Diffusion of Water in Bentonite Clay

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Diffusion of water confined in sodium bentonite clay is studied using the quasi-elastic neutron scattering (QENS) technique. Hydration of bentonite clay is characterized by several methods including X-ray diffraction and thermogravimetric measurements. X-ray diffraction shows that the clay is having a well-defined crystalline structure with an interlayer spacing of 13 Å. The QENS experiment has been carried out on hydrated as well as dehydrated clay at room temperature. Significant quasi-elastic broadening was observed in case of hydrated bentonite clay whereas dehydrated clay did not show any broadening over the instrument resolution. Analysis of QENS data reveals that diffusion of water occurs through jump diffusion. Both Jump diffusion models having random and Gaussian distribution in jump length are used to describe the observed dynamics. Obtained diffusion coefficient is found to be lower than that of bulk water.

1. Introduction

Smectite clay has a layered structure consisting of an octahedral layer of Al and Mg, sandwiched between two tetrahedral alumino-silicate layers. This group of minerals mainly includes bentonite, hectorite, saponite, sepiolite, and sauconite clays. Of these, bentonite and hectorite are the most important because of their swelling properties and availability. Bentonite occurs together with montmorillonite, which exhibits high swelling capacity for water, making this type of clay suitable as a buffer material in sealants and barriers [1]. Each layer of bentonite clay has a thickness of nearly 1 nm and a length of several hundreds of nanometer. The layers possess a net framework negative charge originating from the substitution of one cation for another, either in the tetrahedral or octahedral layers. This charge is compensated by adding suitable cations in the hydrated form in the interlayer spacing of the clay. Due to large specific surface area with small pores, bentonite clays are considered as barriers for the deep geological disposal of radioactive waste. Diffusion of water in bentonite clay is of fundamental interest to the technology for nuclear waste repositories [2]. The dynamics of water confined in clay minerals is important for the understanding of the properties of water within and the transport mechanisms of dissolved components. This has an important bearing on the containment and disposal of radioactive waste. Dynamics of water in various confined

media including clays are suitably studied using quasielastic neutron scattering (QENS) technique [3-8]. It is found that diffusion of water in clay depends on several factors including degree of hydration, type of clays, degree of compaction, interlayer spacing, compensating cations etc [4-8]. Effect of compensating cations on the dynamics of water has been studied in both swelling and non-swelling clays [4]. It is found that compensating cation in swelling clays has only a minor influence on the diffusion of water whereas these cations greatly affect the dynamics of water in non-swelling clay.

Here we report dynamics of water in sodium bentonite clay as studied using QENS technique. The crystalline phases of the clay in both native and hydrated from were studied by X-ray diffraction and Fourier Transformed Infra Red (FTIR) spectroscopy. Phase changes as a function of temperature were also followed by Thermogravimetry and Differential Thermal Analysis (TGA-DTA).

2. Experimental Details

X-ray diffraction of bentonite was studied for dry and hydrated samples using a Rigaku X-ray diffractometer. The diffraction pattern showed crystalline peaks at known angles and the changes in phase after hydration. Infrared spectra were recorded in the range 350 cm^{-1} to 4000 cm^{-1} on an FTIR-8900 SHIMADZU spectrophotometer. Dehydration of clay is studied by thermogravemetric measurements. TGA-DTA curves were obtained with a NETZSCH STA 409 PC instrument. The hydrated clay is heated at a constant rate while recording the change in the weight.

Quasi-elastic neutron scattering measurements were carried out using the QENS spectrometer at Dhruva reactor, Trombay [9]. The spectrometer is used in multi angle reflecting crystal (MARX) mode, which uses a combination of a large analyser crystal for energy analysis and a position sensitive detector for detecting the scattered neutrons. In the present configuration this instrument has an energy resolution of 200 μeV with incident neutron energy of 5 meV as obtained from standard vanadium sample. The quasielastic data were recorded in the wave vector transfer (Q) range of 0.67 Å^{-1}–1.8 Å^{-1} at room temperature. QENS measurements were performed on both hydrated as well as dehydrated bentonite clay. Data from the dehydrated sample were used to estimate the contribution of the sample other than water. For dehydration, the sample was heated to 200 C under vacuum (15 mb) for a period of about 5 h. Weight of the sample is recorded before and after dehydration process. About 12 % sample weight loss was observed after dehydration, which is also independently confirmed by TGA.

3. Results and Discussion

Known reflections are confirmed by X-ray diffraction pattern and the d-spacing is found to be 13 Å for (001) plane (Fig. 1a). When hydrated (5:1 water to clay), the clay partially transforms to an amorphous phase as shown in Fig. 1a. The only peaks present after hydration are those due to montmorillonite while the peaks of kaolinite, calcite and quartz disappear. The presence of water causes swelling within the layers and changes the structure. Hydrated clay has been heated to 400 C to check the irreversibility of the phase. From FTIR spectra (Fig. 1b), it is observed that for dehydrated clay, intensity of the band at 3428 cm^{-1}, which correspond to H-O-H stretching decreases. This band

corresponds to water molecules present in the interlayer spacing. The strong band at 1034 cm^{-1} is due to the Si-O-Si stretching vibration.

A two-step weight loss is observed in DTA–TGA plots (Fig. 1c). The peak at 116 C shows weight loss (~12 %) due to loss of adsorbed water. The removal of structural OH and weight loss due to lattice water occurred at around 420 C. In the DTA plot, an endothermic peak appears at 749 C, which is followed by a small exotherm, peak around 920 C. These peaks are characteristics of both montmorillonite and illite.

In a QENS experiment with water-clay system, the measured intensity is proportional to the incoherent scattering law S(Q, ω) due to large incoherent scattering cross section of hydrogen. Here Q is the wavevector transfer and ω is the angular frequency corresponding to the energy transfer, $\hbar\omega$. In general, this scattering law can be written as [3]

$$S(Q,\omega) = A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma,\omega) \qquad (1)$$

where A(Q) is elastic incoherent structure factor (EISF) and L(Γ,ω) is a Lorentzian function with Γ as a half width at half maxima (HWHM).

The quasielastic spectra were recorded for both water sorbed clay and its dehydrated form. Significant quasi elastic broadening was observed in case of hydrated clay whereas dehydrated clay did not show any broadening over the instrument resolution. Thus, the broadening observed in case of water sorbed clay is related to the dynamical motion of water molecules. To analyse the data, first the contributions of the elastic and quasielastic components were estimated using eq. 1. QENS data obtained from dehydrated clay were used to estimate the elastic contribution from the clay alone. The parameters, $A(Q)$ and $\Gamma(Q)$ were obtained by least squares fit. The resulting fits are shown in Fig. 2a.

In the present case, the elastic intensity other than that from the dehydrated clay is found to be negligible and a single Lorentzian function is good enough to describe the quasielastic part. Increase of HWHM of the Lorentzian (Γ) with Q, indicates that the observed dynamics correspond to the translational diffusion of the water molecules. The simplest model of translational motion is Brownian diffusion, which is described by Fick's law ($\Gamma(Q) = DQ^2$), where D is the self-diffusion coefficient of water. At large wave
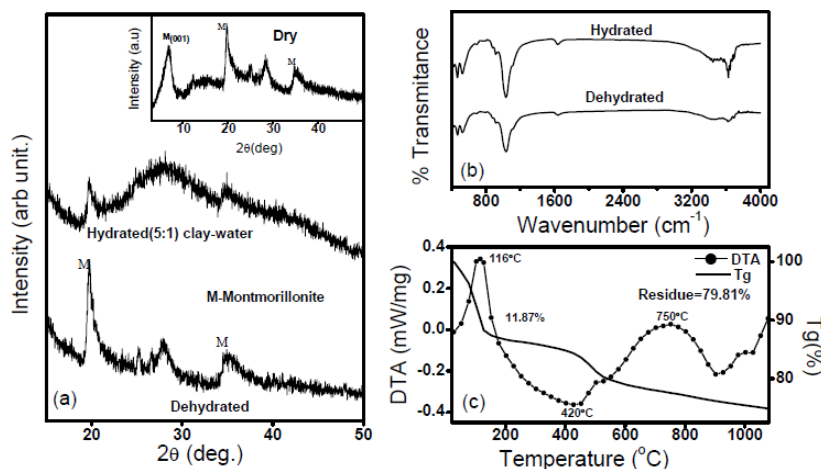
Fig. 1. (a) X-ray diffraction pattern of hydrated and dehydrated sodium bentonite clay. Insert shows diffraction pattern for dry bentonite (b) IR spectrum of hydrated and dehydrated clay. (c) Thermogravimetric curves of bentonite clay.

vector transfer, Fick's law is no longer applicable since diffusion process at atomic scale becomes important. This behaviour is described by jump diffusion models where the particle spends considerable time at a site called the residence time (τ), before instantly jump to another site. The distance covered by the particle in a jump is called the jump length. This model of jump diffusion can then be classified depending upon the degree of order in the environment, which in turn determines the distribution of jump lengths. In case of a more disordered environment, the distribution of jump lengths could be random or Gaussian. The corresponding jump diffusions are known as Singwi-Sjölander (SS) [10] and Hall and Ross (HR) [11] jump diffusions respectively. It may be noted that in these two jump diffusion models, the difference is that of a microscopic detail. In case the system is studied at a larger length scales or equivalently at smaller Q values, the information about finer details is lost and the mechanism of the diffusion resembles to that of Brownian motion. The variation of $\Gamma(Q)$ with Q^2 is therefore linear at low Q values and the diffusion coefficient can be obtained simply from the slope of this curve in the region of small Q values. However, at higher Q values, as finer details of the jump diffusion start to emerge, the variation of $\Gamma(Q)$ with Q^2 remains no more linear and saturates to a value, which is indicative of the residence times involved in the jump process. Both the jump diffusion models have been used earlier to describe water dynamics in clay minerals [4,5]. In the present case, we have employed both jump diffusion models to describe the variation of experimental obtained $\Gamma(Q)$ with Q^2. The SS model, which employs a random distribution of jump lengths, variation of $\Gamma(Q)$ with Q^2 is given by [10]

$$\Gamma(Q) = \frac{D_{ss}Q^2}{1 + D_{ss}Q^2\tau_{ss}} \qquad\qquad (2)$$

The HR model assumes a Gaussian distribution of jump length, which results the variation of $\Gamma(Q)$ [11]

$$\Gamma(Q) = \frac{1}{\tau_{HR}}\left\{1 - \exp(-Q^2 D_{HR}\tau_{HR})\right\} \qquad\qquad (3)$$

The variation of Γ, as obtained from QENS data, with Q^2 is shown in Fig 2b. The solid and dashed lines in Fig. 2b correspond to the least squares fit with Eq. 2 (SS model) and 3 (HR model) respectively.

Table I. **Comparison of the residence time (τ) and diffusion coefficient (D) obtained for water molecules in different clay systems along with bulk water**

System	Interlayer spacing (Å)	SS model		HR model	
		D_{SS} ($\times10^{-5}$cm^2/sec)	τ_{SS} (ps)	D_{HR} ($\times10^{-5}$cm^2/sec)	τ_{HR}(ps)
Sodium Bentonite [Present work]	13	1.8 ± 0.3	3.6 ± 0.4	1.7 ± 0.2	5.0 ± 0.5
Native saponite [6]	14	1.3 ± 0.3	4.5 ± 1.0	1.2 ± 0.3	6.2 ± 1.0
Intercalated saponite [6]	18	1.8 ± 0.4	3.6 ± 1.0	1.5 ± 0.3	5.0 ± 1.0
Na-Montmorillonite [4]	14.8	1.21 ± 0.12	11.9 ± 1.0	0.98 ± 0.05	13.8 ± 0.6
Kaolinite [4]	7.16	2.81 ± 0.19	2.1 ± 0.1	2.50 ± 0.12	2.8 ± 0.1
Bulk water [4]	-	2.37 ± 0.08	1.0 ± 0.06	2.30 ± 0.10	1.6 ± 0.1
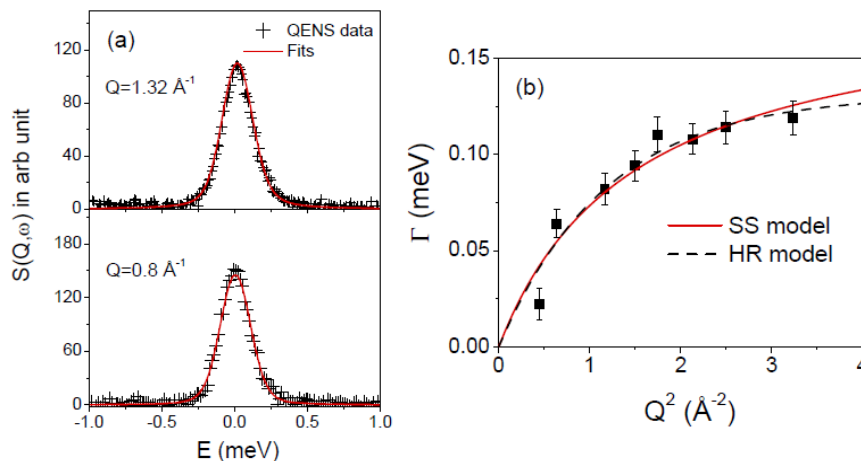
Fig. 2. (a) Fitted QENS spectra from the hydrated bentonite clay at some typical Q values. (b) Variation of HWHM, Γ with Q^2.

The values of the parameters, diffusivity (D) and residence time (τ) as obtained from the fits are given in Table I. Mean jump length (l) can be obtained by using Einstein relation, $D = l^2/6\tau$. Obtained results are compared with the bulk water and water in other clay systems and are shown in Table I. It is found that diffusion coefficient of water in bentonite clay is reduced compared to bulk water. Slower diffusion is mainly caused by the longer residence time, which is partly compensated by the larger jump length. Diffusion coefficient of water in bentonite clay is found to be larger than in sodium montmorillonite and lower than in kaolinite clay. Diffusivity is found to be more or less similar to the intercalated saponite clay. We have earlier studied the effect of hydration on the dynamics of water in hydrotalcite clay [7]. It was found that as the water content is increased, the residence time approached to that of bulk. It was also found that the translational diffusivity decreases with the decrease of the amount of excess water. Therefore, it is of interest to see the effect of different level of hydration on the dynamical behaviour of water in bentonite clay, which is being pursued by our group.

4. Conclusion

X-ray diffraction patterns have shown the presence of montmorillonite along with kaolinite, calcite and quartz in the dry sample. After hydration, the clay partially transforms to an amorphous phase. The only peaks present after the hydration are those due to montmorillonite, which is the major component of bentonite clay. The vibration modes are studied by IR spectroscopy. TGA-DTA results showed that the dehydration of the clay occurs at 116 C and 420 C, the latter relating to the loss of bound water. Dynamics of water in sodium bentonite clay is studied using neutron scattering technique. It is found that the motion of the water can be described by jump diffusion models. Values of residence-time and diffusion coefficient of confined water have been obtained. The dynamics of water in clays is found to be hindered in comparison to the bulk phase. Slower diffusion is mainly caused by the longer residence time, which is partly compensated by the larger jump length.

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