THE DIFFUSION OF INTERLAMELLAR WATER IN THE 23.3 Å Na-MONTMORILLONITE:PYRIDINE/H₂O 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 \( \times \) 10⁻⁹ cm² 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 10⁻⁸ 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themselves; this also can be considerably reduced by the use of synthetic clays in which the hydroxyl groups have been replaced by fluorine (e.g., Hecht and Geissler, 1970).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 ω and the solid angle of scatter Ω is identical to the differential scattering cross section \( \frac{\partial^2\sigma}{\partial\Omega\partial\omega} \):

\[
\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = b^2 \frac{k}{k_0} \frac{1}{2\pi} \int \int \exp[i(Q \cdot r - \omega t)] \cdot G_s(r,t) dr dt
\]
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; $Q = k - k_0$ and is the momentum transfer in the collision. $G_s(r,t)$ is the space-time autocorrelation function describing the motion of the atom containing the scattering nucleus. $G_s(r,t)$ is the probability of finding a nucleus at $r$ at time $t$ if it was at the origin at time $t = 0$.

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

The functional relationship between $r$ 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 $G_s(r,t)$ (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

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

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 $\omega$) and gives an energy broadening ($\Delta E$) proportional to the momentum transfer squared:

$$\Delta E = 2 \frac{1}{N} - DQ^2.$$
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 α term depending upon the angular difference in orientation between the silicate layers and the Q vector (α, 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 Q² 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 cm²s⁻¹ at 23.5, 36.0, and 42.0°C, respectively. These values can be compared with a diffusion constant of 25 × 10⁻⁷ cm²s⁻¹ given by Olejnik et al. (1970) (although their measurements were made at higher Q values) for a sodium montmorillonite with a water content (wt H₂O/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
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


Resumen—Die Diffusion von Wasser in der Titeleinschiebung wurde mit quasi-elastischer Neutronenstreuung gemessen. Der Diffusionskoeffizient (6,1 × 10⁻⁷ cm²/s bei 23,5°C) ist um eine Ordnung niedriger als der welcher vorher für ein Natriumausgetauschtes Montmorillonit gefunden wurde, welches allerdings viermal soviel Wasser im interlamellaren Raum enthält. Die Aktivierungsenergie für die Bewegung wurde auf 18 kJ/mol geschätzt. Es wurde auch demonstriert, dass auf der Zeitskala der Neutonenstreuungseignisse (schneller als 10⁻⁹ s), die Hydroxylgruppen des Tongitters sich nicht bewegen.

Резюме—Диффузия воды в прослойку 23,3 Å Na-монтмориллонит:пиридин/H₂O измерялась с помощью квази-эластичного рассеяния нейтронов. Диффузионный коэффициент (6,1 × 10⁻⁷ cm²/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 kдж/моль. Было также продемонстрировано, что в масштабе временных событий нейтронного рассеяния (быстрее, чем 10⁻⁹ сек) гидроксильные группы решетки глины не находятся в движении.

Résumé—La diffusion d’eau dans la matière intercalée mentionnée dans le titre a été mesurée par dispersion quasi-élastique de neutrons. Le coefficient de diffusion (6,1 × 10⁻⁷ cm²/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 événements 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.