Hydration level dependence of the microscopic dynamics of water adsorbed in ultramicroporous carbon

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ABSTRACT – Even when not functionalized intentionally, most carbon materials are not hydrophobic and readily adsorb water molecules from atmospheric water vapor. We have equilibrated an ultramicroporous carbon at several levels of relative humidity, thereby attaining various hydration levels. The water molecules were adsorbed on the pore walls (but did not fill completely the pore volume) and thus could be better described as hydration, or surface, rather than confined, water. We used quasielastic neutron scattering to perform a detailed investigation of the dependence of microscopic dynamics of these adsorbed water species on the hydration level and temperature. The behavior of hydration water in ultramicroporous carbon clearly demonstrates the same universal traits that characterize surface (hydration) water in other materials that are surface-hydrated. Thus, unless special treatment is intentionally applied to ultramicroporous carbon, the species filling its pores in various applications, ranging from hydrogen molecules to electrolytes, likely find themselves in contact with non-freezing water molecules characterized by rich microscopic dynamics.

1. Introduction

Adsorption of water on porous carbons has been approached from both the experimental point of view [1-3] and the theoretical side [4-7]. Several comprehensive reviews on the experimental results, semi-empirical analytical approaches, and modeling studies are available [8, 9]. What distinguishes adsorption of water on activated carbons from that of other fluids (nitrogen, carbon dioxide, hydrocarbons) is the strong association of water molecules through hydrogen bonding, along with weak carbon-water interactions, except for a few adsorption sites (such as oxygen-containing functional groups) that interact with water strongly via hydrogen bonding. These features lead to type V isotherms (S-shape) in water-carbon systems. In contrast with other wetting fluids, the step of micropores filling is usually absent from water adsorption isotherms on porous carbons. The sudden rise of the isotherm at about $0.4 - 0.6 P/P_0$ (relative humidity) is caused by capillary condensation in mesopores. Moreover, water adsorption not only correlates with the pore structure, but also is sensitive to carbon's surface chemistry. Although carbon-based materials are traditionally considered hydrophobic, it has been argued [10, 11] that hydrophobicity of graphite is not intrinsic, but occurs due to adsorption of a small amount of hydrocarbons from the environment. It is well known that most carbon materials adsorb water molecules from atmospheric water vapor under normal conditions, whether because of intrinsic hydrophilicity [10, 11], or surface groups, defects, etc. In porous carbon materials, unintentionally adsorbed water can exert great influence not only on the matrix, but also on the species utilized to fill the pores to provide application functionality, such as molecular hydrogen for hydrogen storage, electrolytes for electrochemical applications, etc. For example, self-diffusion of methane confined in carbon aerogel slows down significantly after residual water is removed from the native matrix [12]. For a given carbon material, the attainable hydration level depends on the relative humidity. Because carbon materials can be used in applications over a very broad temperature range, it is of interest to analyze the behavior of hydration water in carbon as a function of both temperature and hydration level, as also

suggested by the existing reviews of water adsorptions in carbon materials [8 ,9]. Such analysis is the major objective of the current study.

Figure 1. Pore size distribution of UMC material. The data were calculated from CO₂ (273 K, red lines) and N₂ (77 K, blue lines) adsorption, using NLDFT slit pore model (CO₂) and QSDFT slit-cylindrical pore model (N₂). The arrows point to the left axis for the continuous curves data and the right axis for the dashed curves data.

The ultramicroporous carbon (UMC) investigated in this work was made available by MeadWestvaco Corp. (Charleston, SC). UMC was obtained from a hard wood precursor by two-step activation with phosphoric acid and potassium hydroxide [13]. Chemical analysis showed that as-received UMC contains 4.7 wt. % oxygen and < 0.5 wt. % hydrogen, along with traces of K (1200 ppmwt), Fe (920 ppmwt), Na (540 ppmwt), Cr (500 ppmwt), Cl (450 ppmwt), Ni (180 ppmwt), and Ca (110 ppmwt). The ash content measured by combustion method is 0.53 wt. %. Fig. 1 shows results of standard N₂ (77 K) and CO₂ (273 K) adsorption measurements. UMC has high BET surface area (2540 m²/g) and large total pore volume (1.42 cm³/g at 0.995 P₀) distributed between micropores (70 %) and mesopores (30 %). The micropore volume consists of 0.21 cm³/g in ultramicropores (≤ 7 Å) and 0.71 cm³/g in supermicropores (7 – 20 Å) [14]. These properties recommend UMC as a close equivalent of best activated carbons (Maxsorb and AX-21) recognized as top class microporous adsorbents. UMC's

high uptake capacity for hydrogen (0.8 wt. %) [15], methane (15 wt. %) [16], and carbon dioxide (75 wt. %) [17] at 20 bar and 25 °C stimulated further characterization studies. It was proposed that the unusual, hysteretic H₂ adsorption at room temperature and the restricted H₂ mobility at cryogenic temperatures [14] are both correlated with the presence of defective graphene sheets [18], very short range atomic order [19], and its particular pore morphology [20]. The bright-field scanning transmission electron microscopy (STEM) images of this carbon show (002) fringes representing curled graphene sheets perpendicular to the image plane and assembled in very disordered structures (Fig. 2a). The annular dark-field STEM images in Fig. 2b suggest multiple stacking of undulated graphene sheets in quasi-parallel arrangement. At even higher magnification (Fig. 2c) the atomic structure of graphene sheets shows only short range ordered domains (about 10-15 Å) interrupted by topological defects that induce curvature and define domain boundaries.

A detailed structural analysis of water filling the pores of UMC carbon has been reported in a companion paper [21]. There, using small-angle neutron scattering (SANS), it was determined unambiguously that, even at the highest hydration level attained, water does not completely fill the

Figure 2. Electron microscopy images of UMC material: (a) bright-field STEM image; (b, c) annular dark-field STEM images.

pores. Instead, it resides on, and near the walls, in clusters of almost constant size. As it will be shown below, this conclusion is also supported by our measurements. SANS results also show that water adsorption is a slow process. During the first 10 hours of hydration, the number density of these clusters increases, but their size remains approximately constant (8-9 Å). This finding provides an important insight regarding water adsorbed in UMC. Nominally, this water is confined in carbon pores. However, considering the UMC structure revealed by high resolution SEM images (Fig. 2), we argue that it should be considered a special case of surface-bound water, which bears more resemblance to surface water in various systems rather than confined water that would completely fill the pores. In many systems, surface water is exohedral (e.g., in the case of non-porous nanoparticles with a hydrophilic surface), but there are examples of endohedral surface water (e.g., in porous silica), which exhibits the same traits as exohedral surface water.

In studies of microscopic dynamics, the distinction between surface and confined water is somewhat methodological. Confined water is characterized by two parameters: the pore size determined by the rigid host walls and the “soft” confinement of the quickly dissipating and reforming transient cage of the neighbor water molecules [22]; the latter parameter is often similar for confined and bulk water. The morphology of confinement volume is known to play an important role for the microscopic water dynamics [23]. On the other hand, surface water is not confined in the lateral directions and lacks a well-defined “rigid” confinement dimension, which is not well approximated by the thickness of the hydration layer. From preparation standpoint, surface water is usually added to the matrix not by mixing with water, but through controlled vapor exposure, in order to achieve the target hydration level. Exposure of porous matrices to ambient atmosphere often leads to formation of surface water species from water vapor. We argue that this is also the case of water vapor adsorption on high surface area, ultramicroporous carbon material (UMC).

2. Experiment

A series of binary aqueous saturated salt solutions about 20 mL prepared in open dishes were tightly sealed in glass containers and allowed to equilibrate at 25 °C for one week in a limited air volume. Simultaneously, powdered UMC material was dried at 150 °C for one week. Then pre-weighed amounts of dry UMC material (about 400 mg) were loaded in flat-plate aluminum holders, which were quickly placed in the same containers, next to the open dish saturated salt solutions, and tightly sealed. After one more week at 25 °C it was assumed that the moisture content in carbon samples reached adsorption equilibrium with the air moisture at the relative humidity of each saturated salt solution [24]. At this time the sample holders were sealed with indium gaskets for measurements. The moisture uptake in each sample was determined from the weight variations. It was found that the oven-dried carbon stored near the saturated LiCl solution (8 % RH) actually lost some weight, indicating that oven-drying (150 °C) did not remove all moisture from carbons. Vacuum drying (< 5 Pa) at 300 °C was more efficient, and a sample thus prepared was used as the driest base line (0 % RH) in the series of humidified carbons. It was verified that vacuum outgassing at 300 °C did not alter the pore structure of the carbon. The salts used and the corresponding relative humidity levels are shown in Table 1 along with the carbon weight changes and the absolute moisture uptakes corrected versus the driest carbon reference.

Table 1. Saturated salt solutions and corresponding moisture uptakes by carbon. Corrected moisture uptakes were calculated versus the vacuum-dried carbon as a reference. Only four samples (from salt solutions shown in bold fonts) were used for neutron scattering experiments.

Salt	RH %	weight change wt. %	corrected uptake wt. %	water adsorption mmol/g
NaOH	8	-4.9	0.1	0.05
LiCl	11	-4.3	0.1	0.06
MgCl₂	32	2.8	7.2	4.00
K₂CO₃	43	7.3	11.7	6.50
Mg(NO ₃) ₂	53	19.4	23.8	13.22
KI	68	54.9	59.3	32.94
NaNO ₃	74	70.5	74.9	41.61
NH ₄ Cl	78	78.8	83.2	46.22
KCl	84	92.5	96.9	53.83
K ₂ SO ₄	97	97.3	99.9	55.50

Because of the time constraints, only a few selected samples could be used for neutron scattering experiments, besides the reference baseline dry sample (0 % RH). A low thickness of the carbon samples (0.5 mm) was selected in order to control the amount of sample in the neutron beam, thus reducing the effects of multiple scattering. Quasielastic neutron scattering (QENS) measurements were performed on backscattering spectrometer BASIS [25]. The energy resolution was 3.4 μeV (full-width at half-maximum for the Q -averaged resolution value), regardless of the dynamic range of accessible energy transfer, which, depending on the spectrometer settings, was either from $-100 \mu\text{eV}$ to $+100 \mu\text{eV}$, or from $-100 \mu\text{eV}$ to $+500 \mu\text{eV}$ (the latter range could be used at the expense of the signal statistics). For each sample, we measured at first the sample-specific resolution function at the baseline temperature of 10 K, followed by measurements at higher temperatures. Besides, for each sample we collected the elastic intensity scan data, with “elastic” intensities (within $\pm 3.4 \mu\text{eV}$ energy transfer window) recorded on warming up from the baseline temperature at a rate of 1 K/min.

Throughout the paper error bars represent one standard deviation. When error bars are not visible in a figure, they are within the symbol size.

3. Results and discussion

Fig. 3 shows the evaluation of water uptake by the samples linked to the elastic intensity scan data. Water uptake data (Table 1) describe the typical sigmoidal adsorption isotherm of water [26], as expected. Adsorption is driven by hydrogen bonding between water molecules and not by van der Waals dispersion forces. As shown in Fig. 3a, the initial part of the isotherm can be fitted by the Dubinin equation [26], $a = a_o c h / (1 - c h)$. Here a is the amount of water adsorbed at relative humidity $h = P/P_o$, c is the adsorption equilibrium constant, and a_o is the concentration of primary adsorption sites. The latter was obtained by fitting ($a_o = 6.38 \text{ mmol/g}$). This value is about twice the concentration of oxygen atoms (2.94 mmol/g) from elemental analysis, suggesting that each O atom is capable of binding about two H_2O molecules at saturation. The gradual rise or water uptake at $h > 0.6$ is associated with gradual cluster development on the primary adsorption sites, but is different from capillary condensation.

Assuming that the water density in carbon pores is not much different from bulk water density, one can estimate from Table 1 that the maximum water uptake at the highest humidity level is close to $1.0 \text{ cm}^3/\text{g}$. This is smaller than the total pore volume in UMC ($1.42 \text{ cm}^3/\text{g}$) measured by a wetting fluid, such as N_2 at 77 K. Water does not fill completely the available porosity in UMC. The ratio between the maximum adsorbed water volume and the volume measured by an adsorptive that does completely wet the surface (liquid N_2) defines a hydrophilicity index (HI) [27]. The HI value for UMC is 0.70, comparable to other partially hydrophilic porous carbons [27-29]. Incomplete filling by water of the porosity accessed by nitrogen adsorption was also observed by small angle X-ray scattering for several granular activated carbons [30].

Figure 3 (a) (left panel). Water adsorption as a function of relative humidity. Filled symbols (red and blue), left axis: data from Table 1, last column. Solid line: a fit by the Dubinin equation [26]. Red symbols indicate samples measured by neutron scattering. Open symbols (red), right axis: the relative water content estimated from the elastic intensities measured at the baseline temperature (with the dehydrated sample intensity subtracted); see plots in the right panel. **(b) (right panel).** Elastic intensity scan data averaged over $0.4 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$. Inset: hydration water elastic intensities, each multiplied by a constant, to bring them to unity at 20 K.

Because of the large incoherent neutron scattering cross-section of hydrogen compared to all other elements, all scattering intensities measured in this work are dominated by protons in the sample. The elastic scattering intensity provides a good measure for the relative amount of protons in the sample, but only at low temperatures, when there is no measurable broadening of the scattering signal, because the diffusion-type mobility has ceased. Fig. 3b demonstrates the scattering intensity at the baseline temperature progressively increasing as a function of hydration level. The dehydrated sample exhibits sizable elastic scattering, suggesting the presence of a significant amount of hydrogen-bearing species that could not be removed from the sample despite the treatment. This incoherent elastic scattering might be associated with protons in oxygen-containing functionalities ($-\text{COOH}$, $-\text{OH}$, etc.), C–H bonds, or even H_2O molecules that are immobilized near the carbon walls.

When the baseline intensity originating from this hydrophilic residue is subtracted, the relative water content in the sample as a function of relative humidity can be estimated as shown in Fig. 3a (right axis). For comparison, the data from Table 1 are also shown in Fig. 3a (left axis). Fig. 3b demonstrates that the hydrophilic residue in the dehydrated sample does not exhibit diffusion-like mobility even at ambient temperature, as evidenced by purely vibrational (Debye-Waller) temperature dependence of its elastic scattering intensity.

The temperature dependence of the neutron scattering data in Fig. 3b, especially prominently seen for the RH = 84% sample, but also visible to some extent in the lower hydrated samples, is archetypical of hydration water, essentially ruling out the presence of pores of ca. 20 Å and larger diameter completely filled with water, which would have manifested itself in a freezing transition. The rapid decrease in the elastic scattering beginning for the RH = 84% sample at about 200 K is due to super-Arrhenius temperature dependence of hydration water structural relaxation [31]. It is well known empirically that hydration water in various systems behaves as a glass-forming liquid characterized by non-Arrhenius structural relaxation, avoiding crystallization on cooling down. Moreover, the dynamic arrest at 228 K, which would be associated with the completion of the tetrahedral network in supercooled water [32, 33], is also avoided in surface water due to disruption of the hydrogen bonding

network. Therefore, the scattering intensity perceived as elastic rapidly decreases with temperature due to super-Arrhenius broadening of the scattering signal (which is inversely proportional to the relaxation time). At ambient temperature, the fast structural relaxation of hydration water yields the scattering signal so broad that it does not contribute anymore to the elastic line. Hence, the elastic intensity curves practically merge at 300 K, since only the immobilized hydrogen-bearing species on the carbon pore walls still scatter elastically at this temperature. Super-Arrhenius temperature dependence of the structural relaxation and the concomitant characteristic elastic intensity temperature scan curve, such as observed in Fig. 3b, is conditioned upon sufficient hydration level; if the hydration is too low, super-Arrhenius temperature dependence is not observed [34-36]. Too low hydration level means insufficient “transient caging” effect on water molecules by their neighbors, which is the underlying reason for super-Arrhenius structural relaxation in water [34-36].

Figure 4. Zoomed-in QENS resolution data measured at 10 K (averaged over $0.4 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$).

Figure 5. QENS data measured at 300 K (averaged over $0.4 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$).

For the later discussion, it is important to make sure that even the lowest hydrated sample, RH = 11%, possesses the amount of hydration water that gives rise to the scattering intensity in excess of the baseline scattering from the dehydrated sample. This is evident from Fig. 4, which shows the sample-specific resolution function data at 10 K, and Fig. 5, which presents the QENS data at 300 K. The excess elastic intensity measured at 10 K for the RH = 11% sample with respect to the dehydrated sample (Fig. 4) transforms into the visible excess QENS signal at 300 K (Fig. 5). Qualitatively, the width of QENS signal in Fig. 5 rapidly increases with the hydration level, which corresponds to the rapidly decreasing average relaxation time as the hydration level is increased. The hydration water molecules become progressively more mobile at the increasing distances from the walls. The QENS signal in Fig. 5 does not merely increase in strength as a function of hydration level while retaining its width, but indeed becomes broader, as evidenced by the signals from the dehydrated and the RH = 11% samples that merge at high energy transfers, which is clearly not the case for the higher hydrated samples.

Figure 6. Temperature dependence of QENS data (averaged over $0.4 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$) for the lowest-hydrated sample.

The detailed analysis of the temperature dependence of the relaxation times in hydration water will be presented below. However, certain conclusions can be drawn readily from plotting the QENS signal as a function of temperature. Fig. 6 and Fig. 7 show such temperature dependence for the lowest and highest hydrated samples, respectively. The temperature dependence of the QENS signal is much more pronounced for the highest hydrated sample, in agreement with the rapidly changing elastic scattering intensity from this sample as presented in Fig. 3b. As mentioned above, the strong (super-Arrhenius) temperature dependence of the relaxation time is conditioned upon the hydration level being sufficiently high for a pronounced “transient caging” effect to be experienced by water molecules.

Figure 7. Temperature dependence of QENS data (averaged over $0.4 \text{ \AA}^{-1} < Q < 1.8 \text{ \AA}^{-1}$) for the highest-hydrated sample.

While relaxations in hydration water can be readily measured by various spectroscopic techniques, a major strength of QENS as a scattering technique is due to its ability to deduce the geometry of relaxation processes from the dependence of the scattering signal on the scattering momentum transfer, Q . A Q -independent signal width is a signature of localized mobility, whereas Q -dependent broadening is characteristic of translational diffusion [37]. Converting scattering intensities, $I(Q, E)$, into dynamic susceptibilities, $\chi''(E) = I(Q, E)/n_b(E)$, where $n_b(E)$ is the thermal Bose factor, is a powerful way to elucidate the Q -dependence of QENS broadening without resorting to elaborate data fitting. This is due to the fact that a maximum in $\chi''(E)$ represents a characteristic relaxation time, $\tau \sim \hbar/E$, where $\hbar$ is the reduced Planck constant. The dynamic susceptibilities for the highest hydrated sample at 300 K are presented in Fig. 8 as a function of Q . The relaxation dynamics in hydration water measured over a broad energy transfer range (up to +500 μeV) cannot be viewed as a single process, but must be described instead as a superposition of two processes, as evidenced by the minimum in the susceptibility spectra. This minimum separates the faster dynamics visible at higher energy transfers,

traditionally (though overly simplistically, as discussed in [38]) described as “rotational”, from the slower dynamics visible at lower energy transfers. The translational character of this slower dynamic process is evident from the pronounced Q -dependence of the first maximum position (at low energy transfers). At higher Q values, this maximum position moves outside the range of energy transfers accessible in the experiment. Regardless, the minimum separating slower translational from faster “rotational” dynamics always becomes less pronounced at higher Q due to blurred distinction between these two processes on the short length scale [39]. The important conclusion drawn from the susceptibility spectra presented in Fig. 8 is that, with a sufficiently wide dynamic range available in an experiment on hydration water, a two-component fit would always be needed, whereas one-component fit might suffice for a measurement over narrower dynamic range. The translational character of the slower of the two dynamic components is also evident.

Figure 8. Q -dependence of QENS data measured for the highest-hydrated sample at 300 K converted to dynamics susceptibilities, $\chi''(E) = I(Q, E)/n_b(E)$, where $n_b(E)$ is the thermal Bose factor.

Until now we have made qualitative observations of hydrated water dynamics. To perform quantitative analysis, we fit the QENS data using DAVE package [40] with the following expression:

$$I(Q, E) = [x(Q)\delta(E) + (1 - x(Q))S(Q, E)] \otimes R(Q, E) + B(Q, E) \quad (1)$$

where $\delta(E)$ is a delta function centered at zero energy transfer ($E = 0$), $x(Q)$ represents the fraction of elastic scattering in the signal, $B(Q, E)$ is a linear background term, $B(Q, E) = C_1(Q)E + C_2(Q)$, $R(Q, E)$ is the resolution function, and $S(Q, E)$ is the model dynamic structure factor. Because the data fits were performed for the data collected with high statistics over ± 100 μeV energy transfer, the background term described both the measurement background and the contribution from the processes too fast for the ± 100 μeV dynamic range, including the “rotational” mobility. Even though the data collected over ± 100 μeV describe only one (translational) component, this component is somewhat “stretched” compared to a Lorentzian, and thus requires the use of a Cole-Cole distribution function:

$$S(Q, E) = \frac{1}{\pi E_0(Q)} \frac{(E / E_0(Q))^{-\alpha(Q)} \cos \frac{\pi\alpha(Q)}{2}}{1 + 2(E / E_0(Q))^{1-\alpha(Q)} \sin \frac{\pi\alpha(Q)}{2} + (E / E_0(Q))^{2(1-\alpha(Q))}} \quad (2)$$

Here the parameter $E_0(Q)$ is analogous to the half-width at half maximum (HWHM) of a Lorentzian function, which is the limiting case of Eq. (2) when the “stretching” parameter $\alpha(Q) = 0$. At each measurement temperature, the QENS broadening parameter $E_0(Q)$ was determined at $Q = 0.5, 0.7$, and $0.9 \text{ \AA}^{-1}$. Then the Q dependence of the relaxation time, computed as $\hbar/E_0(Q)$, was plotted as shown in Fig. 9. It is evident that relaxation times extracted from the fits represent a translational diffusion process with a pronounced Q dependence down to the lowest temperatures we could analyze, which was 220 K for the RH = 84% sample and 260 K for the RH = 11% sample. The longest measurable relaxation time is limited by the spectrometer resolution (3.4 μeV , FWHM, which corresponds to ca. 0.4 ns). Furthermore, the translational process is well approximated by continuous Fickian diffusion (rather than, e.g., jump diffusion), as evidenced from the exponent, γ , being close to 2 in the power law fit $\tau(Q) = \tau_0 Q^{-\gamma}$, as shown in Table 2.

Figure 9. Hydration water relaxation times obtained using fits with Cole-Cole model scattering.

Table 2. Power law fit of the Q -dependence of the relaxation times, fit $\tau(Q) = \tau_0 Q^{-\gamma}$.

Sample	T [K]	τ_0 [ps]	γ
RH = 84%	300	6.6 ± 0.2	2.0
	280	10.7 ± 0.3	2.1
	260	21.8 ± 0.7	2.1
	240	59.7 ± 2.1	1.8
	220	218.3 ± 14.7	2.0
RH = 43%	300	11.3 ± 0.1	2.2
RH = 32%	300	17.2 ± 0.3	2.4
RH = 11%	300	50.4 ± 2.9	1.9
	280	69.4 ± 7.0	2.1
	260	113.2 ± 10.6	1.9

Figure 10. Temperature dependence of the average relaxations times for hydration water.

The so obtained average relaxation times, τ_0 , which are related to translational diffusivity of hydration water, are plotted in Fig. 10 as a function of temperature. At 300 K, the relaxation times become shorter with the increased hydration level, as was already evident from the data in Fig. 5. The five temperature points measured for the RH = 84% sample clearly demonstrate a super-Arrhenius temperature dependence of the relaxation time, as we already mentioned above in discussion of Fig. 3b. Super-Arrhenius temperature dependence of the relaxation time for confined water has been observed in a variety of carbon-based materials probed over the temperature range comparable to ours [41-44]. Yet hydration water in UMC is remarkable in that it does not fill the pores completely. This is due to the peculiar water adsorption properties of UMC, as discussed in the companion paper [21]. The hydration water in UMC does not freeze; instead, its relaxation time rapidly becomes longer at lower temperatures, leading to the disappearance of the QENS broadening within the resolution line and the concomitant leveling off of the elastic scattering intensity at low temperatures. Even lacking a sufficient number of temperature data points for the other samples, we nevertheless can infer from Fig. 3b, that the

lower hydrated samples behave in the same qualitative manner as the RH = 84% sample, as far as the temperature dependence of the relaxation time is concerned. The data in Fig. 10 suggests that the relaxation times temperature dependence becomes stronger (that is, more super-Arrhenius) as hydration level is increased. This observation is corroborated by the data in Fig. 3a onset, where the elastic intensities put on the same zero-to-unity scale change with temperature much faster for the higher hydrated samples. The stronger super-Arrhenius dependence of the relaxation time for higher hydrated samples is a consequence of the more developed hydrogen bonding network [34-36]. This suggests that at low temperatures, unlike under ambient conditions, the relaxation rate will scale not directly, but inversely, with hydration level [34-36]. That is, at sufficiently low temperatures, the higher hydrated samples should exhibit slower dynamics compared to the lower hydrated samples.

4. Conclusion

The hydration level attained by UMC depends on the relative humidity during sample exposure. At low humidity, the initial hydration is due to the presence of hydrophilic species immobilized on the pore walls. Further hydration is facilitated by interactions of vapor water molecules with the water molecules already present in the sample. Water in ultramicropores ($< 7 \text{ \AA}$) appears as immobile on the resolution scale of quasielastic neutron scattering, giving rise only to elastic scattering signal. On the other hand, water in micropores ($< 20 \text{ \AA}$) exhibits rich dynamics measurable by quasielastic neutron scattering, which strongly depends on the hydration level. Even in the highest hydrated sample, hydration water does not fill those micropores completely, in agreement with the results of the SANS structural study of water in UMC [21], which indicates peculiar properties of UMC among carbon-based materials. Regardless of the hydration level, from the lowest to the highest, water molecules adsorbed on the pore walls exhibit Fickian long-range translational diffusion, along with the localized “rotational” mobility. Hydration water in UMC does not freeze. The characteristics traits of the microscopic

dynamics of hydration water in UMC are qualitatively the same as for hydration water in many hydrophilic matrices with variable hydration levels that are surface-hydrated. In particular, the diffusion rate, related to the main structural relaxation time of hydration water, exhibits super-Arrhenius temperature dependence, which becomes a stronger function of temperature as the hydration level is increased. At ambient temperature, the diffusive mobility scales with the hydration level. However, extrapolation of the temperature dependence suggests the opposite trend at very low temperatures, where the higher hydrated samples should exhibit a lower relaxation rate compared to the lower hydrated samples, due to the more developed hydrogen bonding network. Thus, molecules hosted by ultramicroporous carbon in various applications will witness a different trend in the microscopic dynamics of their water co-solvent, depending on the application temperature range. For instance, electrolytes, with the ambient and near-ambient application temperature range, will see the diffusivity of the water co-solvent that becomes faster with the increasing hydration level. On the other hand, molecular hydrogen, in low-temperature applications such as hydrogen storage, might see the opposite trend, when the relaxation of water co-solvent becomes slower with the increasing hydration level. Since a complete dehydration of carbon is difficult to achieve, the microscopic dynamics of hydration water should always be taken into consideration as a factor potentially influencing other guest molecules in applications of carbon-based materials.

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