Excess water dynamics in hydrotalcite: QENS study

S MITRA[1], A PRAMANIK[2], D CHAKRABARTY[2] and R MUKHOPADHYAY[1]
[1]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[2]Hindustan Lever Research Centre, Chakala, Andheri (East), Mumbai 400 099, India
E-mail: smitra@apsara.barc.ernet.in

Abstract. Results of the quasi-elastic neutron scattering (QENS) measurements on the dynamics of excess water in hydrotalcite sample with varied content of excess water are reported. Translational motion of excess water can be best described by random translational jump diffusion model. The observed increase in translational diffusivity with increase in the amount of excess water is attributed to the change in binding of the water molecules to the host layer.

Keywords. Porous materials; diffusion; neutron scattering.

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1. Introduction

Hydrotalcite (HT), viz. the magnesium aluminium hydroxycarbonate, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, one of the representative materials belonging to the family of layered double hydroxides (LDH), have attracted much attention in recent times [1] due to their practical applications as catalysts, catalyst supports, ion exchangers and composite materials [2]. The structure of HT is similar to brucite, $Mg(OH)_2$, which consists of layers of Mg^{2+} ions coordinated octahedrally to six oxygens. Partial substitution for Mg^{2+} by the isomorphous Al^{3+} leads to the generation of positively charged metal assembly layers and the stacked metal assemblies are held together by the presence of charge balancing anions, like carbonate anions present in the interlayer region along with molecules of water of crystallization. Most of the previous investigations on hydrotalcites have centred on understanding the nature of different anions present in the interlayer region of the framework or in the study of their thermal behaviour.

Hydrotalcite-based layered double hydroxide materials offer a unique advantage in terms of studying water dynamics in the interlayer region of the hydrotalcite frameworks [3]. Since these materials provide three-dimensional structures characterized by superior porosity and ion exchange properties, these materials found some industrial applications. LDHs containing carbonate anions have been used as antacids [4]. Those containing chloride anions are used as adsorbents of the phosphate ions contained in the human intestine [5]. The crystallized water

molecules are expected to have different dynamics than the extraneous hydration water present in the HT. Our preliminary experimental investigations have revealed that the extra hydration water, i.e., the water other than that of crystallization water exhibit slightly reduced thermodynamic water activities, and, thereby reduced tendency for water loss from hydrated HT materials. Earlier QENS studies dealt with the dynamics of crystalline water in hydrotalcite [6,7]. Here, we decided to probe the dynamics of this extraneous hydrated water associated with the HT structure by employing the quasi-elastic neutron scattering (QENS) technique. Our earlier study on the dynamics of water molecules in porous alumina showed that the dynamics of water inside the pores is very different from that of bulk water [8].

2. Experimental details

Hydrotalcite sample was prepared by combining a co-mixture of water soluble Mg^{2+}/Al^{3+} salts with Na_2CO_3 at elevated temperatures followed by normal work-up of the precipitate obtained. Hydrotalcite with 9, 21, 30 and 50% (wt%) of excess water $(Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O + xH_2O)$ and hydrotalcite with no excess water $(Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O)$ are studied by QENS technique at room temperature. Sample with no excess water is studied to account for the contributions from immobile hydrogen atoms. Experiments were carried out using medium resolution quasi-elastic spectrometer at Dhruva reactor in Trombay [9]. The spectrometer is having an energy resolution of 200 μeV with incident neutron energy of 5.1 meV. The quasi-elastic spectra were recorded in the wave-vector transfer (Q) range of 0.8–1.8 Å^{-1} at 300 K.

3. Results and discussion

In a neutron scattering experiment from hydrogeneous systems, the observed dynamics mainly corresponds to the self-correlation function of the hydrogen atoms. In that case the incoherent scattering law, $S_{\mathrm{inc}}(Q,\omega)$, alone describes the dynamics. $\mathbf{Q}$ ($=\mathbf{k}-\mathbf{k_0}$) is the wave-vector transfer and $\hbar\omega = E - E_0$ is the energy transfer. However, if both rotational as well as translational motion are present in the system, total scattering function will be a convolution of rotational and translational components assuming the two motions are uncorrelated. As in hydrotalcite sample, there are hydrogen atoms in the layered sheet, which are not mobile and will give rise to elastic scattering. Total scattering function can then be written as

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

The first term is the elastic scattering from the fixed hydrogen atoms and the second term is for quasi-elastic scattering from the mobile hydrogen atoms. Rotational motion of water is known to follow isotropic rotational diffusional model [10] which can be described by

$$S_{\mathrm{rot}}(Q,\omega) = B_0(Q)\delta(\omega) + \sum_{l=1}^{\infty} B_l(Q)\frac{1}{\pi}\frac{l(l+1)D_{\mathrm{R}}}{\omega^2 + [l(l+1)D_{\mathrm{R}}]^2}, \tag{2}$$

where B_0 and B_l can be calculated exactly knowing the radius of rotation [8]. D_R in eq. (2) is the rotational diffusion constant. The translational motion of water molecules can be described by a Lorentzian with half-width at half-maximum (HWHM) $\Gamma(Q)$ as

$$S_{\text{tran}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\omega^2 + \Gamma^2(Q)}. \tag{3}$$

Hydrotalcite with no excess water ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) did not show any quasi-elastic broadening over the instrumental resolution ($\Delta E = 200 \ \mu eV$). However, quasielastic broadening was seen in 9, 21, 30 and 50% excess water sample. Fraction of immobile to mobile hydrogens and thus $A(Q)$ in eq. (1) can be estimated by taking ratio of intensity of QENS spectra from the sample with no excess water and the sample with excess water at all the Q values. Finally, data analysis involve convolution of eq. (1) with instrumental resolution and determining D_R and $\Gamma(Q)$ by least square fit with the experimental spectra. Since rotational motion of small water molecule (size $\sim$2 Å) is not expected to get affected due to confinement between two layers with separation of about 8 Å, we assumed the rotational diffusion constant to be the same as that of bulk water [11]. The QENS spectra of excess water sample are then fitted with a scattering function (eq. (1)) which consists of both rotational and translational motion of water molecules. The only parameter to be found is the HWHM of the translational component ($\Gamma(Q)$) at each Q value. QENS spectra can be fitted very well with this assumption at all the Q values. Figure 1 shows the typical fitted QENS spectra with elastic (dotted) and quasi-elastic (dashed) components separated. With many other models for translational motion, the obtained $\Gamma(Q)$ is found to follow the random translational jump diffusion model [8] which can be described by

$$\Gamma(Q) = \frac{D_T Q^2}{1 + D_T Q^2 \tau}, \tag{4}$$

where D_T and τ are the translational diffusion constant and residence time in between jumps. Variation of $\Gamma(Q)$ with Q^2 is shown in figure 2. Solid lines are the fit with eq. (4). Translational diffusion constants and residence time in between jumps obtained for 9, 21, 30 and 50% excess water are given in table 1. While the mean jump lengths have not changed much with different water content, residence time showed an increase when the water content is less. This essentially indicates that with the increase in water content, water molecules move faster. These values can also be compared with corresponding values obtained for bulk water. Mean jump length and residence time obtained for bulk water at 20°C were found to be 1.29 Å and 1.25 ps respectively [11]. One may conclude that even in 50% water content sample, though diffusion constant of excess water molecules is having a similar value as that of bulk water, residence time is still larger than that of bulk water. It is also found that the translational diffusivity decreases with the decrease in the amount of excess water. This is mainly due to the fact that when the amount of excess water is small they are mostly bound to the host layer. With increased amount of excess water, more and more water molecules are available away from the layer surface and are relatively free. ^{1}H T_1 relaxation measurements by NMR
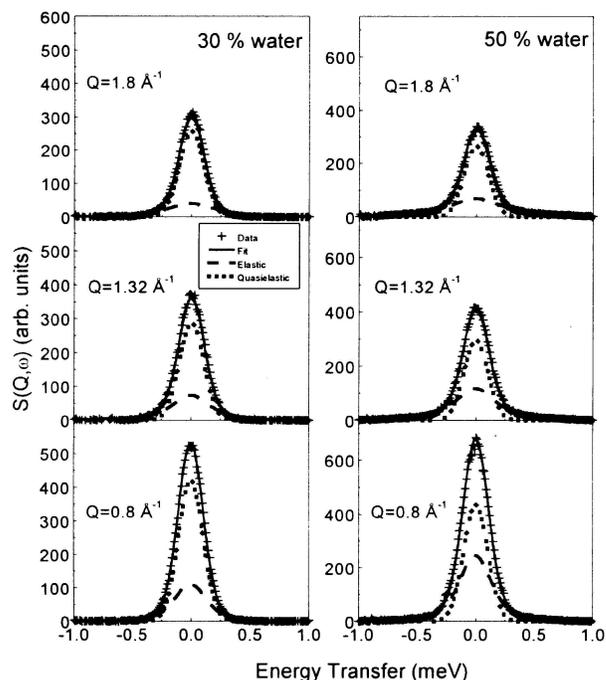
Figure 1. Typical fitted QENS spectra along with separated elastic (dotted) and quasi-elastic (dashed) components for 30 and 50% excess water in hydrotalcite.
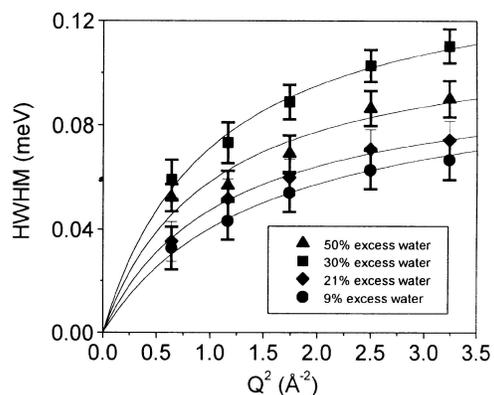
Figure 2. Variation of translational HWHM with Q^2 for different excess water sample. Solid lines are fit with random jump diffusion model (eq. (4)).

have also clearly indicated that the hydration water at lower percentages (up to ∼30%) shows that this water appears to be in a more bound state. Earlier study on dynamics of crystalline water also showed that the diffusion constant of crystalline water is significantly lower than that of the bulk water [7].

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Table 1. Dynamical parameters for translational motion of water molecule adsorbed in hydrotalcite.

Water content (wt%)	Jump length ($\langle l \rangle$) (Å)	Residence time (τ) (ps)	Diffusion constant $= l^2/6\tau$. ($\times 10^{-5}$ cm^2/s)
9	2.2	7.0	1.1
21	2.3	6.6	1.3
30	2.5	5.7	1.9
50	2.4	4.6	2.1

4. Conclusion

Results of this study have provided considerable insight into the dynamical properties of excess water in hydrotalcite. QENS measurements carried out on the excess water in hydrotalcite sample with varied amount of excess water showed that the translational motion for excess water can be best described by random translational jump diffusion model. Translational diffusion constants are found to increase with increasing amount of excess water suggesting that by increasing the amount of excess water, more and more molecules are available away from the layer surface and are relatively free to move. In other words, there is a clear difference in the magnitude of the translational motions between the layers that is attributable to the bonding interactions between water and the interlayer species. The assumption that rotational motion is unchanged is also found to be consistent with the QENS data.

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