

DIFFUSION OF WATER IN Li-MONTMORILLONITE STUDIED BY QUASIELASTIC NEUTRON SCATTERING

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Abstract—The diffusion of water in Li-montmorillonite was studied by incoherent quasielastic neutron scattering. Experiments were carried out on sedimented samples equilibrated at relative humidities of 32%, 58%, and 98%, corresponding approximately to 1, 2, and 3 molecular layers of water in the clay. At all three humidities, although the mobility of the water molecules is less than in bulk water, all water molecules in the system undergo translational diffusion, at least over short distances ($>5 \text{ \AA}$), with correlation times shorter than 5×10^{-11} sec.

Various models of molecular motion have been used to account for the exact shape of the scattering. The only completely successful model is one where a water molecule undergoes jump-translational diffusion and rotational diffusion. The mean square jump length is $10\text{--}15 \text{ \AA}^2$ with a residence time between jumps of $4\text{--}2 \times 10^{-11}$ sec. The translational diffusion coefficient increases with humidity, having values of 4, 7, and $10 \times 10^{-10} \text{ m}^2/\text{sec}$ for the three humidities. These values can be combined with values previously obtained by tracer measurements to give an estimate of 0.75–0.8 for the tortuosity factor. Although the samples are anisotropic, there is no clear evidence that the diffusion of water over distances 5–20 \AA is anisotropic. An upper limit of 3 can be deduced for the rate of diffusion parallel to the direction perpendicular to the platelets.

Key Words—Diffusion, Montmorillonite, Neutron scattering, Water.

INTRODUCTION

In previous papers Cebula *et al.* (1979a, 1980) described the application of neutron scattering to the determination of the structure of montmorillonite-water systems varying from relatively dry samples with 30% water by weight to sols containing 99% water. In this paper the dynamical properties of water in these systems are examined by incoherent quasielastic neutron scattering.

In incoherent quasielastic neutron scattering the small changes in energy resulting from scattering of neutrons by nuclei in motion are measured. Because protons have a much higher incoherent scattering cross section than any other nucleus, the spectrum is dominated by the motion of protons in the system and therefore, for montmorillonite-water samples, by the motion of water molecules. Olejnik *et al.* (1970) and Olejnik and White (1972) showed how the technique may be used to measure the diffusion coefficient of water in swollen clay-water samples. Since then great improvements have been made in energy resolution, and it is now possible to measure smaller energy transfers and hence to study the slower motions of water in clays con-

taining only a few molecular layers of water. At these low concentrations the nature of the cation becomes important. This investigation considers Li-montmorillonite for which preliminary results have already been published (Cebula *et al.*, 1979b). Similar experiments on Ca-montmorillonite were made by Hall *et al.* (1978, 1979) and on Na-montmorillonite containing pyridine and water by Adams *et al.* (1979).

EXPERIMENTAL METHODS

The clay material used was bentonite from Clay Spur, Wyoming (A.P.I. No. 26). Samples of the lithium homoionic form prepared by Cebula *et al.* (1979a) were used. Pellets 5 cm in diameter and 0.5–1 mm thick were prepared to transmit more than 90% of the neutron beam, obviating the need to correct for secondary scattering events. The relatively strong absorption of Li also reduces multiple scattering in these systems. The samples were maintained at constant humidity and temperature throughout the experiment in an aluminum container as described by Cebula *et al.* (1979a). The relative humidities (RH) used were 32%, 58%, and 98%, corresponding approximately to 1, 2, and 3 molecular layers of water as discussed by Cebula *et al.* (1979a). Although the incoherent scattering of the water in the clay was dominant, some background scattering from the clay resulted partly from its irregular structure and

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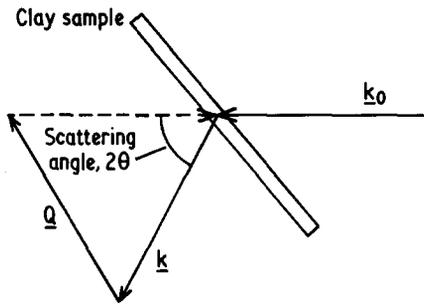


Figure 1. Vector diagram showing the orientation of incident (k_0) and final (k) neutron wavevectors on the flat clay sample. At a scattering angle of 90° , the momentum transfer, Q , is exactly parallel to the plane of the sample.

partly from protons in the clay itself. This background contribution was measured by using a sample equilibrated at 15% RH of D_2O , deuterium having a relatively small incoherent cross section.

Spectra were recorded on the IN5 multichopper time of flight spectrometer at the Institut Laue-Langevin (Institut Laue-Langevin, 1977) with an incident wavelength of 8.5 \AA and an energy resolution of $41 \mu\text{eV}$ (full width at half maximum). To avoid coherent scattering effects, the spectra were recorded at scattering angles, 2θ , between 40° and 130° , corresponding to values of the momentum transfer $Q (= 4\pi \sin \theta/\lambda)$, between 0.5 and 1.3 \AA^{-1} . There are no Bragg peaks in this range to interfere with the analysis (Hawkins and Egelstaff, 1980). The flat samples were oriented at an angle of 45° to the incident beam so that, for scattering at 90° to the beam, Q was parallel to the surface of the sample (Figure 1). The spectrometer was calibrated with a vanadium sample cut to the same shape and size as the clay samples. Instrumental corrections were applied to the spectra, the background from the D_2O sample subtracted, and the intensities were normalized to vanadium using standard computer programs available for users at the Institut Laue-Langevin.

RESULTS AND ANALYSIS

Fully corrected quasielastic spectra from the montmorillonite sample equilibrated at the three RHs are shown in Figure 2. The background scattering that has been subtracted to obtain these spectra is shown in Figure 3(b). It is equivalent to about half the total scattering from a sample containing one molecular layer of water, that is, about 33% of the total scattering from a two water-layer sample and about 12% of that from a three-layer sample. Errors in the subtraction will be largest close to the center of the peaks because it is here that the background spectrum is strongest. However, the area of the peaks in Figure 2 is proportional to the known amounts of water in the three samples showing that the subtraction procedure is satisfactory.

The measured spectrum, $M(Q, \omega)$, is a convolution

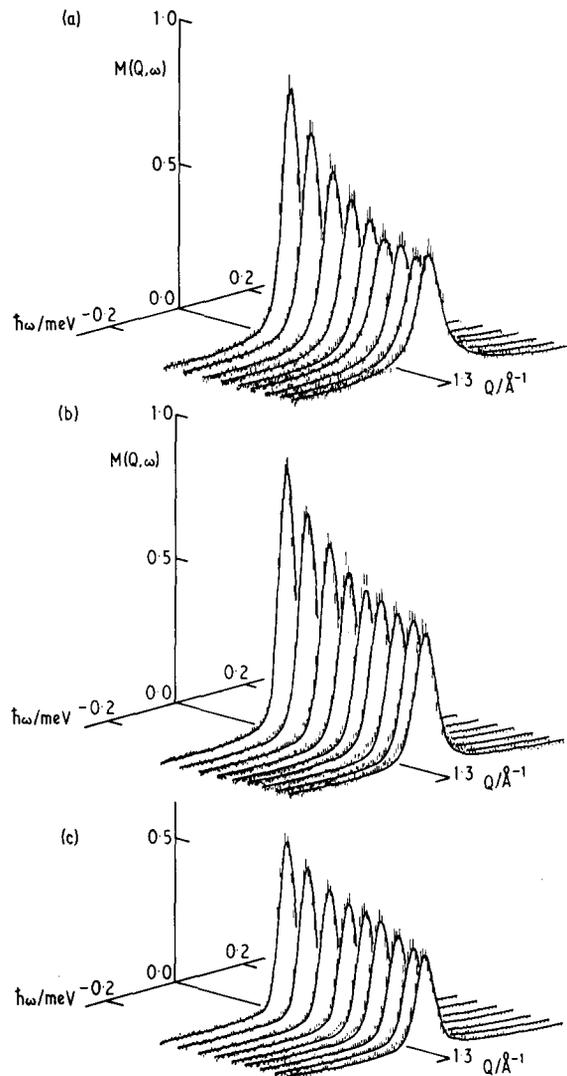


Figure 2. Quasielastic spectra of water in Li-montmorillonite at three different relative humidities. (a) 98% RH, 3 layers of molecular water, (b) 58% RH, 2 layers of water, and (c) 32% RH, 1 layer of water. Intensities have been normalized to the spectrum of a vanadium standard. Error bars are shown for the data, and the full lines show the fits obtained using a model of isotropic translational and rotational diffusion (see text).

of the scattering law, $S(Q, \omega)$, with the resolution profile of the machine, $R(\omega)$. In a time of flight experiment the true convolution is a function of 2θ and t , but it is more convenient to work with Q and ω because most models of the scattering are formulated in terms of Q and ω . Over the range of ω used for the experiments, the use of Q and ω introduces a negligible error. The observed spectrum is then

$$M(Q, \omega) = \int S(Q, \omega - \omega')R(\omega') d\omega',$$

and the main problem of the analysis is the extraction of $S(Q, \omega)$ from the data. A qualitative comparison of

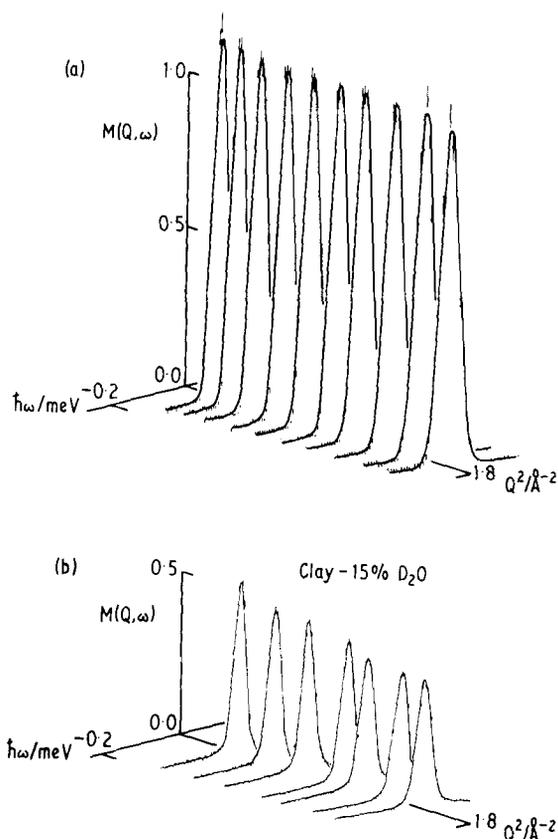


Figure 3. (a) The resolution function (vanadium spectrum) of the spectrometer and (b) the background spectrum from a Li-montmorillonite-D₂O sample at 15%.

the resolution function with the three sets of spectra shown in Figure 2 shows that there is pronounced quasielastic broadening in all three. The broadening increases both with $|Q|$ and with the amount of water in the clay showing that the water molecules are undergoing some kind of rapid diffusion.

Several methods exist that, in principle, could be used to extract $S(Q, \omega)$ from the observed spectrum. The most convenient method of analysis, however, is to calculate $S(Q, \omega)$ from a model, convolute it with the known resolution function, and compare the resulting $M(Q, \omega)$ with the observed spectrum. It is particularly simple here because the resolution function is well represented by a triangle; all the appropriate models of $S(Q, \omega)$ are either Lorentzian in ω or a sum of Lorentzians, and the convolution of a triangle with a Lorentzian can be represented analytically (Volino *et al.*, 1975). In this way possible models of the motion of water in the system can be fitted to the observed data using non-linear least squares to optimize the fit. By matching the area of the computed to the observed spectrum, only the shape of the quasielastic scattering was analyzed. This was done separately at each value of Q , leading to a coefficient characterizing the partic-

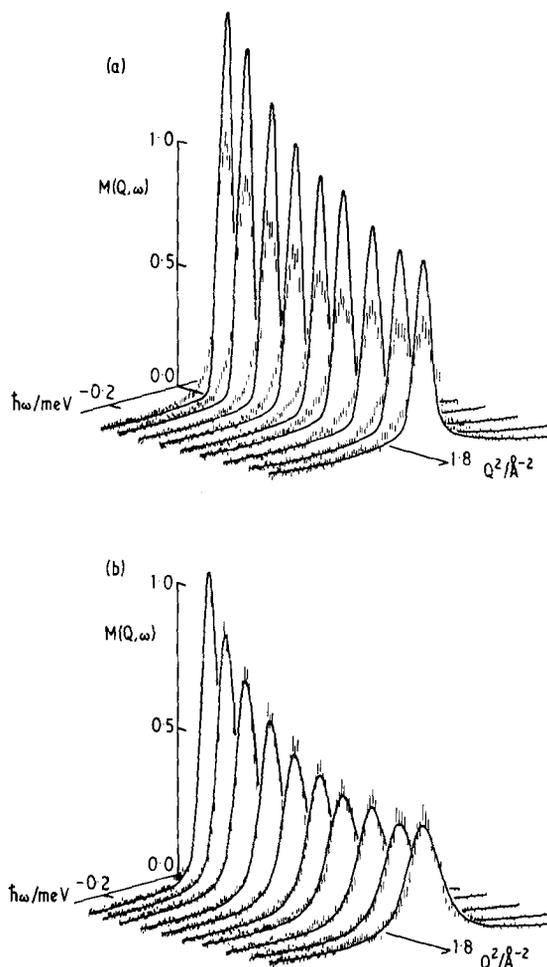


Figure 4. (a) The fit of a model of isotropic rotational diffusion to the data at 98% RH. $\tau_r = 5 \times 10^{-11}/\text{sec}$. (b) The fit of a model of translational diffusion in two dimensions to the same data. $D_t = 7.9 \times 10^{-10} \text{ m}^2/\text{sec}$. In both cases the area of the computed spectrum has been scaled to the area of the observed spectrum at each value of Q .

ular type of diffusive motion $D_{\text{eff}}(Q)$. The variation of $D_{\text{eff}}(Q)$ with Q was then analyzed graphically.

The different expressions for $S(Q, \omega)$ resulting from various types of diffusion were summarized by Thomas (1979). For the range of Q used here and for a molecule as small as water, isotropic translational diffusion should give a single Lorentzian whose width increases with Q^2 (at least at the lower values of Q), and isotropic rotational diffusion should give an elastic peak together with a Lorentzian quasielastic component whose width does not depend on Q but whose intensity does. Thus, for isotropic diffusion

$$S(Q, \omega) = \frac{1}{\pi} \cdot \frac{D_t Q^2}{\omega^2 + (D_t Q^2)^2},$$

and for isotropic rotational diffusion

$$S(Q, \omega) \sim j_0^2(Qr)\delta(\omega) + j_1^2(Qr)\frac{2D_r}{\omega^2 + (2D_r)^2},$$

where D_t and D_r are translational and rotational diffusion coefficients, r is the radius of gyration, and j_0 and j_1 are spherical Bessel functions. $S(Q, \omega)$ for rotational diffusion generally contains higher terms but, for a molecule as small as water and the range of Q used in these experiments, the higher terms may be neglected.

Because the basic structure of the clay is lamellar, any translational diffusion of water molecules in such thin layers of water is expected to be anisotropic with an insignificant rate of translational diffusion perpendicular to the clay platelets. The quasielastic broadening is then determined by the component of Q parallel to the platelets

$$S(Q, \omega, \alpha) = \frac{1}{\pi} \frac{D_t Q^2 \sin^2 \alpha}{\omega^2 + (D_t Q^2 \sin^2 \alpha)^2},$$

where α is the angle between Q and the normal to the platelets. Unfortunately, the platelets within the sample are not well oriented, and $M(Q, \omega)$ must then be computed by averaging $M(Q, \omega, \alpha)$ over all values of α , taking into account the distribution function, $g(\alpha)$, that characterizes the mosaic spread of the platelets. This was done. The function $g(\alpha)$ was determined by neutron diffraction and, for these samples, is approximately a Gaussian of full width at half maximum of 40° plus a small component independent of angle (Cebula *et al.*, 1979a).

The models of isotropic rotational or isotropic translational diffusion taken separately do not explain the shapes of the observed spectra. The fit of the rotational model is shown in Figure 4(a). It cannot be improved by including any anisotropy in the motion because this would sharpen the calculated peaks even more. On the other hand, the model of two-dimensional translational diffusion in a partially oriented sample is a reasonable, though not perfect, fit to the observed scattering, as can be seen in Figure 4(b). Thus, the dominant contribution to the quasielastic broadening is translational diffusion of water molecules between the clay platelets. The diffusion coefficients vary from about an eighth of that for bulk water in the one-layer sample to about a quarter in the three-layer sample.

Although a model of rotational diffusion alone cannot account for the observed spectra, models allowing simultaneous rotational and translational diffusion fit the data extremely well. The quasielastic broadenings are explained by either isotropic or anisotropic translational diffusion with a value of the rotational diffusion coefficient in the range $2\text{--}5 \times 10^{-10}/\text{sec}$ (similar to D_r for bulk water (Packer, 1977)). In these experiments therefore, neutron scattering does not distinguish any anisotropy in the translational motion. There are three possible reasons for this. First, the observation length of neutrons is approximately $2\pi/Q$, which for the present

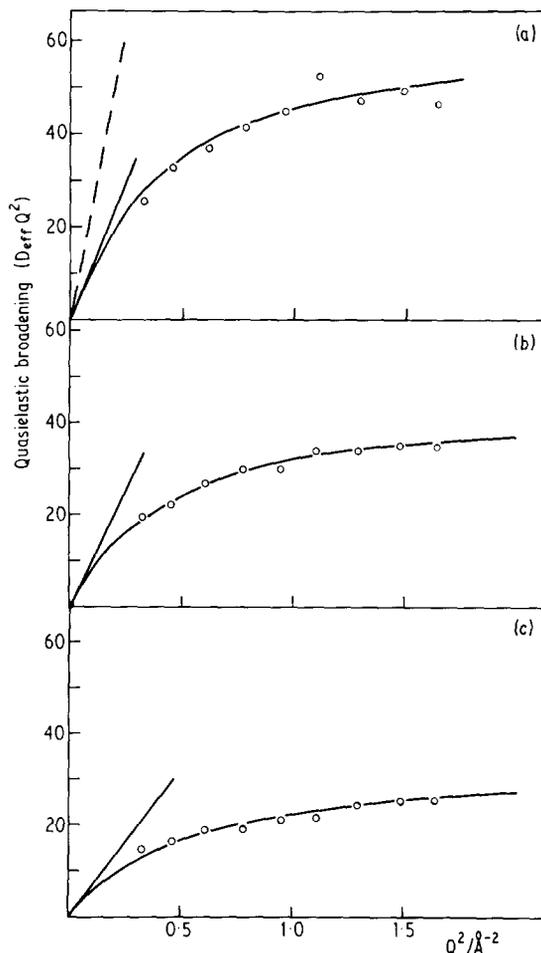


Figure 5. Plots of $D_{\text{eff}}Q^2$ against Q^2 for the three clays equilibrated at relative humidities. The values of D_{eff} were obtained from the best fits of a model of isotropic translational and rotational diffusion to the data in Figure 1. Relative humidities are (a) 98%, (b) 58%, and (c) 32%. Also shown in (a) is the equivalent plot for bulk water at room temperature with $D_t = 2 \times 10^{-9} \text{ m}^2/\text{sec}$.

experiments is 6–12 Å. This is similar to the thickness of the water layer, and thus the neutrons will only “see” motion within the layer which may not be very sensitive to the boundary presented by the platelets (Ross and Hall, 1978). Second, the clay has many defects (Cebula *et al.*, 1979a). In some of these, especially those that might be described as micropores, the diffusion should be approximately isotropic. Third, the large mosaic spread of clay particles averages the scattering laws for different orientations. When allowance is also made for the instrumental resolution, it can be assumed that neutron quasielastic scattering will only be sensitive to the anisotropy if the diffusive motion perpendicular to the platelets is, at most, one third as fast as that parallel to the platelets (Gamlen *et al.*, 1979). Although the experiment cannot distinguish an-

Table 1. Parameters characterizing the diffusion of water in Li-montmorillonite.

Relative humidity (%)	Translational diffusion coeff. (m ² /sec) ($\pm 1 \times 10^{-10}$)	Rotational correlation time (sec) ($\pm 5 \times 10^{-12}$)	Mean square jump length (Å ²) (± 4)	Mean square amplitude of oscillation (Å ²) (± 0.05)	Residence time (sec) ($\pm 0.5 \times 10^{-11}$)
32	4×10^{-10}	1.5×10^{-12}	10	0.17	4.3×10^{-11}
58	7×10^{-10}	1.5×10^{-12}	15	0.16	3.3×10^{-11}
98	10×10^{-10}	1.5×10^{-12}	14	0.22	2.3×10^{-11}

The model used to fit the quasielastic scattering data is described in the text.

isotropic and isotropic diffusion, there is no ambiguity in the determination of its rate. For given mean-square-jump lengths and frequencies of jumps, $D_{2D} = 3/2D_{3D}$. The best fits of the two models to the data give diffusion coefficients in this ratio to one another. The solid lines shown in Figure 2 are the final fits of the model of isotropic translational and rotational diffusion to the data.

The result of the analysis is to give a value of the translational diffusion coefficient at each value of θ , $D_{\text{eff}}(Q)$. The formulae used so far to analyze the translational diffusion predict that $D_{\text{eff}}(Q)$ is independent of Q . That this is not so can be seen in Figure 5 where $D_{\text{eff}}(Q)Q^2$ is plotted against Q^2 for the three clay samples. If the diffusion were to obey Fick's law, the graphs would be straight lines of slope D_t , the translational diffusion coefficient. However, it is only appropriate to apply Fick's law when the observation length, $2\pi/Q$, is much larger than the mean-square-jump length associated with the diffusion. Thus, D_t is given only by the limiting slope as Q tends to zero. These limiting slopes together with the graph expected for bulk water are shown in Figure 5.

At higher values of Q the observation length becomes comparable with intermolecular distances in the sample and the quasielastic scattering is then sensitive to the finer details of the molecular motion. A model that is physically reasonable is that a water molecule oscillates with a mean square amplitude $\langle u^2 \rangle$ about an equilibrium position for an average time τ_0 and then jumps a mean square distance $\langle \ell^2 \rangle$ in a time τ_1 to another equilibrium position. If the time taken to jump between equilibrium positions is much shorter than the residence time ($\tau_1 \ll \tau_0$), the scattering law according to Singwi and Sjölander (1960) is

$$S(Q, \omega) = \frac{1}{\pi} \cdot \frac{\Gamma}{\omega^2 + \Gamma^2} \exp(-Q^2 \langle u^2 \rangle),$$

where $\Gamma \rightarrow D_t Q^2$ as $Q \rightarrow 0$, and $\Gamma \rightarrow 1/\tau_0$ when $Q^2 \gg 1/\langle \ell^2 \rangle$.

Provided that $\langle \ell^2 \rangle$ is also much greater than $\langle u^2 \rangle$, which is also physically reasonable, $D_t \approx \langle \ell^2 \rangle / 6\tau_0$. This

scattering law is the same at low values of Q as that derived from Fick's law, but predicts that at high Q the quasielastic broadening tends to a constant value depending only on the residence time of a water molecule in an equilibrium position. This is exactly the behavior of the graphs in Figure 5, and the dashed lines represent the best fit of the jump model of the observed quasielastic broadening. The analysis gives $\langle \ell^2 \rangle$ and τ_0 . The mean square amplitude of oscillation about an equilibrium position, $\langle u^2 \rangle$, is obtained by plotting the log of the total intensity of the quasielastic peak against Q^2 . The final values are given in Table 1. It can be seen that the condition $\langle \ell^2 \rangle \gg \langle u^2 \rangle$ is fulfilled.

DISCUSSION

Neutron quasielastic scattering measures the manner and rate of diffusion of protons in the water layer. The result from the experiments described here is that the protons are all undergoing translational diffusion. In principle, this could take place by proton transfer without any translational motion of the water molecules themselves (Hougardy *et al.*, 1976). However, the concentration of hydrogen ions in the Li-montmorillonite system is far too low for proton transfer to contribute significantly to the scattering law. The unambiguous conclusion is that the observed quasielastic broadening results from moderately fast translational diffusion of all the water molecules in the system. The finer details of the process are less definite, for example, whether the diffusion is anisotropic or not. Before examining the finer details, the overall result is compared with those from other techniques.

Two difficulties arise in making such comparisons. First, experiments have been made on a variety of clays with different silicate layer structures, different cations, and different cation-exchange capacities. Measurements have been made at different points on the adsorption isotherm and on samples prepared in quite different ways. The latter might influence the measured diffusion coefficient by, for example, changing the ratio of micropores to channels (Cebula *et al.*, 1979a). The second difficulty is that the three main techniques cover quite different ranges of observation, both in time and in space. Neutrons measure diffusion at the molecular level, over distances smaller than the heterogeneities in the system; nuclear magnetic resonance (NMR) measures processes at the molecular level, but over times sufficiently long that the molecule may experience a wide range of different environments; and tracer and related techniques measure diffusion on the macroscopic scale. Nevertheless, it is worth making comparisons in the search for general features of water diffusion in clays.

Kemper *et al.* (1964) measured the rate of diffusion of water through bulk samples of Na- and Ca-bentonites containing different amounts of water. They interpreted their results in terms of a tortuosity factor, β , and

a factor, α , relating the intrinsic rate of diffusion of water in the clay to its value in bulk water. They estimated that β , which relates the actual pathlength of diffusion to the pathlength in real space, lies between 0.8 and 0.9. Taking β to be 0.8 gives diffusion coefficients of 6×10^{-10} and 8×10^{-10} m²/sec for water in the 2- and 3-layer Na-bentonites, respectively. These values are slightly smaller than the present values of 7×10^{-10} and 10×10^{-10} m²/sec. The differences may well be caused by the difference in cation. The overall results, that water diffuses much more slowly near the mineral surface than in bulk water, agree well. It is worth noting that, because neutron scattering measures α directly, a comparison of the two techniques gives the tortuosity, β , directly. Using the neutron scattering results of Olejnik and White (1972) for swollen Na-montmorillonites together with the data of Kemper *et al.* (1964), a value of 0.75–0.8 for β can be calculated, in close agreement with the value estimated less directly by Kemper *et al.* (1964).

An extensive series of NMR experiments on clay water systems was carried out by Fripiat and co-workers (Fripiat, 1977; Hougardy *et al.*, 1976). Although the clays studied were not montmorillonites, making a strict comparison with the present results impossible, those containing monovalent counterions show features in common with each other, which suggest that these features are also to be expected for the montmorillonites. For a two water-layer Na-vermiculite and a one-layer Li-hectorite, two T_1 minima occur, which correspond to correlation times for proton motion at room temperature of about 10^{-7} and 10^{-10} sec for the Na-clay and 10^{-9} and 5×10^{-11} sec for the Li-clay. Hougardy *et al.* (1976) interpreted the shorter of these correlation times as arising from translational diffusion of protons in the system. They correlated their value of 10^{-10} sec for the Na-vermiculite with a value estimated from the translational coefficient of diffusion of water in Na-montmorillonite measured by Olejnik *et al.* (1970) using neutron scattering. The present data for the one-layer Li-montmorillonite are $\langle \ell^2 \rangle \approx 10 \text{ \AA}^2$ and $D_t = 4 \times 10^{-10}$ m²/sec, giving a correlation time for translational diffusion of 4.3×10^{-11} sec, almost perfect agreement with the shorter of the two values obtained by Hougardy *et al.* (1976). It therefore seems certain that both experiments observed translational diffusion of water molecules, and that the diffusion is somewhat slower than in bulk water. However, the longer correlation time observed by Hougardy *et al.* (1976) cannot easily be reconciled with the neutron results. Hougardy *et al.* (1976) interpreted this correlation time to be associated with a slow rotation of the hydration shell of the cation. For this motion to have a significant effect on the spin lattice relaxation of the protons, the rate of exchange of molecules between the hydration shell and free water in the system must be less than the reciprocal of the correlation time, as indeed found by Hougardy

et al. (1976). This requires that on the shorter time scale of the neutron experiment a water molecule in the hydration shell will not be seen to move at all. As discussed further below, the unambiguous result of the neutron experiment is that *all* the water molecules in the system are moving with correlation times shorter than about 5×10^{-11} sec. The only way that this can occur for water molecules bound in the hydration shell is by rapid translational diffusion of the counterion plus the hydration shell or by rapid rotation of the whole hydration shell. Although counterions are known to diffuse moderately rapidly (Lai and Mortland, 1961), it is unlikely that translation of the hydration shell would be four orders of magnitude faster than its rotation. It is therefore probable that the slow correlation time observed by Hougardy *et al.* (1976) has another origin.

The conclusion that *all* the water molecules in the system are moving with correlation times shorter than about 5×10^{-11} sec rests in the simple observation that the quasielastic scattering spectrum contains no elastic component. Any water molecule with a longer translational correlation time, even if that molecule is rotating rapidly, will contribute an elastic peak, irrespective of the model that is used to fit the exact shape of the scattering. However, it must be emphasized that translational motion here refers to a spatial scale appropriate to neutron scattering. This is sufficiently small that true translational diffusion would be difficult to distinguish from the motion of a water molecule resulting from the rotation of a hydrated ion. Nevertheless, the absence of an elastic peak still requires the correlation time to be shorter than 5×10^{-11} sec, and this must apply to all water molecules in the sample.

The present results are an extension of the earlier low resolution experiments of Olejnik and White (1972). Although Olejnik and White (1972) estimated the diffusion coefficients of water in 1, 2, and 3 water-layer Li-montmorillonites, they could not expect to obtain very accurate values. The values measured here are generally higher than the original estimates. Olejnik and White (1972) derived a simple model of diffusion of water in a layered system based on the Kelvin equation and Eyring's model of diffusion in a liquid. This model predicts a linear variation of $\log D_t$ with $1/d$ where d is the separation between the platelets. The slope was predicted to be -10 \AA , and the intercept should correspond to the diffusion coefficient of water molecules in the bulk. Replacement of their values of D_t at low values of d by the new values obtained here gives a closer agreement with the original theoretical prediction but, at the two lowest values of d , the plot deviates markedly from a straight line. At these values of d an equation based on macroscopic properties is less likely to be successful.

The results of two other high-resolution neutron scattering experiments have recently been published. Adams *et al.* (1979) measured the rate of diffusion of

protons in Na-montmorillonite intercalated with pyridine. They interpreted their spectra in terms of a model of two-dimensional translational diffusion, in which case their value of D_i should be compared with the present values multiplied by $3/2$. They obtained a value of $6 \times 10^{-11} \text{ m}^2/\text{sec}$ at 23°C , an order of magnitude smaller than our lowest value for the one-layer Li-montmorillonite. The diffusion of water is obviously completely changed in the presence of pyridine. Hall *et al.* (1979a, 1979b) studied the diffusion of water in montmorillonites and vermiculites containing divalent counterions and either two of three molecular layers of water. They interpreted their spectra in terms of a model of simultaneous rotational and translational diffusion of water molecules bound to the counterion and more rapid translational diffusion of free water molecules. There are some points of similarity between their results and those of the present study. For example, there was no marked anisotropy in the diffusion, and their results are equally at variance with the interpretation of the slow correlation time observed in the NMR spectra (Hougardy *et al.*, 1976). The most surprising similarity between the two sets of measurements is that the mean rate of diffusion of water in the two systems is about the same, although earlier tracer results (Kemper *et al.*, 1964) suggest that the rate of translational diffusion in montmorillonites containing Ca should be about a fifth of that in montmorillonites containing Na. The comparison of the two sets of results on Ca and Li with the earlier ones of Olejnik and White indicates that the counterion hardly affects the diffusion of water molecules. However, this conclusion must remain uncertain until Hall and colleagues publish their final analysis.

The overall picture that emerges of water in Li-montmorillonites is that it is liquid-like, although it has a translational diffusion coefficient much smaller than in bulk water. This agrees with the conclusions of a recent neutron diffraction study (Hawkins and Egelstaff, 1980), that there is no highly structured interlayer water. It seems probable from the present analysis that the water molecules also rotate relatively freely. That there is some change in the character of the translational diffusion from that in the bulk is revealed by Figure 5, where it is seen that a plot of $D_{\text{eff}}Q^2$ against Q^2 flattens off where $Q \sim 0.7 \text{ \AA}^{-1}$, whereas this does not happen for bulk water until Q is almost double this value. This difference indicates that the oscillatory component in the diffusion process is much more important in the clays and that the characteristic jump length of the water molecules is much larger than in the bulk liquid.

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Резюме—Исучалась диффузия воды в Li-монтмориллоните при помощи некогерентного рассеяния квазиупругих нейтронов. Эксперименты были проведены на осажденных образцах, уравновешенных при относительных влажностях 32%, 58%, и 98%, соответствующих приблизительно 1, 2, и 3 молекулярным слоям воды в глинe. При всех трёх влажностях все молекулы воды в системе подвергаются поступательной диффузии, по крайней мере, на коротких расстояниях ($>5 \text{ \AA}$), со временами корреляции короче, чем 5×10^{-11} сек, хотя подвижность водных молекул меньше, чем в основном количестве воды. Различные модели молекулярного движения были использованы для определения точной формы рассеяния. Единственно полностью успешной моделью является модель, в которой молекулы воды подвергаются скачкообразной поступательной диффузии и ротационной диффузии. Средняя квадратичная длина скачка равна $10\text{--}15 \text{ \AA}^2$, при времени пребывания между скачками равным $4\text{--}2 \times 10^{-11}$ сек. Коэффициент поступательной диффузии увеличивается со влажностью, принимая величины 4, 7, и $10 \times 10^{-10} \text{ м}^2/\text{сек}$ для трёх вышеуказанных влажностей. Эти величины вместе с предварительно полученными данными при помощи измерений методом меченых атомов дают для фактора кривизны величины 0,75–0,8. Хотя образцы были анизотропны, нет очевидного доказательства, что диффузия воды на расстояниях $5\text{--}20 \text{ \AA}$ является анизотропной. Для скорости диффузии параллельной направлению перпендикулярному к тромбцитом, может быть выведен верхний предел равным 3. [E.C.]

Resümee—Die Diffusion von Wasser in Li-Montmorillonit wurde mit Hilfe inkohärenter quasielastischer Neutronenstreuung untersucht. Die Experimente wurden mit Sedimentproben durchgeführt, die bei einer relativen Feuchtigkeit von 32%, 58%, und 98% ins Gleichgewicht gebracht wurden, was etwa 1, 2, und 3 Moleküllagen Wasser im Ton entspricht. Bei allen drei Feuchtigkeitsgraden unterliegen alle Wassermoleküle im System einer translatorischen Diffusion, zumindest über kurze Entfernungen ($>5 \text{ \AA}$) mit Korrelationszeiten von kleiner als 5×10^{-11} sec, obwohl die Beweglichkeit der Wassermoleküle kleiner ist als im Wasser an sich.

Verschiedene Modelle für die Molekülbewegung wurden zur exakten Deutung des Streuverhaltens herangezogen. Das einzig wirklich anwendbare Modell ist das, in dem ein Wassermolekül einer sprunghaften translatorischen Diffusion oder rotatorischen Diffusion unterliegt. Die mittlere quadratische Sprunglänge beträgt $10\text{--}15 \text{ \AA}^2$ mit einer Verweilzeit zwischen den Sprüngen von $4\text{--}2 \times 10^{-11}$ sec. Der translatorische Diffusionskoeffizient, der mit dem Feuchtigkeitsgrad zunimmt, zeigt Werte von 4, 7, und $10 \times 10^{-10} \text{ м}^2/\text{sec}$ für die drei Feuchtigkeitsgrade. Diese Werte können mit Werten verglichen werden, die kürzlich bei Tracermessungen erhalten wurden, und eine Schätzung von 0,75–0,8 für den Torsionsfaktor ergeben. Obwohl die Proben anisotrop sind, gibt es keinen eindeutigen Hinweis, daß die Diffusion von Wasser über eine Entfernung von $5\text{--}20 \text{ \AA}$ ebenfalls anisotrop ist. Für die Diffusionsgeschwindigkeit parallel zur Richtung senkrecht auf den Plättchen kann auf eine obere Grenze von 3 geschlossen werden. [U.W.]

Résumé—La diffusion d'eau dans la montmorillonite-Li a été étudiée par éparpillement incohérent quasiélastique de neutrons. Des expériences ont été faites sur des échantillons sédimentés équilibrés à des humidités relatives de 32%, 58%, et 98%, correspondant approximativement à 1, 2, et 3 couches moléculaires d'eau dans l'argile. Pour les trois humidités, quoique la mobilité des molécules d'eau est moins que dans l'eau en masse, toutes les molécules d'eau dans le système subissent une diffusion translationnelle, au moins sur de courtes distances ($>5 \text{ \AA}$), avec des temps de corrélation plus courts que 5×10^{-11} sec.

Des modèles variés ont été utilisés pour rendre compte de la forme exacte de l'éparpillement. Le seul modèle connaissant un succès complet est celui où une molécule d'eau subit une diffusion translationnelle-saut et une diffusion rotationnelle. La distance de saut moyenne carrée est $10\text{--}15 \text{ \AA}^2$, avec un temps de résidence entre les sauts de $4\text{--}2 \times 10^{-11}$ sec. Le coefficient de diffusion translationnelle croît proportionnellement à l'humidité, ayant les valeurs de 4, 7, et $10 \times 10^{-10} \text{ м}^2/\text{sec}$. Ces valeurs peuvent être combinées à des valeurs obtenues précédemment par des mesures de traceur, pour donner une estimation de 0,75–0,8 pour le facteur de tortuosité. Bien que les échantillons sont anisotropiques, il n'y a pas d'évidence claire que la diffusion d'eau sur des distances de $5\text{--}20 \text{ \AA}$ est anisotropique. Une limite supérieure de 3 peut être déduite pour le taux de diffusion parallèle à la direction perpendiculaire aux plaquettes. [D.J.]