**Diffusion of water adsorbed in hydrotalcite: neutron scattering Study**

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**Abstract.** Layered double hydroxides (LDH) are a class of ionic lamellar solids with positively charged layers of two kinds of metallic cations and exchangeable hydrated anions. Quasi-elastic neutron scattering (QENS) measurements are performed in this type of LDH structured hydrated hydrotalcite sample to study the dynamical behaviour of the water in geometric confinement within the layers. Dynamical parameters correspond to the confined water molecules revealed that depending on the amount of excess water present, behaves differently and approaches bulk values at high concentration. Both translational and rotational dynamical parameters showed that at very low concentration of excess water, water molecules are attached to the surfaces and show the confinement effect.

1. Introduction
Water in confined geometries behaves differently from bulk water. Layered double hydroxides with their lamellar structures offer an example of confined geometries in which water can be found. Hydrotalcite (HT), viz the magnesium aluminium hydroxycarbonate, Mg₆Al₂(OH)₁₆(CO₃)₄H₂O, is one of the representative materials belonging to the family of layered double hydroxides (LDH). Hydrotalcites have attracted much attention in recent times [1] due to their practical applications as catalysts, catalyst supports, ion exchangers and composite materials [2]. Most of the previous investigations on hydrotalcites have centered on understanding the nature of different anions present in the interlayer region of the framework or in the study of their thermal behaviour. Hydrotalcites, because of their relatively open hydroxide lattice, offer a unique advantage in terms of studying water dynamics in the interlayer region of the LDH frameworks [3-5]. Our preliminary experimental investigations have revealed that the extra hydration water i.e., the water other than that of crystallisation water exhibits slightly reduced thermodynamic water activities, and, thereby reduced tendency for water loss from hydrated HT materials. This excess water seems to make the structure more stable; therefore it is important to study its behaviour. We had studied the dynamics of the excess water in hydrotalcite earlier [6] but limited to room temperature only. Here, we report study of the dynamics of this extraneous hydrated water associated with the HT structure at different temperatures employing Quasielastic Neutron Scattering (QENS) technique.

2. Experiment
Hydrotalcite sample was prepared by combining a co-mixture of water soluble Mg²⁺/Al³⁺ salts with Na₂CO₃ at elevated temperatures followed by normal work-up of the precipitate obtained. Precipitated

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hydroxylate followed by dehydration of the wet cake to powder samples having 10, 30, 40 wt % of water in excess of the stoichiometric water of crystallization were used for the neutron experiment. Quasielastic neutron scattering experiments were performed using FOCUS spectrometer at Paul Scherrer Institute, Switzerland. The spectrometer allows one to vary the instrumental energy resolution, by changing the incident wavelength of the neutrons. We have used two wavelengths of 5.9 and 4.4 Å providing energy resolutions (at elastic position) of ~ 45 μeV and 145 μeV respectively. Data were recorded at temperatures 300, 280, 260 and 240 K for each sample.

3. Results and discussion
In a neutron scattering experiment from hydroxylate systems, the observed dynamics mainly corresponds to the self-correlation function of the hydrogen atoms. In that case the incoherent scattering law, $S_{incoh}(Q, \omega)$, alone describes the dynamics. $Q = k - k_0$ is the wavevector transfer and $\hbar \omega = E - E_0$ is the energy transfer. However, if both rotational as well as translational motions are present in the system, total scattering function will be a convolution of the rotational and translational components assuming the two motions are uncorrelated. The scattering function can be written as

$$S_{tot}(Q, \omega) = A(Q)\delta(\omega) + [1 - A(Q)]S_{rot}(Q, \omega) \otimes S_{trans}(Q, \omega)$$

(1)

The first term is the elastic component arises due to the immobile hydrogen atoms and the second term is the quasielastic one contribution from the mobile hydrogen atoms. Rotational motion can be described by:

$$S_{rot}(Q, \omega) = B_0(Q)\delta(\omega) + [1 - B_0(Q)]L(\omega, \Gamma_R(Q))$$

(2)

where $L(\omega, \Gamma_R)$ is a Lorentzian with Half Width at Half Maximum (HWHM) $\Gamma_R(Q)$ and $B_0(Q)$ is known as Elastic Incoherent Structure Factor (EISF). The translational motion of water molecules can be described by a Lorentzian, $L(\omega, \Gamma_T)$ with HWHM $\Gamma_T(Q)$. Therefore, Eq. (1) can be written as:

$$S_{tot}(Q, \omega) = A(Q)\delta(\omega) + [1 - A(Q)]B_0(Q)L(\omega, \Gamma_T) + [1 - B_0(Q)]L(\omega, \Gamma_T + \Gamma_R)$$

(3)

In a high resolution instrument (small $\Delta E$) the rotational motion is relatively fast (large $\Gamma_R$), then the third term in Eq. 3 can be approximated by a Q dependent background. In the present case, where rotational motion of water is known to be much faster (~ 0.1meV) than the instrumental resolution used (0.045 meV), Eq. 3 can be rewritten as:

$$S_{tot}(Q, \omega) = A(Q)\delta(\omega) + [1 - A(Q)]B_0(Q)L(\omega, \Gamma_T) + C(Q)$$

(4)

where $C(Q)$ is a background which depends on Q. Therefore, the QENS data is fitted with $A(Q)$, $\Gamma_T(Q)$ and $C(Q)$ as parameters. $B_0(Q)$ can be calculated exactly knowing the radius of gyration of water molecules. Hydrotalcite with no excess water ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3.4\text{H}_2\text{O}$) did not show any quasielastic broadening over the instrumental resolution ($\Delta E = 45$ μeV). However, quasielastic broadening was seen in 10%, 30% and 40% excess water sample. Typical QENS spectra fitted with Eq. (4) for 40 % and 10 % hydrated hydrotalcite for $Q=1.9$ Å$^{-1}$ are shown in Fig. 1. Obtained $\Gamma_T(Q)$ for different hydrated samples at different Q values as obtained by least squares fit of the resolution broadened $S(Q,\omega)$ with the measured data at different temperatures are shown in Fig. 2. $\Gamma_T(Q)$ is found to follow the random translational jump diffusion model [7,8]. Translational diffusion constants and residence time between jumps are obtained for the 10% water. While the translational width for sample with 30 % and 40% excess water content shows very similar behaviour but the width for sample with 10 % water content shows a marked difference as shown in Fig. 2.
**Figure 1.** Typical fitted QENS spectra for 40 and 10 wt % hydrated hydrotalcite using energy resolution of 45 μeV. Solid lines are the total fits. Dashed and dotted lines represent the translational component and instrumental resolution respectively.

**Figure 2.** Behaviour of translational width with $Q^2$ for (a) 40 % (solid) and 30 % (open) and (b) 10 % hydrated hydrotalcite at different temperatures. Solid and dashed lines are the fit with random jump diffusion.

**Figure 3.** Typical fitted QENS spectra for 40 and 10 wt % hydrated hydrotalcite using energy resolution 145 μeV. Solid lines are the total fits. Dashed and dotted lines represent the first and second component of the right hand side of Eq. 5 respectively.
The mean jump lengths did not change very much for samples with different water content, but residence time showed significant increase in the samples with low water content. To compare with the behaviour of bulk water, it is found that the dynamics, particularly the residence time, approached that of bulk as the water content is increased. It is also found that the translational diffusivity decreases with the decrease of the amount of excess water. This is mainly due to the fact that when the amount of excess water is small these water molecules are most likely bound to the host layer. With increase amount of the excess water, more and more of the water molecules are available away from the layer surface and are subjected to relatively lesser interaction with the host. It was seen that with the decrease of temperature the diffusivity decreases at low temperature suggesting hindered translational motion. Effort is also made to estimate the rotational diffusion constant of the confined water using the data taken with low instrumental resolution. Data taken with low instrumental resolution should contain the contribution from both translational and rotational component. Translational diffusivities obtained from high resolution data are assumed to calculate the rotational parameters. Data from the sample with no water content is subtracted properly in order to estimate the dynamical contribution of confined water only. Spectra is then fitted with the following equation,

\[
S_{\text{tot}}(Q,\omega) \otimes R(\omega) = S_{\text{rot}}(Q,\omega) \otimes S_{\text{tran}}(Q,\omega) \otimes R(\omega)
\]

\[
= \left[ A_0(Q)\delta(\omega) + \sum_{n=1,\infty} A_n L_n(\omega, D_r) \right] \otimes L(\omega, D_r) \otimes R(\omega)
\]

\[
= A_0(Q)L(\omega, D_r) \otimes R(\omega) + \sum_{n=1,\infty} A_n L_n(\omega, D_r) \otimes L(\omega, D_r) \otimes R(\omega)
\]

Here \(D_r\) and \(D_c\) are the translational and rotational diffusion constants respectively. Fig. 3 represents the typical spectra and the fit with Eq. 5. The dashed and dotted lines are the first and second component of RHS of Eq. 5. Rotational diffusivity of the confined water in the case of 30 and 40% water content sample is found to be very close to that of bulk water. However, 10% water content sample showed a small decrease of rotational diffusivity compared to the bulk water.

4. Conclusion

Quasielastic neutron scattering studies performed on excess water in LDH structured hydrotalcite system provided considerable insight into the dynamical properties of confined water. Varied content of excess water inside the hydrotalcite sample is used for the study. Both translational and rotational motions are taken into account in analyzing the data. It is seen that the translational motion for excess water can be best described by random translational jump diffusion model. Rotational motion is described by isotropic diffusion model. Both translational and rotational diffusivities are found to increase with increasing amount of excess water suggesting on increase amount of the excess water, more and more of the water molecules are available away from the layer surface and are relatively free to move. It is established that there is a clear difference in the magnitude of the translational and rotational motions between the layers that is attributable to the bonding interactions between water and the interlayer species.

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