was obtained by Fripiat et al.[61] through an analysis of the temperature dependence of the (longitudinal) spin–lattice relaxation time, T_1, of the protons in the one-layer hydrate of Li–hectorite. This parameter is a time constant for the exponential decay of a component of proton magnetization, brought on by interactions between a given proton and all of the nuclear magnets in its surrounding environment. The analysis of T_1 data for water adsorbed by montmorillonites and many other smectites thus is made difficult by the presence, in the clay structure, of Fe^{3+} ions whose interaction with the water protons is ill-defined, but exerts a dominant influence on the value of T_1.[56,62] Hectorite, on the other hand, contains very little Fe and has about half its structural OH replaced by fluorine; in this case, the principal contributor to T_1 is the water proton–proton interaction. This interaction occurs between protons in the same water molecule and between those in different water molecules and, therefore, T_1 contains both "intra" and "inter" contributions.[63] For bulk liquid water, the two contributions are of the same order of magntidue and T_1 is about 3 s at 293 K,[18] indicating a relatively weak coupling between a magnetized proton and its local environment.[49] For water on Li–hectorite, Fripiat et al.[61] found two populations of T_1 values: $T_{1L} = 0.06$ s at 293 K, corresponding to water outside the interlamellar space, and $T_{1C} \approx 0.02$ s at 293 K, corresponding to water inside this space. Both of these T_1 values are about 2 orders of magnitude smaller than T_1 in bulk liquid water and, therefore, they reflect a considerably stronger proton–proton interaction. Fripiat et al.[61] assumed that the "inter" contribution to T_{1C} was much larger than the "intra" contribution and then analyzed the temperature dependence of $1/T_{1C}$ to obtain two oritentational correlation times. One of these was to describe the rotation of the water molecules around their symmetry axes ($\tau_2 \approx 200$ ps at 293 K), whereas the other was purported to describe the rotation of the hydration shell in Figure 7 around its symmetry axis ($\tau_c \approx 10^3$ ps at 293 K). In bulk liquid water, the orientational correlation time (τ_2) associated with the "intra" contribution to T_1 is about 3 ps at 293 K[18] and in ice I_h it is about 10^6 ps at 273 K.[48] Thus water molecules in the interlamellar space of the one-layer hydrate of Li–hectorite appeared to be rotating less freely than in liquid water, but certainly more freely than in ice. Hecht and geissler[54] found the same result in their analysis of T_1 data for the water protons in the one- and two-layer hydrates of a synthetic fluoromontmorillonite in sodium form. They deduced only one population of orientational correlation times, with $\tau_2 \approx 1200$ ps for the one-layer hydrate and $\tau_2 \approx 400$ ps for the two-layer hydrate at 293 K. Perhaps none of these estimates of τ_2 should be taken to have more than qualitative significance, since the temperature dependence of T_1 for adsorbed water is very complicated and the expressions available to calculate τ_2 and τ_c are notoriously model dependent.[47,57] It is important to note again that the self-diffusion coefficient of a monovalent exchangeable cation in a relatively dry smectite is equal to about 10^{-12} m^2/s at 293 K.[42] This means that the cation diffuses a distance equal to its own diameter ($\approx$0.2 nm) in around 10^{-8} s, which is on the same time scale as that probed by an NMR measurement. It follows that NMR spectra must reflect in some way the average effects of cationic motion as well as that of the water molecules. Nonetheless, "static" models, such as that in Figure 7, seem to be useful in the interpretation of line shape and relaxation data.

Woessner[57b] has performed the same kind of experiment with T_1 measurements as Prost[30] carried out with the near-IR spectrum for the water adsorbed by Na–hectorite. The measured values of $1/T_1$, both for adsorbed H_2O and for adsorbed D_2O, were found by Woessner[57b] to be strictly linear functions of the clay content between 0.3 and 11 dm^3 water/kg of clay. These results were interpreted to mean that each added increment of water had the same NMR relaxation characteristics as bulk liquid water for all of the water contents investigated. Given this interpretation, it follows that τ_2 for the adsorbed water molecules can differ from the value for the molecules in bulk liquid water only in the first nanometer away from the clay surface, in agreement with the conclusion reached by Prost.[30] Woessner[57b] estimated that τ_2 for the strongly adsorbed water molecules was only about 5 times larger than the value for bulk liquid water. Halle and Wennerström[51] and Packer[58] cite many experimental NMR studies on water in a variety of heterogeneous systems that lead to the same general conclusion regarding the extent of the influence of surface forces on the reorientational motions of adsorbed water molecules.

B. Electron Spin Resonance Spectra

Electron spin resonance (ESR) spectroscopy probes a molecular environment on the more restricted time scale of 10^{-10} to 10^{-11} s. The theory and the practice of ESR spectroscopy as applied to clay minerals have been described recently by Vedrine[64] and by Hall.[65] The available ESR data for adsorbed species on layer silicates have been reviewed by Pinnavaia,[66] McBride,[67] and Hall.[68]

Clementz et al.[69] were the first to obtain ESR data on the structure of water near Cu^{2+} ions adsorbed by smectites. The ESR spectrum of interlamellar Cu^{2+} in one-layer hydrates indicated clearly the existence of a symmetry axis that was approximately perpendicular to the silicate surfaces and passed through the tetragonal solvation complex, $Cu(H_2O)_4^{2+}$ (Figure 8a). A detailed analysis of the angular dependence of the spectrum by Gutierrez-LeBrun and Gaite[70] indicated that the clay platelets in the oriented samples deviated from a perfectly parallel arrangement by ±18° but that otherwise an axial symmetry in the Cu^{2+} exchange sites was maintained. In a three-layer hydrate, prepared by doping 5% Cu^{2+} into Mg–hectorite, the ESR spectrum indicated the presence of the octahedral complex, $Cu(H_2O)_6^{2+}$, shown also in Figure 8b.[71] At higher water contents, this complex tumbled rapidly on the ESR time scale and a purely isotropic signal was observed.[66,68] The same kinds of results have been found for $Mn(H_2O)_6^{2+}$ cations adsorbed by smectites.[72] Thus, it may be concluded that, on the ESR time scale, the water molecules near bivalent exchangeable cations are well-organized at low water contents in a manner consistent with ion size and the nearby presence of parallel silicate layers. As the water content increases, the behavior of the hydrated cation is similar to that of a cation in an aqueous solution (i.e., rapid tumbling). Hall[68] has suggested that $\tau_c \approx 10^3$ ps for the rigidly oriented water molecules is consistent with the available ESR data. This estimate is also consistent with those made on the basis of NMR spectra.[61]

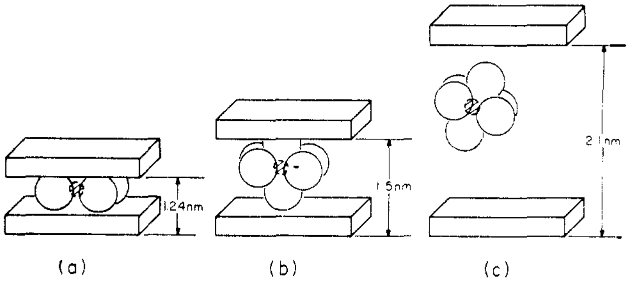

Figure 8. Spatial arrangement of water molecules solvating bivalent exchangeable cations on montmorillonite as indicated by ESR spectroscopy:[66] (a) one-layer hydrate; (b) three-layer hydrate; (c) 2.1-nm hydrate.

V. Dielectric Relaxation

A. The Complex Permittivity

The distribution of electric charge in a water molecule is primarily dipolar in nature.[15] Thus, if a water molecule is subjected to an applied electric field, the molecule will orient itself with its dipole moment pointing along the direction of the field, and if the field is time varying, the molecule will attempt to follow changes in the field direction by reorienting itself sympathetically. The extent to which this is possible, however, depends on the constraints imposed on the molecule by its surrounding environment. Should the molecule be coupled strongly with its neighbors, its ability to follow a fluctuating electric field will be less than if the coupling were weak. Whatever the degree of coupling, it is certain that as the frequency with which an applied electric field changes direction is increased, the water molecule will be less able to reorient in phase and, at some frequency, it will begin to fail altogether to respond. The mean frequency after which the failure becomes complete is expected to be an indicator of the strength of the bonds that constrain the water molecule from freely reorienting its dipole moment. The greater this mean frequency is, the weaker are the constraining bonds between the molecule and its surrounding environment.

The reorientational motions of a water molecule can be studied through measurements of the complex dielectric permittivity, $\epsilon(\omega)$, as a function of ω, the angular frequency of an applied electric field. For liquid water and ice I_h, permittivity data have been interpreted with the help of the *Cole–Cole* equation:[73a]

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau_D)^{1-\alpha}} \tag{7}$$

In eq 7, ϵ_∞ and ϵ_s are the limiting values of $\epsilon(\omega)$ as ω approaches $+\infty$ and 0, respectively, τ_D is the *Cole–Cole dielectric relaxation time*, and α is a parameter that characterizes the distribution of relaxation times about the value τ_D. The mathematical form of the distribution function is[73a]

$$G(\ln \tau) = \frac{1}{2\pi} \frac{\sin \pi\alpha}{\cosh [(1 - \alpha) \ln (\tau_D/\tau)] - \cos \pi\alpha} \tag{8}$$

Equation 8 leads to the Cole–Cole equation after substitution into the standard expression:[73a]

$$\epsilon(\omega) \equiv \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{G(\ln \tau)\, d \ln \tau}{1 + i\omega\tau} \tag{9}$$

If $\alpha << 1$, $G(\ln \tau)$ is a very sharply peaked function centered on $\ln \tau_D$; as α approaches 1.0, $G(\ln \tau)$ becomes a very broad, symmetric function about $\ln \tau_D$.

The failure of a water molecule to reorient in an oscillating, applied electric field is reflected by a drop in the value of the real part of $\epsilon(\omega)$ and ω increases, with a corresponding rise in the value of the imaginary part to a maximum value. This maximum value occurs at $\omega = 1/\tau_D$; hence τ_D is a measure of the nominal time scale on which molecular reorientations can take place. The smaller τ_D is, the easier it is for the water molecule to respond to an applied, time-varying field and the weaker must be the coupling between the molecule and its surroundings. If the parameter α is near 0, the environment of the water molecule is expected to be rather uniform in nature and τ_D describes this environment with respect to orientational motions. If α is near 1.0, a broad distribution of τ values exists and τ_D represents only a mean relaxation time characterizing a broad variety of different molecular environments for the water dipoles.[73a]

Since τ_D is a macroscopic parameter, it cannot be interpreted automatically as the time constant for the reorientational motion of a *single* water molecule. This latter time constant, denoted τ_1, is the case $n = 1$ of the general expression:[73b]

$$\tau_n = \int_0^\infty \langle P_n(\hat{\mu}(0)\cdot\hat{\mu}(t))\rangle\, dt \qquad (n = 1,2,...) \tag{10}$$

where $\hat{\mu}(t)$ is a unit vector pointing in the direction of the dipole moment of the water molecule at time t, P_n is an nth-order Legendre polynomial, and the angular brackets refer to a canonical ensemble average. The case $n = 1$ in eq 10 gives a time constant related to τ_D, whereas the case $n = 2$ (τ_2) gives a time constant related to the NMR spin-lattice relaxation time, T_1, as discussed above. The conditions required for equality between τ_D and τ_1 have been reviewed by Sposito,[18] who showed that they are met reasonably well for liquid water. The same appears to be true for ice I_h.[74]

Dielectric relaxation measurements probe a molecular environment on the rather broad time scale between 10^{-12} and 10^{-2} s, and, therefore, they encompass the domains of both neutron scattering and magnetic resonance spectroscopy, at least with respect to reorientational motions. In the case of liquid water, no drop in the value of the real part of $\epsilon(\omega)$ is observed until $\omega = 10^8$ Hz.[75] The value of the parameter α is 0.01, irrespective of the temperature in the range 273–333 K, and τ_D varies from 18 ps at 273 K to 4 ps at 333 K.[18] For ice I_h, $\alpha \approx 0.025$[73a] and $\tau_D = 1.7 \times 10^6$ ps at 250 K.[74] Thus both liquid water and ice I_h exhibit essentially a single dielectric relaxation time at a given temperature, but that for ice is 6 orders of magnitude larger, reflecting the much stronger coupling between a water molecule and its neighbors in the crystalline structure. This aspect is revealed also in the values of the temperature coefficient, $d \ln \tau_D/d(1/T)$, which is equal to about 7×10^3 K for ice I_h and 2.5×10^3 K for liquid water.[74,75]

B. Dielectric Relaxation in Water Adsorbed by Montmorillonite

The dielectric relaxation of water adsorbed by homoionic montmorillonites has been studied in detail by Mamy and Chaussidon,[76,77] Mamy,[78] and Calvet.[79,80] As discussed by Calvet,[80] the interpretation of data on $\epsilon(\omega)$ for smectite–water systems is made complicated by the fact that several phenomena contribute to the permittivity besides dipolar relaxation. In particular, as the water content of the clay increases, the exchangeable cations begin to move relatively freely near the clay surface. This motion provides a dominant contribution to the imaginary part of $\epsilon(\omega)$ and makes and observation of dipolar relaxation very difficult. Fortunately, at water contents below 0.15 kg of H_2O/kg of clay, the contribution of the exchangeable cations to $\epsilon(\omega)$ can be neglected.[78,80]

Mamy[78] has applied eq 7 to permittivity data obtained for water adsorbed by Li–, Na–, and K–montmorillonite at temperatures between 170 and 200 K. The value of the parameter α was determined from graphs of the imaginary part of $\epsilon(\omega)$ against the real part,[73a] and τ_D could be inferred from the frequency at which the imaginary part became a maximum. Representative values of α and τ_D are given in Table III for $T = 293$ K and at water contents corresponding to a spacing between the clay platelets large enough to accommodate one water layer.[78] Calvet[80] has made the same kind of measurements for adsorbed water on Mg–, Ca–, Sr–, and Ba–montmorillonite. Values of α and τ_D at 293 K for these clays also are listed in Table III for water contents corresponding to a clay platelet spacing large enough for one monolayer between the clay platelets. In terms of cation solvation, these low water contents are equivalent to about three water molecules per Li^+, five per Na^+, six per K^+, and about six per bivalent exchangeable cation.[78,80]

C. Structural Implications

The values of α for adsorbed water on montmorillonite are close to 0.7 regardless of the exchangeable cation, in striking contrast to the situation in bulk liquid

TABLE III. Cole–Cole Dielectric Relaxation Parameters for Adsorbed Water on Homoionic Montmorillonites at 293 K[78,80]

exchange-able cation	water content, kg of H_2O/kg of clay	α^a	τ_D,^{b} s	d ln τ_D/d(1/T), 10^3 K
Li	0.04	0.60	1.7×10^{-8}	5.5
Na	0.06	0.80	3.6×10^{-12}	7.4
K	0.085	0.64	4.9×10^{-12}	6.7
Mg	0.07	0.65	9.5×10^{-6}	11.1
Ca	0.07	0.65	1.1×10^{-6}	9.9
Sr	0.07	0.65	3.2×10^{-7}	8.0
Ba	0.062	0.65	1.6×10^{-5}	6.3
bulk liquid		0.01	9.3×10^{-12}	2.5
ice I_h		0.025	3.0×10^{-6}	7.0

[a] Data for Li–clay at 200 K, Na–clay at 175 K, K–clay at 170 K, ice I_h at 250 K. [b] Data for monovalent cations and for ice I_h have been extrapolated to 293 K.

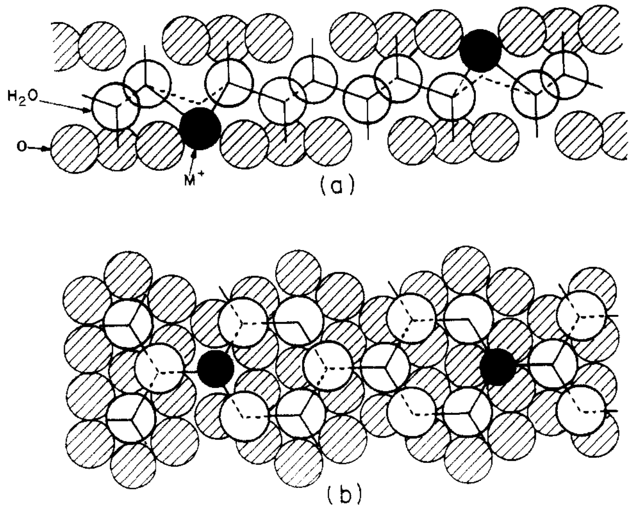

Figure 9. Spatial arrangement of water molecules in the interlamellar space of montmorillonite containing monovalent exchangeable cations, as determined by dielectric relaxation spectroscopy:[78] (a) section view; (b) plan view. The shaded circles denote clay surface oxygen atoms.

water and ice, where α is near zero. This result indicates clearly that a broad variety of molecular environments exists in adsorbed water, as compared to the bulk solid and liquid phases, at least at very low water contents. For montmorillonite saturated with monovalent exchangeable cations, Mamy[78] has suggested that the one-layer hydrate consists of water molecules arranged in a strained, icelike configuration, with bonds formed both with intermolecular interactions and with clusters of oxygen atoms in the silicate surface (Figure 9). The nearest-neighbor distance in this model is 0.32 nm, which agrees well with the jump distance found by Cebula et al.[37] for water molecules on Li–montmorillonite. There are five water molecules assignable to each exchangeable cation in this structure. Since some of the water molecules have a hydroxyl group proton inside a ditrigonal cavity of the silicate surface, the net of hydrogen bonds among the adsorbed water molecules is broken in places. These defects permit a variety of reorientational motions that are not possible in ice I_h or in bulk liquid water. For the one-layer hydrate of montmorillonite saturated with bivalent cations, the same structure may not exist because of the strong solvation of the exchangeable cations. In this case, the significance of the large value of α may be that the reorientational motions of the solvation shell water molecules (about four per exchangeable cation in a one-layer hydrate) are very different from those of the remaining water molecules (about two per exchangeable cation) that are outside the solvation shells.

TABLE IV. Values of the Cole–Cole Parameters at 293 K for Water Adsorbed by Ca–montmorillonite[79]

water content, kg of H_2O/kg of clay	α	τ_D, s
0.038	0.68	3.8×10^{-5}
0.070	0.65	1.1×10^{-6}
0.095	0.66	1.7×10^{-6}
0.130	0.69	3.0×10^{-11}

The values of τ_D in Table III indicate that the reorientational motions of water molecules adsorbed on Na– and K–montmorillonite are on the same time scale as those in liquid water, even in the one-layer hydrate. On the other hand, the time scale of the reorientational motions for water molecules on Li–, Mg–, Ca–, Sr–, and Ba–montmorillonite is comparable to that for ice I_h. It is possible that these trends reflect the tendency of the latter exchangeable cations to bind solvation shell water molecules very strongly, thereby preventing an easy movement of their dipole moment vectors in response to an oscillating, applied electric field. Calvet[79] has determined τ_D as a function of water content and temperature for Ca–montmorillonite. At $T = 293$ K (Table IV), τ_D decreases from about 4×10^{-5} s to 3×10^{-11} s as the water content increases from one-half monolayer to about two layers of water molecules in the interlamellar space, whereas α remains the same. This result suggests that the solvation shell molecules, which probably account for all of the water content at 0.04 kg of H_2O/kg of clay, are reorienting on a time scale that is much longer than that for the adsorbed water molecules that make up most of the water content at 0.13 kg of H_2O/kg of clay.

Hoekstra and Doyle[81] have measured $\epsilon(\omega)$ at 9.8×10^9 Hz for water on Na–montmorillonite at temperatures between 70 and 293 K. Below 263 K, just two layers of water molecules remained in the interlamellar space. An analysis of the behavior of the imaginary part of $\epsilon(\omega)$ with decreasing temperature led to the conclusion that the dielectric relaxation phenomenon in the two-layer hydrate operated on the same time scale as it does in bulk liquid water. This conclusion is in accord with the data in Table III.

VI. Neutron and X-ray Diffraction

Neutron or X-ray diffraction is the coherent, elastic scattering of either neutrons of X-rays by atoms arranged on a periodic lattice. Neutron diffraction is quite analogous to the better known X-ray diffraction, but differs from the latter in two important respects. First, neutron diffraction involves scattering by nuclei, whereas X-ray diffraction involves scattering by atomic electrons. It follows that the scattering power of a given element will be different, in general, for the two processes. For example, deuterium, having but one electron, has a low scattering power for X-rays but a high (coherent) scattering power for neutrons. Secondly, neutron diffraction probes a larger spatial domain in a target sample than X-ray diffraction because of the greater penetration of neutrons into matter. Thus, structural information pertaining to relatively larger units in the sample materials can be obtained.

Since coherent scattering experiments require the collection of data over long time periods, neutron and X-ray diffraction will give a picture of the structure of adsorbed water on an effectively "infinite" time scale. This picture, then, will be an account of the diffusionally averaged structure that, in principle, can be compared with what has been found for liquid water and ice on the basis of neutron and X-ray diffraction studies.[15,82,83] The fundamental experimental and theoretical aspects of neutron diffraction as applied to clay–water systems have been discussed by Ross and Hall.[33] Cebula et al.[84] and Hawkins and Egelstaff[85] have given brief overviews concerning the use of neutrons vs. X-rays in diffraction investigations of adsorbed water on smectites.

A. Smectites at Low Water Contents

Hall et al.,[45] Cebula et al.,[84] and Hawkins and Egelstaff[85] have investigated the (001) reflections of neutrons diffracted by oriented montmorillonites saturated with monovalent or bivalent exchangeable cations and containing up to three layers of water molecules in the interlamellar space. The (001) peak position (basal spacings) of the homoionic clays were observed to increase with water content in the well-known stepwise manner that has been established for smectites repeatedly by X-ray diffraction.[8,20,78,86,87] However, the (001) peak is broader for diffracted neutrons than for X-rays when both kinds of diffraction peak are plotted against Q, the momentum transfer.[84] The reason for this difference lies with the larger spatial domain explored by the neutrons. Beyond the region nearest to the sample surface (the only region that diffracts X-rays), the clay platelets evidently are to be found in a relatively disordered array. Detailed studies of the (001) peak[45,84] show that the clay platelets deviate ±20° about a perfectly parallel arrangement in typical oriented samples, in agreement with what has been inferred from ESR data on cation solvation complexes in montmorillonite.[70]

Hawkins and Egelstaff[85] have investigated the (001) peaks in the neutron diffraction pattern of a deuterated Na–montmorillonite containing either H_2O or D_2O at water contents up to 0.533 kg/kg clay. The scattering density profile along the c axis direction, obtained by Fourier inversion of the (001) peak intensities, showed that the water molecules in the one-layer hydrate are located about 5.5 Å from the plane of Al atoms in the clay structure. This result and other features of the neutron density profile were in excellent agreement with the electron density profile calculated previously by Pézerat and Méring[88] on the basis of X-ray diffraction data for the same montmorillonite in the same hydration state. The relatively large breadth calculated for the water molecule peak in the density profile suggested to Hawkins and Egelstaff[85] that the one-layer hydrate did not have a highly ordered structure and that the water protons were rotating rapidly enough to preclude strong correlations between their positions and those of the oxygen atoms in the silicate structure.

Neutron diffraction intensities at scattering angles up to 120° were determined by Hawkins and Egelstaff[85] for Na–montmorillonite exposed to D_2O at relative humidities between 0 and 100%. With the clay sample maintained in a transmission geometry, the intensity data gave information about the *hk* peaks for the clay as well as the broad diffraction peak expected from the adsorbed D_2O. It was found that the latter was shifted to higher scattering angles relative to the peak for bulk liquid D_2O. Moreover, certain of the clay peaks changed significantly in intensity as the content of D_2O increased. These characteristics led Hawkins and Egelstaff[85] to conclude that at least some of the adsorbed D_2O molecules were correlated spatially with the atoms of the silicate surface but that the effects of these correlations did not change after the one-layer hydrate was formed. The overall view expressed was that the adsorbed water structure on Na–montmorillonite is predominantly liquidlike, subject to the constraints imposed by the nearby presence of the silicate surfaces. This same conclusion was reached by Pons et al.[89] on the basis of a comparative analysis of *hk* peak shapes and intensities in the X-ray diffraction patterns of liquid water and a thick (20% by mass) suspension of Na–montmorillonite. These investigators found that their data were consistent with a model in which some of the molecules in the first monolayer of adsorbed water are bound strongly to the surface oxygen atoms and others are entrained over the ditrigonal cavities in an epitaxy with the clay surface. This strong association did not extend past the initial adsorbed monolayer.

B. Smectite Suspensions

Coherent, elastic neutron scattering can occur from solid particles suspended in an aqueous phase if the diameters of the particles lie in the range 1–500 nm. The intensity of the scattered neutrons can be studied as a function of the momentum transfer, Q, to obtain information about the size distribution of the target particles. Moreover, the fact that the proton and the deuteron have very different coherent neutron scattering cross sections[33] can be exploited to determine the actual dimensions of the particles. These applications and the underlying theory of *small-angle neutron scattering* (so-called because very small Q values are involved) have been discussed by Ross and Hall[33] and by Cebula et al.[90]

Cebula et al.[90,91] have pioneered in the use of small-angle neutron scattering to investigate dilute suspensions of Li–, K–, and Cs–montmorillonite. Measurements of the scattering intensity as a function of Q were made on suspensions containing 0.8% clay by mass and varying proportions of H_2O and D_2O. The data were interpreted with straightforward theoretical expressions derived for thin, disk-shaped aggregates of clay platelets in face-to-face association. The analysis showed that Li–montmorillonite formed single platelets in suspension, whereas K– and Cs–montmorillonites formed aggregates with two and three platelets, respectively. Between each pair of platelets in an aggregate there were two layers of water molecules, and these molecules did not exchange significantly with the solvent surrounding the aggregate during 1 h. Cebula et al.[90] concluded from these results that the structure of a montmorillonite aggregate was controlled by the exchangeable cation and that a barrier to water molecule diffusion exists at the edges of an aggregate, possibly because of the distribution of electric charge there.

Cebula and Ottewill[92] have investigated the behavior of Li–montmorillonite suspensions containing between 2 and 7% clay by mass and concentrations of LiCl between 10^{-3} and 10^{-5} M. The suspensions with the higher salt concentration produced small-angle scattering intensities whose Q dependence was similar to that of the Li–montmorillonite suspensions studied by Cebula et al.[90] At the lower salt concentration, however, Bragg diffraction peaks were observed whose position decreased in a regular manner as the clay concentration increased. The peak positions could be estimated quite well by a formula derived from the assumption that the clay platelets were dispersed individually into ordered stacks of particles aligned in parallel. Electrostatic repulsive forces between the clay platelets were assumed to produce this ordering.

The use of *small-angle X-ray scattering* to study smectite suspensions has been developed by Pons et al.[93-95] In order to obtain an intense, well-collimated beam of X-rays whose wavelength can be varied, these investigators have employed synchrotron radiation from the LURE accelerator at Orsay. The details of this experimental innovation have been described by Tchoubar et al.[96] Measurements of the scattering intensity as a function of Q and the temperature were made on suspensions containing 20% clay by mass. The data were analyzed according to model expressions derived for aggregates comprising parallel plates with variable numbers of water monolayers between adjacent plates. It was found that the montmorillonite gel at ambient temperature contained quasi-crystals with 4–5 platelets in face-to-face association as well as isolated single platelets. Within the quasi-crystals, two monolayers of water molecules separated each clay platelet. The same experiments were performed with K–, Cs–, and Ca–montmorillonite.[93] The data for K-montmorillonite were not described well by the theoretical model employed, but it appeared that the suspension comprised parallel clay platelets both with and without water monolayers interposed between them. The data for Cs–montmorillonite indicated that rather thick aggregates formed with either 0 or 1 water monolayer between the platelets, a result that disagrees with that of Cebula et al.[90] obtained for a more dilute suspension of the same homoionic montmorillonite. For Ca–montmorillonite, quasi-crystals containing 4–5 clay platelets with three monolayers of water molecules between adjacent platelets were found.

Pons[93] also has studied small-angle X-ray scattering by thick suspensions of Na–hectorite, Na–beidellite, and Li–saponite. The hectorite suspension was found to have properties very similar to those of the Na–montmorillonite suspension that had been studied previously, whereas the beidellite and saponite suspensions showed less dispersion, presumably because of the existence of charge deficits in the tetrahedral sheets of these clays.

VII. Thermodynamic Properties

A. Partial and Apparent Specific Properties

Thermodynamic studies of smectite–water mixtures have been carried out often during the past 30 years with the aim of elucidating the structure of adsorbed water.[1,2,4,9,27] The data obtained in these studies refer to the properties of stable states and, therefore, give information pertaining to a time scale that is effectively "infinite" with respect to the dynamics of adsorbed water molecules. Besides this well-known fact, there are two other important features of thermodynamic data that should be mentioned in connection with their interpretation. First, since the objective of chemical thermodynamics is solely the development of exact mathematical relationships among the macroscopic properties of a physical system,[97] thermodynamic data cannot be interpreted directly in terms of molecular structure. Thus, the thermodynamic properties of smectite–water systems cannot provide unambiguous insights into the structural behavior of adsorbed water molecules. Second, the thermodynamic properties of mixtures, such as smectite–water systems, are only formally separable into properties that pertain to the individual components. Consider, for example, any extensive property of a smectite–water system, X (e.g., the volume, entropy, or Gibbs energy). This property can always be expressed:[98]

$$X = m_w \bar{x}_w + m_s \bar{x}_s \tag{11}$$

where m_w and m_s are the masses of water and smectite, respectively, and

$$\bar{x}_w = \left(\frac{\partial X}{\partial m_w} \right)_{T,P,m_s} \tag{12}$$

is the partial specific value of the property X with respect to water, $\bar{x}_s$ being defined similarly with respect to the clay. Equation 11 is an identity, but $\bar{x}_w$ is not simply the amount of X attributable to water. Instead, it is the infinitesimal change in X produced by an infinitesimal addition of water at constant temperature, pressure, and mass of smectite. In general $\bar{x}_w$ will depend on all four variables of state, T, P, m_w, and m_s. Moreover, any variation in $\bar{x}_w$ at constant temperature and pressure is compensated for by a variation in $\bar{x}_s$ according to the generalized Gibbs–Duhem equation:[98]

$$m_w \, d\bar{x}_w + m_s \, d\bar{x}_s = 0 \tag{13}$$

These points are well-known, but they deserve emphasis to make it clear that any attempt to assign, for example, $\bar{x}_w$ solely to the water component must be understood as arbitrary action unless nonthermodynamic evidence exists to support it.

In addition to $\bar{x}_w$, Low[27] has employed the *apparent specific value* of a property to describe smectite–water mixtures. This quantity is defined by the relation

$$X \equiv m_w \phi_X + m_s x_s^0 \tag{14}$$

where ϕ_X is the apparent specific value of X and x_s^0 is the value of X per unit mass of smectite in a system containing only the smectite at a mass of m_s kilograms. Low[27] has pointed out that ϕ_X is an average quantity, whereas $\bar{x}_w$ is a differential quantity. This fact can be seen clearly from the relation between ϕ_X and $\bar{x}_w$ that follows from eq 11, 13, and 14. Because of eq 13, the total differential of X can be expressed:

$$dX = \bar{x}_w \, dm_w + \bar{x}_s \, dm_s = \phi_X \, dm_w + m_w \, d\phi_X + x_s^0 \, dm_s$$

from which one can derive

$$\frac{d(\theta\phi_X)}{d\theta} = \bar{x}_w(\theta) \qquad (T, P \text{ constant}) \qquad (15)$$

where $\theta = m_w/m_c$ is the gravimetric water content. Equation 15 is the differential equation for ϕ_X as a function of θ at constant temperature and pressure. The formal solution of this equation is

$$\phi_X(\theta) = \frac{1}{\theta}\int_0^\theta \bar{x}_w(\theta')\, d\theta \qquad (T, P \text{ constant}) \qquad (16)$$

This expression shows that ϕ_X and $\bar{x}_w$ are not independent quantities and that the former is an average of the latter over the gravimetric water content. Thus, ϕ_X also represents a property of the whole clay-water mixture and cannot be attributed, a priori, to the water component alone.

B. Partial Specific Gibbs Energy

The defined relationship between the partial specific Gibbs energy with respect to water, $\bar{g}_w$, and the relative vapor pressure of water in a smectite-water mixture is[99]

$$\bar{g}_w = g_w{}^\circ + RT \ln (p/p_0) \qquad (17)$$

where $g_w{}^\circ$ is the Gibbs energy of 1 kg of liquid water in the standard state, R is the molar gas constant, T is the standard state temperature, and p/p_0 is the relative vapor pressure. In principle, eq 17 could be used to calculate $\bar{g}_w$ from measurements of p/p_0 for different states of a smectite-water mixture. However, except for $p/p_0 > 0.99$, this calculation is not strictly possible because p/p_0 is a multivalued function of the gravimetric water content, θ.[100-102] Thus, one set of $(p/p_0, \theta)$ pairs is obtained when the clay is taken from a condition of water saturation to a condition of dryness and another is obtained when the process is reversed, giving rise to the well-known hysteresis phenomenon. Since the slopes of the $(p/p_0, \theta)$ curves for smectite-water mixtures always are observed to have positive values, the states of the system they describe are stable,[99] but they are not equilibrium states because infinitesimal changes in the values of $(p/p_0, \theta)$ are not reversible. It follows that the right side of eq 17 has no strict thermodynamic meaning, although it is well-defined experimentally. On the other hand, the difference between the integral of the right side of eq 17 along a desorption curve and along an adsorption curve can be interpreted as the chemical energy lost, irreversibly, as heat when a smectite-water system is brought from a water-saturated condition to dryness, then back again.[99] Tardy et al.[102] have published values of the integral of $RT \ln (p/p_0)$ along desorption and adsorption curves for homoionic hectorite-water mixtures. The resulting irreversible heat losses at 293 K are listed in Table V. The data show no particular trend with cation size, but the heat losses appear to be somewhat larger for the bivalent cations than for the monovalent cations.

At high water contents, hysteresis effects in smectite-water systems do not appear and eq 17 can be applied to calculate $\bar{g}_w$. Alternatively, one can use the expression:[103a,b]

$$\bar{g}_w = g_w{}^\circ - \bar{v}_w P_s \qquad (18)$$

where $\bar{v}_w$ is the partial specific volume with respect to water and P_s is the external pressure that must be applied to a smectite-water system at fixed temperature and water content to prevent pure liquid water from entering (the swelling pressure). Published values of P_s as a function of θ[104-108] indicate that $\bar{g}_w$ can be a few joules per kilogram lower than $g_w{}^\circ$ at 298 K even at water contents approaching 8 kg of H_2O/kg of clay. This difference is a tiny fraction of the value of $g_w{}^\circ$ (-1.32×10^4 J/kg at 298 K).[99]

TABLE V. Values of Q_{hys}, the Irreversible Heat Loss in Traversing a Sorption Hysteresis Loop Once, for Homoionic hectorite-Water Systems at 293 K[102]

exchangeable cation	Q_{hys}, kJ/mol	exchangeable cation	Q_{hys}, kJ/mol
Li	-11.2	Mg	-17.5
Na	-27.1	Ca	-13.5
K	-25.6	Sr	-26.9
Cs	-9.1	Ba	-30.4

C. Partial Specific Enthalpy and Entropy

The partial specific entropy, $\bar{s}_w$, and enthalpy, $\bar{h}_w$, with respect to water can be calculated, in principle, from data on the temperature dependence of $\Delta\bar{g}_w$ in smectite-water mixtures.[98] Because of hysteresis effects, this calculation cannot strictly be done for smectites containing small amounts of water, although standard thermodynamic equations have been employed formally to compute the "isosteric heat of adsorption" for montmorillonite-water systems.[100] On the other hand, the temperature dependences of $\bar{v}_w$ and P_s can be employed legitimately to determine $\bar{h}_w$ and $\bar{s}_w$ as functions of θ.[109,110]

The most common method of measuring $\bar{h}_w$ has involved the determination of the enthalpy change when a smectite of known water content is wholly immersed in pure water.[101,110-113] The slope of a graph of this enthalpy change per unit mass of clay vs. the initial gravimetric water content, i.e., the differential enthalpy change, is equal to $(h_w{}^0 - \bar{h}_w)$. Although both the enthalpy change of immersion and the slope of its graph against water content are well-defined experimental quantities for smectites at low water contents, their thermodynamic significance is doubtful under these circumstances because the stable states of the smectite-water system are not equilibrium states, as discussed above. Nonetheless, the data at low water contents do indicate that cation hydration makes an important contribution to the enthalpy change of immersion and its variation with initial water content.[101,111,112] In particular, Ca-montmorillonite shows larger values of the enthalpy change of immersion per unit mass of clay than does Na-montmorillonite and there is a continuous increase in the enthalpy change with initial water content for the former clay, whereas both Na-montmorillonite and Na-hectorite show approximately steplike increases. These trends have led to the suggestion that the principal mechanism underlying the observed variation of the differential enthalpy change at low water contents is the solvation of the exchangeable cations followed by the adsorption of water molecules in the interlamellar space between cation solvation shells.[101,112,114]

At high water contents, the variation of the enthalpy change of immersion of a smectite with initial water content has thermodynamic meaning. Figure 10 shows

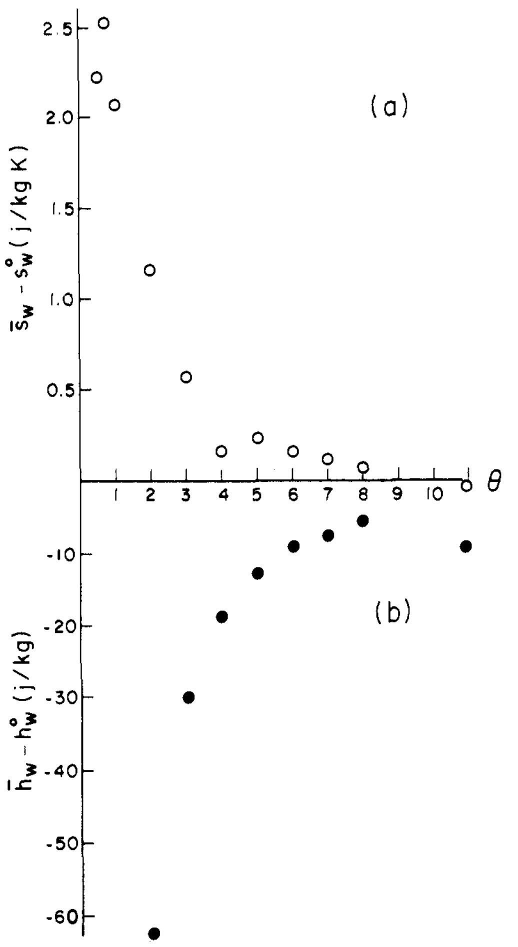

Figure 10. (a) Difference between the partial specific entropy, with respect to water, on Na–montmorillonite and the partial specific entropy of bulk water, as a function of water content.[110] (b) Same as in (a) for the partial specific enthalpy with respect to water on Na–montmorillonite.

a plot of $(\bar{h}_w - h_w^0)$ against θ for Na–montmorillonite at 298 K.[110] A smooth dependence of $(\bar{h}_w - h_w^0)$ on the initial water content is evident, and it appears that $\bar{h}_w$ is detectably different from h_w^0 even at $\theta = 8.0$ kg of H_2O/kg of clay. However, these data do *not* demonstrate that the enthalpy of adsorbed water is less than that of bulk liquid water for $\theta \leq 8.0$ kg of H_2O/kg of clay. They show only that the enthalpy of a Na–montmorillonite–water mixture increases less with an infinitesimal increase in water content than does bulk liquid water, i.e., changes in enthalpy are being compared. Also, one cannot attribute the value of $\bar{h}_w$ a priori to structural characteristics of adsorbed water, since the enthalpy change of immersion is produced by all possible reactions between the clay sample and water. As pointed out by Keren and Shainberg,[101] one expects that the hydrolysis of Na–montmorillonite will be an important contributing reaction at high initial water content. Less severe perturbations of the clay structure, as well as reactions with impurities adsorbed by the clay, can also be important under these conditions, and the role of each reaction competing with simple hydration of the clay must be established experimentally before the values of $\bar{h}_w$ can be interpreted structurally.

If $(\bar{g}_w - g_w^0)$ has been determined from swelling pressure measurements and $(\bar{h}_w - h_w^0)$ is known through enthalpy change of immersion data, then the partial specific entropy with respect to water can be calculated.[98] Figure 10 shows values of $(\bar{s}_w - s_w^0)$ for Na–montmorillonite–water mixtures at 298 K that were calculated in this way by Oliphant.[110] The interpretation of the graph is that the increase in the entropy of a Na–montmorillonite–water mixture with an infinitesimal increase in water content is greater than that for bulk liquid water. Whether the entropy of adsorbed water is greater than that of liquid water cannot be deduced from the data; only the fact that the entropy of the entire mixture increases at a greater rate than does that of liquid water alone can be inferred with certainty.

D. Heat Capacity

The heat capacities of smectite–water mixtures have been measured by Oster and Low[115] and by Eger et al.[116] Oster and Low[115] determined the heat capacity at constant pressure for Li–, Na–, K–, Ca–, and Al–montmorillonite–water systems as a function of water content at about 288 K. Their data permitted the calculation of both $\bar{c}_w$, the partial specific heat capacity with respect to water, and ϕ_C, the apparent specific heat capacity. The values of $\bar{c}_w$ decreased with increasing water content for all five homoionic montmorillonites. At water contents below 0.1 kg of H_2O/kg of clay, $\bar{c}_w$ approached a value about 10% larger than the specific heat capacity of bulk liquid water. For Li– and Na–montmorillonite, $\bar{c}_w$ did not approach c_w^0 until θ was about 2 kg of H_2O/kg of clay; for the other three montmorillonites, $\bar{c}_w \approx c_w^0$ at $\theta \approx 0.4$ kg of H_2O/kg of clay. The trend of ϕ_C with water content was similar to that of $\bar{c}_w$,[27] except that $\phi_C > \bar{c}_w$ at any value of θ.

The partial specific heat capacity, $\bar{c}_w$, is the change in the heat capacity of a smectite–water mixture produced by an infinitesimal increase in the water content. Since $(\bar{c}_w - c_w^0)$ is not negative, the addition of water to a smectite–water system must create more excited modes of motion, or cause a greater temperature dependence of the frequencies of the excited modes, or change the configurations of the molecules more than in bulk liquid water.[117] Whether any of these effects occurs in the water component cannot be deduced from the thermodynamic data alone. The molecules significance of the water content dependence of ϕ_C is even less evident, since

$$\phi_C = \bar{c}_w + (1/\theta)(\bar{c}_s - c_s^0) \qquad (19)$$

according to eq 11 and 14. The interpretation of the second term on the right side of this equation is not straightforward without additional experimental data.

Eger et al.[116] have determined the temperature dependence of the heat capacity at constant pressure for Ca–montmorillonite and Li–hectorite. The data were employed to calculate the quantity $M_w\phi_C$ (i.e., ϕ_C expressed per mole of water) between 100 and 250 K, where M_w is the relative molecular mass of water. Eger et al.[116] assumed that $M_w\phi_C$ was the molar heat capacity of the water component in their smectite–water mixtures. Between 100 and 150 K, the value of $M_w\phi_C$ for Li–hectorite containing one layer of water molecules in the interlamellar space was the same as the molar heat capacity of ice. Thereafter it increased, until it attained about two-thirds the value for liquid water (at 273 K) when the temperature reached 250 K. This latter behavior was interpreted to mean that the two kinds of rotational motions for adsorbed water molecules suggested on the basis of NMR studies of Li–hectorite by Conard[59,60] were reduced to torsional motions around 150 K. This structural interpretation, of course, depends entirely on how good an assumption it is to attribute the temperature variation of ϕ_C only to adsorbed water in smectite–water mixtures.

E. Correlations among Thermodynamic Properties

A number of thermodynamic properties of montmorillonite–water mixtures has been determined during the past 25 years in the laboratory of P. F. Low, who has recently attempted to interpret these data systematically in terms of a unified picture of the structure of adsorbed water.[27,110] Since all of the measured quantities were either partial specific values or apparent specific values of some extensive property of a montmorillonite–water system, Low[27] has made two fundamental assumptions pertaining to the possible structural interpretation of his data. First, he has assumed that any dependence of $\bar{x}_w$, ϕ_X, $(\partial\phi_X/\partial T)_{P,\theta}$, or $(\partial\phi_X/\partial P)_{T,\theta}$ on the gravimetric water content reflects only changes in the structure of adsorbed water. This assumption is based on the fact that most of the data were obtained for θ values in excess of 1.0 kg of H_2O/kg of clay, where no changes in the unit cell dimensions of the montmorillonite crystal as a function of water content have been noted. Moreover, it seems reasonable to believe that changes in θ should affect the water component more than the clay component of the mixture, since the latter has a crystalline structure and the former does not. The second assumption made by Low[27] is that the temperature and pressure derivatives of ϕ_X receive their principal contributions from changes in the configurations of adsorbed water molecules. Changes in the modes of motion of the water molecules (e.g., shifts in vibrational frequencies or changes in the number of excited modes) thus are assumed to be minor or negligible contributors to the values of $(\partial\phi_X/\partial T)_{P,\theta}$ and $(\partial\phi_X/\partial P)_{T,\theta}$.

The absence of changes in the unit cell dimensions of montmorillonite certainly is a necessary condition for the validity of the first assumption made by Low.[27] However, this condition is not sufficient, because perturbations of the clay structure other than changes in unit cell size could occur and contribute importantly to the values of partial specific or apparent specific properties. For example, at high water content, hydrolysis of the clay structure or changes in the state of the exchangeable cations could take place. Even if only a fraction of the exchangeable cations dissociate from the clay, and even if this fraction does not depend on water content, the concentration of the dissociated cations in the interlamellar space must decrease as the water content increases and this change must produce some effect on $\bar{x}_w$ and ϕ_X. It is not evident, without supporting experimental data, that the clay component of a montmorillonite–water mixture remains inert and can be neglected in the interpretation of thermodynamic data.

TABLE VI. Dependence of Some Thermodynamic Properties of Na-montmorillonite–Water Mixtures on the Water Content at 298 K[27,110]

thermodynamic property	observed value as a function of gravimetric water content
$\overline{v}_w$	larger than $v_w°$; decreases to $v_w°$ as θ increases
$(\partial\phi_V/\partial T)_{P,\theta}$	larger than $(\partial v_w°/\partial T)_P$; decreases as θ increases
$-(\partial\phi_V/\partial P)_{T,\theta}$	smaller than $-(\partial v_w°/\partial P)_T$; increases as θ increases
$\overline{c}_w$	larger than $c_w°$; decreases to $c_w°$ as θ increases
ϕ_C	larger than $\overline{c}_w$; decreases to $c_w°$ as θ increases
$(\partial\phi_C/\partial P)_{T,\theta}$	larger than $(\partial c_w°/\partial P)_T$; decreases as θ increases
$(\partial\phi_S/\partial P)_{T,\theta}$	smaller than $(\partial s_w°/\partial P)_T$; increases as θ increases equal to $-(\partial\phi_V/\partial T)_{P,\theta}$ within experimental error
$(\partial\phi_S/\partial\phi_V)_{T,\theta}$	larger than $(\partial s_w°/\partial v_w°)_T$; decreases as θ increases
$(\partial\phi_S/\partial\phi_V)_{P,\theta}$	increases as θ increases

With respect to the temperature and pressure derivatives of ϕ_X, it is known that, in the limit of very high θ values, these quantities must equal the corresponding derivatives of (X/m_w) for bulk liquid water, since, according to eq 14,

$$\phi_X = (X/m_w) - (x_w^0/\theta) \tag{20}$$

Consider, for example, ϕ_S, the apparent specific entropy, whose temperature derivative must become proportional (at a given temperature) to the specific heat capacity at constant pressure of liquid water as θ becomes very large. In this limit, the relative contributions of configurational changes and changes in the modes of motion of the water molecules to the value of $(\partial\phi_S/\partial T)_{P,\theta}$ are well-established.[14,117,118] In fact, it is known that the specific heat capacity of liquid water receives approximately equal contributions from these two components and, therefore, that the component attributable to changes in the modes of molecular motions is by no means negligible. In the case of ice I_h, changes in the modes of molecular motions contribute essentially all of the value of the specific heat capacity.[14] Therefore, to the extent that adsorbed water has a structure resembling either that of liquid water or that of ice I_h, it would seem erroneous to attribute the value of $(\partial\phi_s/\partial T)_{P,\theta}$ solely to configurational changes. This conclusion can be extended to the temperature and pressure derivatives of other ϕ_X. On the other hand, what is of interest in that given by Low[27] is the *change* in the temperature and pressure derivatives of ϕ_X as the water content changes. Perhaps it is valid to argue that configurational changes are the major contributor to the dependence of $(\partial\phi_X/\partial T)_{P,\theta}$ and $(\partial\phi_X/\partial P)_{T,\theta}$ on θ, even if these changes are not the only contributor to the actual values of the two derivatives at a given water content.

Table VI summarizes the trends in several partial specific and apparent specific thermodynamic properties of Na–montmorillonite–water mixtures reported by Low[27] and Oliphant.[110] Differences between the listed properties and the corresponding quantities in bulk liquid water were observed at gravimetric water contents as high as 28 kg of H_2O/kg of clay, although most of the variation with θ was complete by about 10 kg of H_2O/kg of clay. The general conclusion drawn by Low[27] on the basis of his analysis of the trends indicated in

Table VI was that the hydrogen-bonded structure of water adsorbed by Na–montmorillonite is more extensible and compressible, but also less deformable (less bond breaking or bending), than is the hydrogen-bonded structure of bulk liquid water. The greater extensibility is reflected in the behavior of $\bar{v}_w$, $(\partial \phi_V / \partial T)_P$, $\bar{c}_w$, and ϕ_C, whereas the other properties listed in Table VI reflect the greater stability of the adsorbed water structure. These characteristics persist to relatively high water contents, as mentioned above.

Besides these qualitative conclusions, Low[27] has attempted to show that all of the thermodynamic properties in Table VI follow the mathematical relationship:

$$J(\theta) = J^\circ \exp(\beta/\theta) \qquad (21)$$

where J° is the property of bulk liquid water corresponding to $J(\theta)$ and β is an empirical constant. It is not clear that eq 21 should be regarded as more than an approximate way to characterize data on $J(\theta)$ in a numerical fashion. Equation 21 cannot be valid at very low water contents, since it predicts infinite values of $J(\theta)$ as θ approaches zero. Moreover, even though Low[27] has found both $\bar{c}_w$ and ϕ_C follow eq 21 closely, it is physically *impossible*, according to eq 16, that both of these quantities can have the same mathematical dependence on θ unless they are constants, a point also noted by Oliphant.[110] Evidently, as the values of $J(\theta)$ become determined more precisely and the range of θ over which they are measured becomes larger, one would expect that the relation in eq 21 would be found to be only an approximation of the complete expression for $J(\theta)$.

VIII. Discussion and Conclusions

A. The V Structure

The motions of adsorbed water molecules observed in IR, neutron scattering, and ESR experiments take place on a time scale during which the exchangeable cations are translationally stationary (i.e., $<<10^{-8}$ s). These cations then can serve as essentially fixed hydrophilic sites on the smectite surface at low water contents, and it is expected that they can play an important role in organizing the V structure of adsorbed water. At water content corresponding to less than three monlayers in the interlamellar space, the experimental methods that probe the V structure indicate that the spatial arrangement of the water molecules indeed derives mainly from the solvation of exchangeable cations (Figures 3, 4, 5, and 8). Studies on aqueous solutions using magnetic resonance spectroscopy[44,119] show that the mean residence time of a water molecule in the first solvation layer around a monovalent cations is about 10^{-11} s, whereas around a bivalent cation the residence time is about 10^{-8} s. If these results apply to adsorbed water, molecules in direct contact with a monovalent exchangeable cation should be able to diffuse, e.g., on the neutron scattering time scale, but those contacting a bivalent exchangeable cation should not. This hypothesis is confirmed by the data in Tables I and II and by the ESR studies summarized in Figure 8.

Additional information about the V structure can be inferred from NMR and dielectric relaxation spectroscopy experiments. In an aqueous solution, NMR data indicate that the water molecules in the first cation solvation layer rotate around their C_2 axes with a correlation time $\tau_2 \approx 10^{-11}$ s and that the entire solvation complex rotates with a correlation time τ_c between 10^{-11} and 10^{-10} s.[44] These motions also are found for adsorbed water molecules on smectites with magnetic resonance spectroscopy, but it appears that τ_2 and τ_c may be at least an order of magnitude larger. This difference may reflect a smaller number of collisional perturbations of the solvation complex by surrounding water molecules in a smectite at low water contents. Since the residence time of an adsorbed water molecule *not* in the solvation complex is about 10^{-11} s under these conditions (Tables I and II), whereas that in bulk water is about 10^{-12} s,[18] fewer translational jumps and, therefore, fewer intermolecular collisions in adsorbed water may occur.

The dielectric relaxation data in Tables III and IV also confirm the important role of the exchangeable cation in determining the structure of adsorbed water on smectites. The values of τ_D for water on montmorillonites bearing strongly solvating exchangeable cations are characteristics of rigidly bound molecules that cannot reorient easily. Evidently the strong electric fields of these cations produce this result. As the water content increases (Table IV), the reorientational time decreases rapidly, suggesting a decreased influence of the cationic field. In aqueous solutions containing monovalent cations, τ_D for the first solvation layer is not a great deal larger than τ_D for bulk liquid water, and there is a rapid (on the picosecond time scale) exchange of the solvation layer molecules with those in the bulk liquid.[120] These characteristics are consistent with the data for Na– and K–montmorillonite in Table III. At the low water content of the Li–montmorillonite in Table III, aqueous solution behavior is not yet manifest and the solvation complex behaves as a rigid unit—an effect seen also in some neutron scattering experiments.[43]

Despite the great significance of the exchangeable cations for the structure of adsorbed water on smectite, the role of the silicate surface cannot be neglected. Both IR and NMR spectroscopic data indicate clearly that the adsorbed water molecules maintain a preferred orientation relative to the opposing planes of oxygen atoms bounding the interlamellar space. The nature of the interaction between the silicate surface and water molecules in the V structure depends on the degree of localization of charge deficits created by isomorphous substitutions in the smectite. If the deficit originates in the octahedral sheet, the excess negative charge tends to be delocalized around the oxygen atoms forming the ditrigonal cavities in the silicate surface and water molecules can form proton bonds with this charge distribution, as illustrated in Figures 4 and 9. If the deficit occurs in the tetrahedral sheet, the excess negative charge tends to be localized on single oxygen atoms, and conventional hydrogen bonding between a water molecule and the surface is possible (Figure 5). Thus the V structure of adsorbed water can be regarded principally as a result of superposed electric fields originating from the silicate surface and the exchangeable cations, when the water content is relatively low.

B. The D Structure

A detailed comparison between the D structure of adsorbed water on smectites and that of bulk liquid water is not possible at the present time because the latter is not known with certainty. Stillinger[17] has characterized liquid water as "a macroscopically connected, random network of hydrogen bonds, with frequent strained and broken bonds, that is continually undergoing topological reformation". He adds that liquid water is unique in exhibiting "a competition between relatively bulky ways of connecting molecules into local patterns, characterized by strong bonds and nearly tetrahedral angles, and more compact arrangements characterized by more strain and bond breaks". There is very clearly implied in these statements the idea that the structure of liquid water is a dynamic concept. Moreover, the properties of this structure result from perturbations of the local tetrahedral arrangement that is realized permanently in ice I_h.

The results of both neutron and X-ray diffraction experiments on smectite–water systems[85,89] indicate that the D structure of adsorbed water in these systems is not exactly the same as that in the bulk liquid, even at water contents up to 4 kg of H_2O/kg of clay. The interpretation of these data, however, has been that the structural differences are created by an epitaxy of the molecules in the first and second adsorbed monolayers, with a transition to an essentially liquid water state (as defined above) thereafter. This point of view, which has been emphasized recently by Tarasevich,[9] is in agreement with the limited near-IR and NMR spectroscopic data available,[30,57b] as well as with dielectric relaxation results (Table IV). Since the range of time scale covered by all of these experiments includes both the V and the D structures of adsorbed water, it could be concluded that a meaningful difference exists between the vibrational, rotational, and translational motions of adsorbed water molecules and those in the bulk liquid. However, a principal cause of this difference is the exchangeable cation and, therefore, the difference is limited to a region close to the smectite surface. Put another way, the properties of water on smectite surfaces compare more with those of an aqueous solution, not pure liquid water. With respect to an aqueous solution, the only important structural difference in adsorbed water occurs in the first nanometer next to the smectite surface, especially when the film of adsorbed water is not yet continuous. At high water content, the interlamellar space contains essentially an aqueous solution, and classical double-layer effects, such as the order–disorder transition observed by Cebula and Ottewill,[92] then are possible. As the D structure of water in aqueous solutions becomes better understood, the ways in which the smectite surface can influence the water solvating exchangeable cations should also become better understood by comparison. On the basis of recent neutron diffraction data,[119,121] it appears that water molecules do not orient themselves around cations in aqueous solutions in exactly the manner that a simple picture of point charge–lone-pair interactions would predict. Thus, deviations from this picture in adsorbed water on smectites may not reflect the influence of the silicate surface alone.

C. Thermodynamic Properties: Cooperative Effects

The conclusions just summarized are not in good accord with the data in Figure 10 and with the trends summarized in Table VI, if the partial specific properties of smectite–water systems are attributed entirely to the liquid phase. One alternative to remove the diagreement is to assume that the partial specific quantities reflect changes in the smectite (particularly the exchangeable cations), as well as in the water, and that the former kinds of change become dominant as the water content increases. This point of view cannot be rejected in the present absence of conclusive experimental evidence against it. On the other hand, if the partial specific properties do only represent the adsorbed water, as assumed by Low,[27] what can be said to bring the results of thermodynamic measurements into agreement with the other data reviewed in this paper?

With respect to the spectroscopic data, the difference in time scales can be indicated. Thermodynamic data refer to effectively "infinite" scales of time and space, characteristic of the D structure, whereas spectroscopic measurements probe either the V structure or some predessor of the D structure. The degree of ordering of these latter structures may be less because the time scale on which they exist is shorter, and the thermodynamic properties may truly reflect the multiplicity of *cooperative* interactions that can be perceived only after a long-time measurement. This still leaves a question concerning the neutron and X-ray diffraction data, which refer to the same time scale as the thermodynamic properties, but appear to be in conflict with them. In the case of bulk liquid water, it is known that the D structure as deduced from diffraction patterns measured at 273 K differs only a little from that in ice I_h, whereas the thermodynamic properties of liquid water at 273 K differ greatly from those of ice I_h.[15] If this comparison applies to adsorbed water as well, then perhaps the partial specific properties are more sensitive to structural changes than are the diffraction patterns. The small differences from zero at high water content indicated in Figure 10 are consistent with this idea. At any rate, the conclusion drawn by Low,[27] that hydrogen bonds in adsorbed water on Na–montmorillonite are more extensible than in bulk liquid water, even at very high water contents, is not unreasonable. As Stillinger[17] has remarked, the mere presence of a space-filling macromolecule in liquid water will cause the structure to be strained, while strengthening some of the hydrogen bonds. In effect, some of the topological freedom in the liquid disappears and the fluctuations between bulky and compact networks of water molecules shift to favor the bulky configurations. This picture could be an accurate description, on the level of molecular structure, of how the trends listed in Table VI come about.

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