

Translational diffusion of water in compacted clay systems

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Abstract. The translational diffusion of water in compacted clays at a high hydration level has been investigated by quasielastic neutron scattering at a time-of-flight spectrometer FOCUS (SINQ). Four compacted clays with systematic structural differences have been studied: Na-montmorillonite, Na-illite, kaolinite and pyrophyllite. The QENS experiments were performed using two different incident wavelengths in order to access a larger Q range and verify the data analysis. The translational diffusion coefficient for water in Na-montmorillonite and Na-illite are lower than those for bulk water, whereas the preliminary results for kaolinite and pyrophyllite show larger diffusion coefficient.

1 Introduction

The long-term disposal of radioactive waste in an underground geological repository is based on a multibarrier concept. Compacted clay minerals are widely used as one of these barriers. The mineral-water systems have to be well characterized in order to understand the migration of radionuclides. Classical studies show how properties of water at the mineral-water interfaces deviate from that of the bulk water. Water absorbed by minerals presents greater viscosity [1], and heat capacity [2] than that of bulk water. Diffusion of water in clays has been studied, by means of neutron spectroscopy [3], NMR [4] and through diffusion techniques [5]; these different approaches agree in a reduction of the mobility of water molecules in contact with clay surfaces. A comparison of water dynamics in compacted clays with systematic structural differences is shown here. We examined by quasi-elastic neutron scattering (QENS) the dynamics of water molecules over a time scale of pico- and nanoseconds and over a length scale in the order of Ångströms. In this paper, the first QENS results are discussed.

2 Materials and methods

The clays studied were Na-montmorillonite (from Milos montmorillonite [6]), Na-illite (from illite Du Puy [7]), kaolinite (from Georgia, KGa-2 [8]) and pyrophyllite (from North Carolina, Ward Natural Science 46E4630). They have different structures, and consequently, water is confined in different ways: the pore chemistry and pore size vary from one clay to another. Clays are layer silicate minerals [9] where several layers stack together and form clay particles.

These particles have a diameter in the order of microns and a thickness of several tens of nanometers. Isomorphic substitutions (replacement of ions in the crystals without change of the structure) can result in a net negative charge, which is balanced through the electrostatic adsorption of cations. The cations and, depending on the type of clay, water molecules form

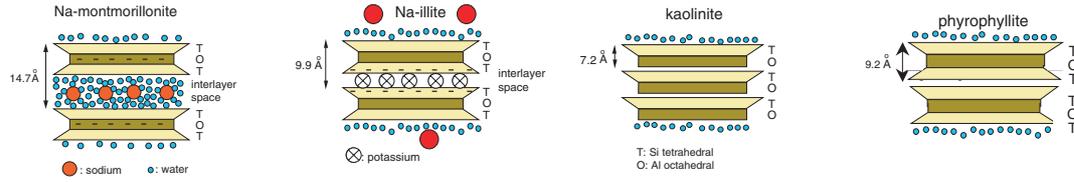


Fig. 1. Schematic clay structure. The lattice d-spacing (given in Å) was measured by X-ray diffraction.

the so-called interlayers. In montmorillonite water is located in between particles and in the interlayer space. In illite, water is found only in between particles, because the interlayer surfaces are tightly linked by potassium cations. Pyrophyllite and kaolinite, with a significantly different clay structure, are uncharged clays; consequently, water is only located in between particles.

Montmorillonite and illite were converted to the homoionic Na form. They were chemically analyzed by ICPAES, obtaining for Na-montmorillonite: CaO (0.3%), Na₂O (2.45%); for Na-illite: CaO (0.71%), Na₂O (0.77%). The pellets (5 × 1.5 × 0.1 cm), with a bulk dry density of $\rho = 1.8 \text{ g/cm}^3$ [3] (30% porosity) were pressed from hydrated powder (equilibrated at 95% relative humidity). The X-ray measurements show a water bilayer formed in the interlayer of Na-montmorillonite [10].

Quasielastic neutron scattering experiments were performed on the time-of-flight spectrometer, FOCUS [11] (SINQ, Switzerland). The measurements were carried out at room temperature, 45° slab angle (transmission), and using different incident wavelengths. The resolution function was measured with vanadium and approximated to a linear function of Q (for $\lambda = 3.65 \text{ Å}$: $fwhm \approx 0.25 \text{ meV}$ and for $\lambda = 5.75 \text{ Å}$: $fwhm \approx 0.05 \text{ meV}$). The two wavelengths were selected to be able to better distinguish the translational and rotational diffusive motions. For $\lambda = 3.65 \text{ Å}$ the rotational component dominates, whereas for $\lambda = 5.75 \text{ Å}$ the translational one; however the two data sets were analyzed as a combined translational-rotational motion. The following model was fitted to the measured intensity as a function of Q (momentum transfer) and E (energy transfer):

$$I(Q, E) = \{A(Q) \cdot \delta(E) + S(Q, E)\} \otimes G(Q, E) + C(Q) \quad (1)$$

Here $A(Q) \cdot \delta(E)$ is a correction for a non perfect background subtraction, $S(Q, E)$ is a model quasielastic scattering function, $G(Q, E)$ is the spectrometer resolution function and $C(Q)$ is a constant background. In the first experiments (Na-montmorillonite and Na-illite) the dry clay material was taken as background. However a small shift of the elastic line was detected, hence for the other clays (kaolinite and pyrophyllite) the empty instrument was also measured and used as background. The data was not corrected for absorption and multiple scattering. Assuming that the rotational and translational motions of the water are independent and thus can be treated separately in time and space, the scattering function $S(Q, E)$ can be approximated by the convolution of the rotational and translational components of the motions. We applied a general model for the combined rotational and translational diffusion which can be derived based on [12] and makes no assumption about the rotational component. This is an important fact for Na-montmorillonite and Na-illite, where the interaction water-ions-clay surface may affect the rotational motion qualitatively. The main goal was to obtain the translational diffusion. A rotational motion can be expressed in general as a sum of series of Lorentzians, which broadening is given by: $0(\delta \text{ function}), \Gamma_1^R(Q), \Gamma_2^R(Q), \dots, \Gamma_n^R(Q)$. The total scattering function then yields:

$$S(Q, E) = \sum_{n=0}^{n=\infty} B_n(Q) \frac{[\Gamma_n^R(Q) + \Gamma^T(Q)]}{E^2 + [\Gamma_n^R(Q) + \Gamma^T(Q)]^2}; \quad \text{with } \Gamma_0^R(Q) = 0 \quad (2)$$

where $B_n(Q)$ is the scaling factor, $\Gamma^T(Q)$ and $\Gamma_n^R(Q)$ are the broadening of the Lorentzian curve due to the translational and rotational movement respectively. For $n = 0$ the broadening is caused only due to the translational diffusion; $\Gamma_0^R(Q) = 0$. For $n \geq 1$ both

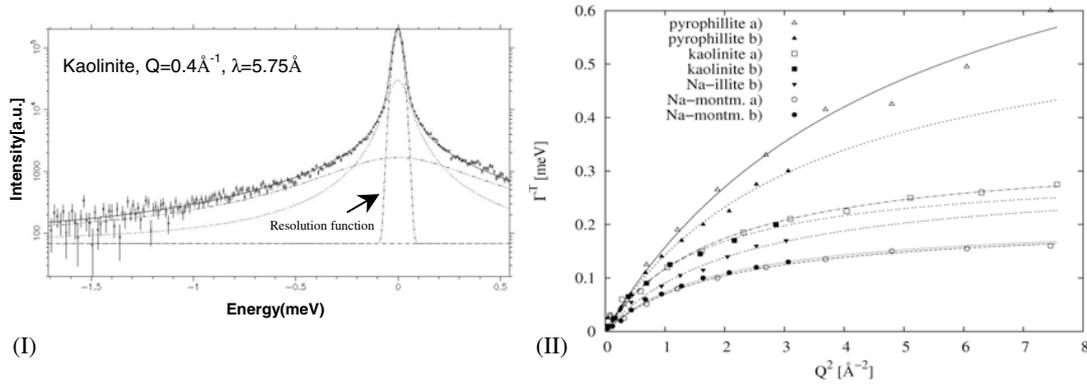


Fig. 2. (I) Fitted raw TOF data by 2 Lorentzian curves, $n = 1$. (II) Linewidth of the QENS spectra $\Gamma^T(Q)$ measured at room temperature. a) $\lambda = 3.65 \text{ \AA}$, $n = 2$, b) $\lambda = 5.75 \text{ \AA}$, $n = 1$.

components, translation and rotation contribute to the broadening of the Lorentzian curves. Diffusion coefficients D were calculated by the three-dimensional jump diffusion model [12], $\Gamma^T(Q) = (\hbar D Q^2)/(1 + \tau D Q^2)$, with τ the average residence time between two consecutive jumps. This model describes well bulk water behaviour and is considered as a good starting point.

3 Results and discussion

Due to a large number of free parameters, we compare here fitted results using $n = 1$ and $n = 2$ (in equation (2)) for both λ . Table 1 presents the translational diffusion coefficients and residence times. For $\lambda = 3.65 \text{ \AA}$ three Lorentzian curves ($n = 2$) were required to obtain a good fit, therefore the fitted values for $n = 1$ were not evaluated. For $\lambda = 5.75 \text{ \AA}$, two Lorentzians ($n = 1$) were enough to describe properly the translational motion of the system; the third Lorentzian appears only as a constant in the energy range relevant for the translational motion (i.e. in the range of the first Lorentzian). This is plausible because the rotational contribution, as expected, is more significant at the lower incident λ .

Table 1. Translational diffusion coefficients and residence times for different clays at room temperature. The crossed out values were not used in computing the average (see argument above).

$\lambda(\text{\AA})$	Na-montmorillonite		Na-illite		kaolinite		pyrophyllite	
	$D/10^{-9}$ (m^2s^{-1})	$\tau(ps)$	$D/10^{-9}$ (m^2s^{-1})	$\tau(ps)$	$D/10^{-9}$ (m^2s^{-1})	$\tau(ps)$	$D/10^{-9}$ (m^2s^{-1})	$\tau(ps)$
3.65	n=1	1.99	2.39		2.95	0.7	4.32	2.05
	n=2	1.60	3.18		2.70	1.93	2.87	0.70
5.75	n=1	1.71	3.14	1.98	2.24	2.88	2.17	2.81
	n=2	1.71	3.14	1.89	2.18	2.90	1.88	3.14
average	1.65±.1	3.16±.1	1.93±.1	2.21±.1	2.8±.2	2.05±.25	2.94±.25	0.75±.5

Similar diffusion coefficients were obtained for the two wavelengths. This gives some confidence that the evaluation of the diffusion coefficients is reliable, despite the large number of fitting parameters.

The translational diffusion coefficients obtained at the two wavelengths differ by less than 10% which can be taken as an estimate of the uncertainty of the measurement. In the same way the uncertainty for τ was estimated. The residence times for kaolinite and pyrophyllite have larger uncertainty than those for Na-montmorillonite and Na-illite. This is reasonable if

we assume that the rotational motion of the water molecules is less influenced by the clay than the translational. The smaller line widths in the translational motion ($I^T(Q)$) in the case of Na-montmorillonite and Na-illite can be better separated from the rotational component. The mean jump diffusion length was also calculated [13]. For pyrophyllite it reaches the value $1.15 \pm 0.86 \text{ \AA}$. For the other clays it varies between 1.6–1.9 \AA , which is close to that in bulk water $jdl = 1.6 \text{ \AA}$ [13].

The data analysis for pyrophyllite and kaolinite will be re-examined, this time assuming a model for the rotational motion since the current data treatment did not lead to self-consistency. An isotropic rotational motion model on a sphere should be realistic for these two clays.

The cations in the structure (for the Na-form clays) slow down the water motions [14]. In case of Na-montmorillonite, the cation concentration is significantly higher than in Na-illite, therefore D is even lower. Furthermore the water-surface interaction is more dominant here since the water is mainly in the interlayer space. In contrast the water in uncharged clays (kaolinite and pyrophyllite) shows more a bulk-like behaviour and the preliminary values for the diffusion coefficients are even larger than those of bulk water $D = 2.23 \cdot 10^{-9} \text{ (m}^2\text{s}^{-1})$ ¹⁵. The D values for Na-montmorillonite and Na-illite are well supported by further measurements (TOFTOF, FRM-II, $\lambda = 10 \text{ \AA}$, $\text{res} \approx 13 \mu\text{eV}$). A deeper analysis of the rotational component will be done in the near future in order to get more accurate information.

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