



QINS studies of water diffusion in Na-montmorillonite

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Abstract

We have used quasielastic incoherent neutron scattering (QINS) to study the diffusion of interlayer water in partially orientated Na-montmorillonite samples. In order to observe the anisotropy of the motion we performed measurements for two orthogonal sample orientations and for two different energy resolutions. Fits to the spectra yield phenomenological translational line widths which, for the 135° orientation, can be fitted by a two-dimensional Chudley–Elliott model with a diffusion coefficient $D = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and a mean square jump distance $l = 1.7 \text{ \AA}$. © 2000 Elsevier Science B.V. All rights reserved.

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Montmorillonite is a smectite (swelling) clay consisting of stacks of negatively charged aluminosilicate layers separated by charge-balancing cations in the interlayer region. Hydration of the interlayer cations and internal surfaces leads to swelling in a series of steps known as one-, two- and three-layer hydrates. The behaviour of the interlayer water is important for the understanding of the mechanical, colloidal and ion-exchange properties of the clays, of interest in the paint and cosmetics industries, environmental remediation and radioactive waste disposal.

Previous quasielastic incoherent neutron scattering (QINS) studies [1] of partially oriented hydrated Li-montmorillonite show that the interlayer water undergoes translational diffusional motion with a diffusion coefficient two to six times smaller than for bulk water. Since these authors measured spectra for only one sample orientation, they could not prove that the diffusion is anisotropic as would be expected for 2D diffusion of the water between the clay platelets. We present here QINS studies of partially oriented samples of hydrated

Na-montmorillonite, using two sample orientations of 135° and 45° with respect to the incident beam, corresponding to Q parallel and Q perpendicular to the clay layers at a scattering angle $2\theta = 90^\circ$, in order to probe the anisotropy of the proton motion.

The Wyoming montmorillonite used (Swy-2, Clay Minerals Society) has the idealised formula $\text{Na}_{0.75}(\text{Si}_{7.75}\text{Al}_{0.25})(\text{Al}_{3.5}\text{Mg}_{0.5})\text{O}_{20}(\text{OH})_4$. Partially oriented samples were produced by deposition onto a filter under pressure, giving disc-shaped samples with the individual platelets tending to orient parallel to the plane of the disc, but with a large mosaic spread: (see Fig. 1). Measurements on the V1 lamellar diffractometer at HMI gave the interlayer spacing of the sample as 16.8 Å, corresponding to approximately three layers of interlayer water. The rocking curve around the interlamellar peak was found to be approximately a Gaussian with FWHM of 40°. QINS spectra were recorded on the V3 time-of-flight neutron spectrometer at HMI at nominal energy resolutions of 120 μeV ($\lambda_0 = 5.1 \text{ \AA}$) and 36 μeV ($\lambda_0 = 6.2 \text{ \AA}$) for each sample orientation.

We fitted the spectra with an elastic term based on a fit to an analogous D₂O-hydrated sample plus a quasielastic term containing both rotational and translational contributions [2]. We fixed the rotational line width at the physically reasonable value [3] of 50 μeV (attempts to fit this parameter led to unreasonably high values) and

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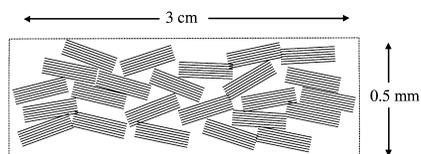


Fig. 1. Schematic cross-section of the partially oriented Na-montmorillonite hydrate sample. The individual crystallites ($\sim \mu\text{m}$ dimensions) align preferentially parallel to the plane of the disc.

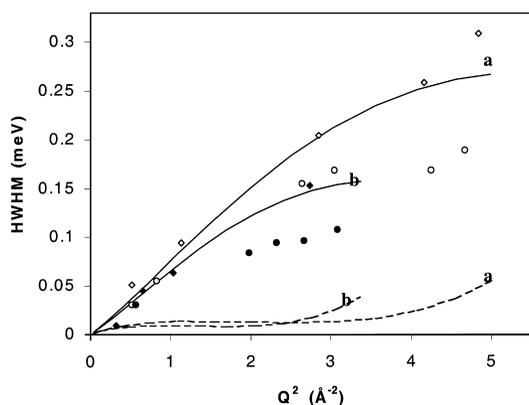


Fig. 2. Translational line widths and corresponding fitted curves (see text) obtained for Na-montmorillonite for sample orientations of 135° (diamonds full lines) and 45° (circles, dashed lines) at nominal energy resolutions of $120 \mu\text{eV}$ (lines a) and $36 \mu\text{eV}$ (lines b).

obtained a phenomenological translational linewidth for each spectrum (Fig. 2). The smaller line widths for the 45° sample orientation ($Q \perp$ to the clay layers for $2\theta = 90^\circ$) indicate that we do indeed observe the 2D water diffusion between the clay platelets. We therefore applied a 2D Chudley–Elliott [4] model, taking account of the mosaic spread of the sample by calculating an overall line width from the weighted average of the line widths for a range of platelet orientations. The curves in Fig. 2 correspond

to fits with a diffusion coefficient, $D = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and a jump distance, $l = 1.7 \text{ \AA}$. These values fit the data for a sample orientation of 135° very well, and reproduce the observed splitting of the high- and low-resolution values (due to the different wavelengths at the different resolutions, the projection of Q parallel to the clay layers is different for a given Q value [3]). The diffusion coefficient is about half the value for bulk liquid water, and is close to the value obtained for the three-layer Li-montmorillonite hydrate by Cebula et al. [1]. The fit to the 45° sample orientation is very poor: the observed anisotropy of the linewidth is much smaller than predicted by the model. This could be because the jump-length in the diffusion process is relatively short compared to the interlayer spacing (the thickness of the interlayer water is around 10 \AA) so that the diffusion is not entirely two dimensional. Alternatively, we may observe an isotropic contribution from non-interlayer water molecules diffusing between the clay particles. In a future publication we will consider lower hydration states, with smaller interlayer spacings, for which the anisotropy should be more marked. We will also make a more rigorous analysis, fitting the individual spectra with a sum of Lorentzians corresponding to different particle orientations, rather than fitting a single line width averaged over these orientations.

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