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# THE DIFFUSION OF INTERLAMELLAR WATER IN THE 23.3 Å Na-MONTMORILLONITE:PYRIDINE/$H_2O$ INTERCALATE BY QUASIELASTIC NEUTRON SCATTERING

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**Abstract**—The diffusion of water in the title intercalate has been measured by quasielastic neutron scattering. The diffusion coefficient ($6.1 \times 10^{-7}$ $cm^2$ $s^{-1}$ at 23.5°C) is one order less than that found previously for a sodium-exchanged montmorillonite which, however, contained 4 times as much water in the interlamellar space. The activation energy for the motion has been deduced to be 18 kJ $mol^{-1}$. Also it has been demonstrated that upon the time scale of the neutron scattering events (faster than $10^{-9}$ s) the hydroxyl groups of the clay lattice are not in motion.

**Key Words**—Diffusion, Intercalate, Montmorillonite, Neutron, Pyridine, Quasielastic.

## INTRODUCTION

The motion of water molecules constrained between the sheets of layered silicates has been the subject of a considerable amount of study, particularly by pulsed Nuclear Magnetic Resonance (NMR) (e.g., Boss and Stejskal, 1965, 1968; Hecht et al., 1966; Hecht and Geissler, 1970; Hougardy et al., 1970; Touillaux et al., 1968). There are problems associated with this technique, primarily the effect of paramagnetic impurities which can be reduced—if not eliminated—by using synthetic clays. Any residual paramagnetism can then be treated by procedures such as that adopted for vermiculites by Hougardy et al. (1970). In addition there is the effect of hydroxyl groups—which contribute to the NMR signal—in the clay layers themselves; this also can be considerably reduced by the use of synthetic clays in which the hydroxyl groups have been replaced by fluorine (e.g., Hecht and Geissler, 1970). Fripiat (1977) has extended these studies in related systems to the motion of different types of hydroxylic species. A somewhat different approach has been adopted by Calvert who has investigated the motion of the interlayer cations themselves (Calvert, 1971); he has also studied the interlayer water molecules by dielectric methods (Calvert, 1975).

Yet another approach in a very short time scale region ($<10^{-9}$ s) is afforded by the use of neutron scattering; inelastic spectra give information comparable in some ways with infrared or Raman measurements, whereas the energy broadening of the elastically scattered neutron peak (quasielastic scattering) coupled with its angular dependence can be interpreted in terms of the diffusive motions of atoms (see e.g., White, 1972). Since $^1H$ has a much larger incoherent scattering amplitude than any other nucleus found in clay intercalates, to a good approximation the information is about the diffusive motions of hydrogen atoms and, in particular, of the interlayer water hydrogen atoms. Olejnik et al. (1970), Hunter et al. (1971), and Olejnik and White (1972) have used such techniques to evaluate diffusion constants for interlamellar water in montmorillonites and vermiculites of different water content.

Early work on the system $Na^+$-montmorillonite: pyridine (Greene-Kelly, 1955) had shown that the 23.3 Å basal spacing pyridine complex with montmorillonite (formed with excess pyridine) must contain some water in order to be stable—a minimum of two water molecules per sodium cation is necessary for the intercalate to be formed (see Figure 2). The aim of this work was to measure the mobility of these interlamellar water molecules. Since other studies have been made on this system using a wide variety of techniques (e.g., Adams et al., 1975) it was hoped to make further progress towards a more complete description of the intercalate.

## THEORETICAL BACKGROUND

For an incident neutron beam with a small range of energies, the observed intensity distribution of the scattered neutrons from an incoherent scatterer (such as hydrogen) as a function of the energy transfer $\omega$ and the solid angle of scatter $\Omega$ is identical to the differential scattering cross section $\partial^2\sigma/\partial\Omega\partial\omega$:

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = b^2 \frac{k}{k_0} \frac{1}{2\pi} \iint \exp[i(\mathbf{Q}\cdot\mathbf{r} - \omega t)] \cdot G_s(\mathbf{r},t)d\mathbf{r}dt$$

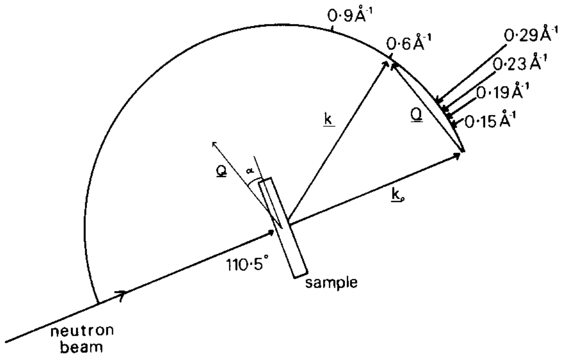

Figure 1. The experimental arrangement on the IN10 back-scattering spectrometer with sample and detector positions.

where b is the scattering length of the nucleus; k and $k_0$ are the magnitude of the scattered and incident wave vectors of the neutron respectively; $\mathbf{Q} = \mathbf{k} - \mathbf{k}_0$ and is the momentum transfer in the collision. $G_s(\mathbf{r},t)$ is the space-time autocorrelation function describing the motion of the atom containing the scattering nucleus. $G_s(\mathbf{r},t)$ is the probability of finding a nucleus at $\mathbf{r}$ at time t if it was at the origin at time t = 0.

$$G_s(\mathbf{r},t) = \frac{1}{N} \sum_n \{\delta[\mathbf{r} + \mathbf{r}_n(0) - \mathbf{r}_n(t)]\}$$

The functional relationship between $\mathbf{r}$ and t may be sinusoidal for a vibrator, or it may have a complicated form as for diffusive motions in liquids or solids. A number of models have been proposed to describe the molecular motions and $G_s(\mathbf{r},t)$ (e.g., Springer, 1972). Using these it is possible to analyze the shape and angular dependence of the scattering to obtain the self-diffusion coefficients associated with a particular scattering center. For a molecule obeying Fick's Law of diffusion the differential scattering cross section is

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = K \cdot \frac{DQ^2}{(DQ^2)^2 + \omega^2}$$

where K is a constant and D is the self-diffusion constant defined by Fick's Law. This model is satisfactory in many cases for long time behavior (i.e., small values of Q and ω) and gives an energy broadening (ΔE) proportional to the momentum transfer squared:

$$\Delta E = 2\frac{1}{N} - DQ^2.$$

To obtain ΔE, the energy broadening (taken to be Lorentzian, see above) and the incident spectrum are deconvoluted. Slopes of ΔE vs. $Q^2$ curves can then be used to obtain D. For quasielastic scattering $k \approx k_0$ and

$$\mathbf{Q} = \frac{4\pi}{\lambda} \sin(\theta/2)$$

where λ is the neutron wavelength and θ is the scattering angle.

## EXPERIMENTAL

The spectrometer used, IN10, at the High Flux Reactor at the Institut Laue-Langevin, Grenoble (Figure 1) is a development of an earlier high resolution back scattering neutron spectrometer constructed at Munich (Birr et al., 1971). The neutron wavelength used was 6.28 Å and the doppler drive frequency for the energy modulation of the incoming neutrons was 5 Hz. Detectors were arranged at Q values of 0.15, 0.19, 0.23, 0.29, 0.60, and 0.90 $Å^{-1}$.

The montmorillonite used was supplied by Volclay (Wallasey, Cheshire) and was sedimented to give the <2 μm fraction and cation exchanged for sodium. Analysis of this fraction gave 53.72% $SiO_2$, 17.63% $Al_2O_3$, 2.45% MgO, 2.62% $Fe_2O_3$, 0.09% F. The cation exchange capacity was determined as 66 meq/100 g air dry clay by a flame photometric method (Adams et al., 1977). The weight of clay used in the runs varied with total hydrogen content (including structural OH groups) so that a maximum of 20% absorption of the incident neutrons occurred.

The intercalate sample was prepared by immersing the calculated weight of oriented flakes of the sedimented clay in deuterated pyridine (99% d) for 10 min followed by wiping off excess pyridine and then allowing the sample to dry at room temperature and humidity for a further 10 min before sealing it in the sample chamber. The intercalate formed by this procedure had a basal spacing of 23.3 Å—it is stable over long periods provided that it does not come into contact with excess moisture. (A different, distinct, intercalate with 14.8 Å basal spacing is formed after some time when exposed to water vapor. We have confined our studies here to the 23.3 Å form.) The spectra were collected over a period of 10 hr.

## RESULTS AND DISCUSSION

The low angle scattering region was covered by the detectors since this region is that for which the simple relationship between peak broadening and momentum transfer could be expected to hold. The resolution function of the spectrometer at different detector positions was determined using a vanadium standard, vanadium giving almost completely incoherent scattering. Spectra obtained using a clay sample in which the interlayer water had been replaced by $D_2O$ were superimposable upon those for vanadium showing that the structural hydroxyl groups of the clay are not in motion on the time scale of the neutron events (faster than $10^{-9}$ s). This result is of great importance for the future examination of layered silicates by neutron scattering since it shows that it is not necessary to use a clay in which the hydroxyl groups have been replaced by fluorine.

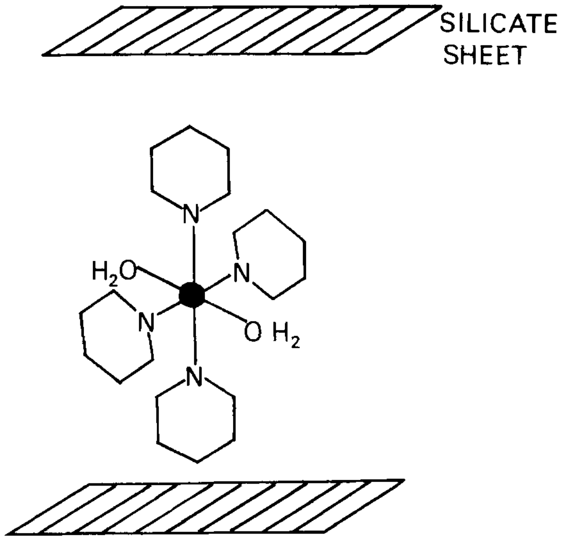

Figure 2. Arrangement around the interlamellar $Na^+$ cations suggested by Greene-Kelly (1956).

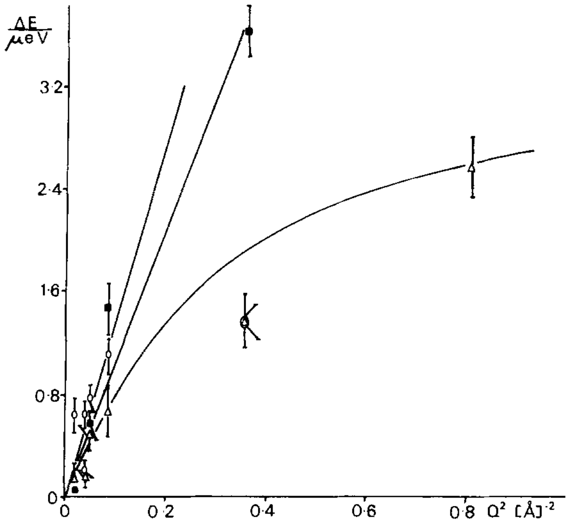

Figure 3. Graph of the broadening of the elastic signal vs. $Q^2$ for the 23.3 Å intercalate (corrected for the angle between **Q** and the clay sheets). (Error bars shown are 1σ.) △ 23.5°C, ■ 36.0°C, ○ 42.0°C.

The intercalated sample was prepared using deuterated pyridine so that all of the signal from protons (except the stationary OH groups) would originate in the water molecules present. The broadening of the quasielastic peaks as a function of the square of the momentum transfer was determined over the temperature range studied (23.5–42°C). The clay samples had been made up of flakes which were highly ordered—the orientation with respect to the neutron beam and detectors was as shown in Figure 1. Since the rate of diffusion of water molecules perpendicular to the clay sheets would be very much smaller than that parallel to the sheets, we have neglected the perpendicular component and derived the parallel component by using a cos $\alpha$ term depending upon the angular difference in orientation between the silicate layers and the **Q** vector ($\alpha$, Figure 1). This procedure is an extension of the earlier work on neutron scattering of clay:water systems where Olejnik and White (1972) stated that since their clay flakes were arranged at 45° to the neutron beam the momentum transfer vector must make angles of less than 45° with the basal plane. They noted that the diffusion coefficients they derived were more strongly affected by the parallel diffusive component.

The peak broadening as a function of the square of the momentum transfer (Figure 3) was reasonably linear except at high $Q^2$ where, as expected, there is a deviation from a continuous diffusion model in this region of shorter time behavior. The peak broadenings are all very small (μeV) and have quite large e.s.d.'s. Although the plots have a high scatter they represent the limit of the present generation of machines. From the initial slopes of the graphs, diffusion coefficients were estimated as 6.1, 7.5, and 10.2 × $10^{-7}$ $cm^2s^{-1}$ at 23.5, 36.0, and 42.0°C, respectively. These values can be compared with a diffusion constant of 25 × $10^{-7}$ $cm^2s^{-1}$ given by Olejnik et al. (1970) (although their measurements were made at higher **Q** values) for a sodium montomorillonite with a water content (wt $H_2O$/wt clay) of 0.228 (samples used in this work had a water content of 0.05). Since, in the presence of excess moisture, the 23.3 Å intercalate is unstable and collapses in a matter of hours to a 14.8 Å form, the samples were checked by X-ray diffraction after the neutron experimental period. Such a conversion had not occurred, confirming that there was no free, excess, water present. The only water studied by the neutron scattering was that essential for the formation of the 23.3 Å intercalate and there was no contribution to the spectra from free, surface, water. This situation is very different from that in many previous studies (NMR or neutron) of interlamellar water motion in clays where a prime objective has been to study the effect of variation in the water content. Boss and Stejskal (1968), for instance, studied clays massively swollen with water such that a major fraction could not have been bonded to the interlayer cations. They found that there was a component of the diffusion which was similar to that found for bulk water and another component which was much retarded.

An activation energy of 18 ± 5 kJ $mol^{-1}$ for the diffusion process parallel to the silicate sheets can be derived from the diffusion coefficients (Figure 4). Although the error in this value is high, it is the first time that such a motion has been studied in a clay intercalate by neutron scattering. Since neutron scattering is sensitive to hydrogen nuclei and not whole molecules it would seem difficult at the present to determine if the

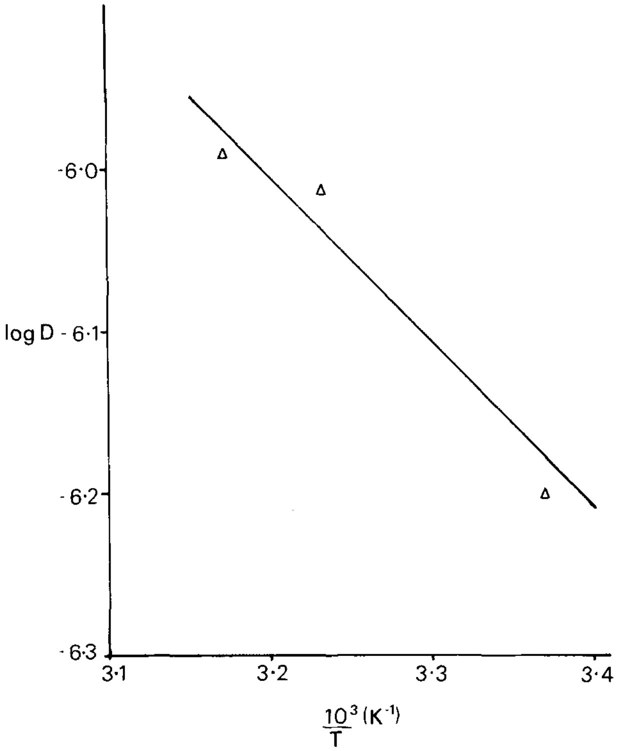

Figure 4. Graph of $\log_{10}$ (diffusion coefficient) vs. $10^3/T$ for the water mobility parallel to the clay sheets for the 23·3 Å 'phase.'

motion is that of water molecules themselves presumably hopping from one site (attached to a $Na^+$ cation) to another or whether the motion is a proton migration which would have to involve reorientation of the water molecules surrounding the interlayer cations or rotation of the whole cation coordination sphere (see e.g., Figure 2). In this connection it has recently been shown (Adams et al., 1978) by neutron diffraction and infrared measurements that when deuterium generating species are blown over the title intercalate there is a fast (~15 min at room temperature) H/D exchange process. This suggests strongly that the motion is of protons rather than whole water molecules.

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## REFERENCES

Adams, J. M., Breen, C., and Rickel, C. (1978) Deuterium/hydrogen exchange in interlamellar water in the 23.3 Å $Na^+$-montmorillonite:pyridine/water intercalate: *J. Colloid Interface Sci.* (in press).

Adams, J. M., Reid, P. I. and Walters, M. J. (1977) The cation exchange capacity of clays: *Sch. Sci. Rev.* 722–723.

Adams, J. M., Thomas, J. M. and Walters, M. J. (1975) Surface and intercalate chemistry of layered silicates. Part IV. Crystallographic, electron-spectroscopic and kinetic study of the sodium-montmorillonite:pyridine system: *J. Chem. Soc. Dalton Trans.* 1459–1463.

Birr, M., Heidemann, A. and Alefeld, B. (1971) A neutron spectrometer with extremely high energy resolution: *Nucl. Instrum. Methods* 435–439.

Boss, B. D. and Stejskal, E. O. (1965) Anisotropic diffusion in hydrated vermiculite: *J. Chem. Phys.* **43,** 1068–1069.

Boss, B. D. and Stejskal, E. O. (1968) Restricted, anisotropic diffusion and anisotropic nuclear spin relaxation of protons in hydrated vermiculate crystals: *J. Colloid Interface Sci.* **26,** 271–278.

Calvert, R. (1971) Properties of montmorillonite: role of the interactions between interlayer cations and water molecules: *Bull. Groupe Fr. Argiles* **23,** 181–190.

Calvert, R. (1975) Dielectric properties of montmorillonites saturated with bivalent cations: *Clays & Clay Minerals* **23,** 257–265.

Fripiat, J. J. (1977) Mobility of physically adsorbed hydroxylic molecules in surfaces made from oxygen atoms: *J. Colloid Interface Sci.* **58,** 511–520.

Greene-Kelly, R. (1955) An unusual montmorillonite complex: *Clay Miner. Bull.* **2,** 226–232.

Hecht, A. M., Dupont, M. and Ducros, P. (1966) Study of the transport of adsorbed water in certain clay minerals by NMR: *Bull. Soc. Fr. Mineral. Cristallogr.* **89,** 6–13.

Hecht, A. M. and Geissler, E. (1970) Nuclear magnetic resonance and relaxation of adsorbed water in synthetic fluor-montmorillonite: *J. Colloid Interface Sci.* **34,** 32–35.

Hougardy, J., Serratosa, J. M., Stone, W. and Van Olphen, H. (1970) Interlayer water in vermiculite: thermodynamic properties, packing density, nuclear pulse resonance, and infra-red absorption: *Spec. Discuss. Faraday Soc.* **58,** 187–193 and 204–205.

Hunter, R. J., Stirling, G. C. and White, J. W. (1971) Water dynamics in clays by neutron spectroscopy: *Nature (London) Phys. Sci.*, **230,** 192–194.

Olejnik, S., Stirling, G. C. and White, J. W. (1970) Neutron scattering studies of hydrated layer silicates: *Spec. Discuss. Faraday Soc.*, **58,** 194–201.

Olejnik, S. and White, J. W. (1972) Thin layers of water in vermiculites and montmorillonites—modification of water diffusion: *Nature (London) Phys. Sci.* **236,** 15–16.

Springer, T. (1972) *Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids:* Springer Tracts in Modern Physics No. 64, Springer Verlag, Berlin.

Touillaux, R., Salvador, P., Vandermeersche, C. and Fripiat, J. J. (1968) Study of water layers adsorbed on sodium and calcium montmorillonite by the pulsed nuclear magnetic resonance technique: *Isr. J. Chem.* **6,** 337–348.

White, J. W. (1972) Some applications of inelastic neutron scattering spectroscopy to surface chemistry and catalysis: *Neutron Inelastic Scattering Proc. Symp., IAEA,* Vienna, 315–344.

**Резюме**—Диффузия воды в прослойку 23,3 Å Na-монтмориллонит:пиридин/$H_2O$ измерялась с помошью квази-эластичного рассеивания нейтронов. Диффузионный коеффициент ($6{,}1 \times 10^{-7}$ cm$^2$/s при 23,5°C) на один порядок меньше, чем было обнаружено ранее для монтмориллонита с обменным натрием, который однако содержал в четыре раза больше воды в межслойных промежутках. Была вычислена активационная энергия для перемещения, которая оказалась равной 18 кдж/мол. Было также продемонстрировано, что в масштабе временных событий нейтронного рассеивания (быстрее, чем $10^{-9}$ сек) гидроксильные группы решетки глины не находятся в движении.

**Resümee**—Die Diffusion von Wasser in der Titeleinschiebung wurde mit quasi-elastischer Neutronenstreuung gemessen. Der Diffusionskoeffizient ($6{,}1 \times 10^{-7}$ cm$^2$/s bei 23,5°C) ist um eine Ordnung niedriger als der welcher voher für ein Natriumausgetauschtes Montmorillonit gefunden wurde, welches allerdings viermal soviel Wasser im interlamellaren Raum enthält. Die Aktivierungsenerdie für die Bewegung wurde auf 18 kJ/mol geschätzt. Es wurde auch demonstriert, daß auf der Zeitskala der Neutronenstreuungsereignisse (schneller als $10^{-9}$ s), die Hydroxylgruppen des Tongitters sich nicht bewegen.

**Résumé**—La diffusion d'eau dans la matière intercalée mentionée dans le titre a été mesurée par dispersion quasi-élastique de neutrons. Le coefficient de diffusion ($6{,}1 \times 10^{-7}$ cm$^2$/s à 23,5°C) est un ordre de grandeur plus bas que celui trouvé dans le passé pour une montmorillonite échangée pour du sodium qui, pourtant, contenait quatre fois plus d'eau dans l'espace interfeuillet. On a déduit que l'énergie d'activation pour le mouvement était 18 kJ/mol. Il a aussi été démontré que sur l'échelle de temps des évenements de la dispersion de neutrons (plus rapide que $10^{-9}$ s) les groupes hydroxyles du réseau cristallin de l'argile n'étaient pas en mouvement.