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# Clustering of water molecules in ultramicroporous carbon: In-situ small-angle neutron scattering☆

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## ABSTRACT

The adsorption of water is central to most of the applications of microporous carbon as adsorbent material. We report early kinetics of water adsorption in ultramicroporous carbon using in-situ small-angle neutron scattering. It is observed that adsorption of water occurs via cluster formation. Interestingly, the cluster size remains constant throughout the adsorption process whereas the number density of clusters increases with time. The role of surface chemistry of microporous carbon on the early kinetics of adsorption process was also investigated. The present study provides direct experimental evidence for cluster assisted adsorption of water molecules in microporous carbon (Do-Do model).

## 1. Introduction

Microporous carbon continues to be one of the most important adsorbents for the removal of organic compounds and is a promising material for storage of $H_2$ and $CO_2$ because of its high surface area, tailored surface chemistry and pore size, as well as low cost [1–4]. The adsorption of water molecules on carbon surfaces is a phenomenon that is pertinent to a wide variety of commercial applications [5,6]. The presence of water vapor adversely affects the adsorption capacity of microporous carbon [7] and limits its effectiveness as an adsorbent material in humid environments. In spite of the variety of commercial applications of microporous carbon, the fundamental understanding of water adsorption in carbon is still incomplete.

Adsorption mechanism of water in carbon micropores is strikingly different from that of non-polar fluids [8]. The adsorption of non-polar fluids is governed by strong dispersion interactions, leading to significant adsorption even at low relative pressures [1,3]. In contrast, water adsorption on carbon is determined by the balance between fluid-solid and fluid-fluid interactions. A recent investigation of the hydrophobicity of carbon surfaces by Kozbial and Wei et al. [9,10] showed that clean (oxygen-free) carbon sites on basal plane edges are intrinsically more hydrophilic than the rest of carbon sites on basal planes. Numerous experimental and theoretical studies on adsorption of water in carbon micropores [11–18] have shown how much sensitive is water adsorption behavior to the nature of hydrophobic or hydrophilic environment [19,20]. The strength of hydrogen bonds between water molecules increases in hydrophobic environments, whereas the hydrogen bonding between water molecules decreases in hydrophilic environments [21–23]. Understanding water behavior in a confined hydrophobic environment may potentially provide insights into the cellular mechanism of water channels in a lipid membrane [24].

The adsorption isotherms of water vapor on carbon-based materials have been studied extensively both experimentally and theoretically [8,15,25–32]. Early work on water adsorption in microporous carbon was done by Dubinin [8] and subsequently by Dubinin and Serpinsky (DS) [25]. Recently, Do et al. [26,33] proposed a new adsorption mechanism of water in microporous carbon. In this model it is assumed that oxygen containing functional groups on the carbon surface are the primary sites for adsorption of water molecules. Adsorbed molecules act as nucleation sites for

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further adsorption of water *via* hydrogen bonds which eventually leads to penetration of water clusters into the micropore. Indeed, occurrence of ordered water clusters inside carbon micropores was confirmed by X-ray diffraction [34,35] and small-angle X-rays scattering [31,35,36] at various relative humidity levels and under equilibrium saturated conditions. However, experimental evidence on formation of clusters during early stage of adsorption kinetics is still lacking. Further, in-situ measurements to probe the kinetics of adsorption of water molecules and its clustering behavior on porous carbon has not been yet reported.

Small angle neutron scattering (SANS) takes advantage of the high neutron sensitivity towards hydrogen isotopes. This allows for water adsorption kinetics measurements of greater accuracy compared to small angle X-rays scattering (SAXS), which is less sensitive for water. This work presents results of in-situ SANS experiments of water adsorption in microporous carbon. Direct evidence was obtained of cluster formation during early-stage of adsorption kinetics. In a parallel study [37] the dynamics of water molecules adsorbed at equilibrium conditions from various levels of humidity on the same microporous carbon was investigated by quasielastic neutron scattering (QENS). It was found that the hydration water in this carbon does not freeze, and does not fill the pores completely, even at the highest hydration levels. This strongly suggests that cluster structures are always formed by long time equilibration at all levels of hydration, from low to high. These results complement the picture obtained from the present study. Combined, these observations confirm the Do-Do model [22] of water adsorption on microporous carbons.

## 2. Experimental details

### 2.1. The UMC carbon

The experimental ultramicroporous carbon (UMC) was obtained from MeadWestvaco Corporation (Charleston, SC). It was prepared through phosphoric acid activation of wood followed by secondary activation with KOH [38]. The detailed properties of UMC such as surface area, porosity and morphology have been reported elsewhere [1,39–43]. In summary, this is a high surface area (2540 $m^2$/g) porous carbon (1.42 $cm^3$/g total pore volume) with a significant volume of ultramicropores (0.21 $cm^3$/g) and supermicropores (0.71 $cm^3$/g) [40]. Elemental analysis showed that as-received UMC contains 4.7 wt % oxygen and <0.5 wt % hydrogen along with ppm traces of K, Na, Fe, Ni, Cr, Cu Cl, Ca (total ash content 0.53 wt %). To understand the role of surface chemistry on the adsorption kinetics of water, a UMC sample was analyzed by temperature-programmed desorption (TPD) in helium (10 °C/min) combined with simultaneous mass spectroscopic (MS) detection (Fig. 1). An Autosorb 1C (Quantachrome) instrument coupled with a Prisma (Pfeiffer) mass spectrometer was used. It was found that desorption of weakly bound, physically adsorbed water was complete below about 200 °C. Water release continued between 200 °C and 800 °C but with much lower intensity, and was accompanied by simultaneous release of $CO_2$ followed by that of CO. The latter species originate from decomposition of carboxylic, lactone, and phenolic groups on carbon. Release of CO from decomposition of ketones and pseudoquinone groups reached the maximum rate at about 900 °C and ended above 975 °C. Small amounts of $H_2$ were released above 900 °C. Globally, the TPD-MS result shows that all hydrophilic oxygen-containing groups decompose below 950–1000 °C. Using this information, the hydrophobic UMC sample used in the SANS experiment was prepared by heat treatment at 975 °C for 30 min in a flow of inert gas. The hydrophobic UMC sample thus prepared was kept in desiccator and was additionally dried overnight at 200 °C in a vacuum furnace before loading in the SANS cell.

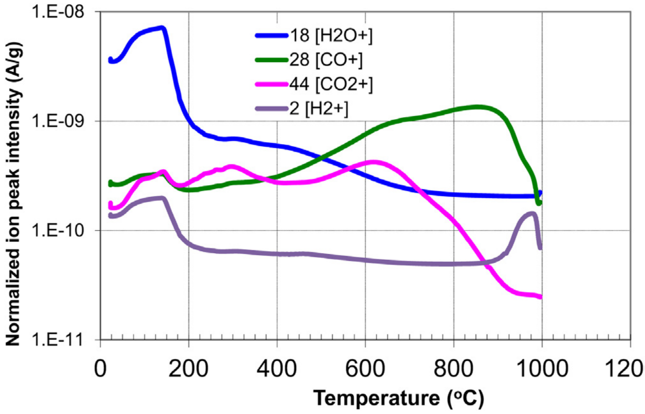

**Fig. 1.** Temperature-programmed desorption analysis of oxygenated surface groups on UMC. Note the logarithmic scale of mass-spectrometer signals corresponding to various desorbed gas species. (A colour version of this figure can be viewed online.)

### 2.2. Initial SANS characterization of UMC under vacuum

SANS experiments were carried out in the Bio-SANS instrument at the High-Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory [44]. Two different instrument configurations were used to cover a wide range of scattering wave vector $Q = 4\pi \sin\theta/\lambda$, where $2\theta$ is the scattering angle and $\lambda$ is the wavelength of the neutrons. The sample-to-detector distances of 1.13 m and 12.83 m at a wavelength of 6 Å gave a *Q* range of0.005 $\AA^{-1} \le Q \le 0.55\ \AA^{-1}$. The wavelength spread $\Delta\lambda/\lambda$ was set to 0.15 by a neutron velocity selector. The scattering intensity profiles *I*(*Q*) versus *Q*, were obtained by azimuthally integrating the processed 2D, $Q_x \times Q_y$ *images*, which were normalized to incident beam monitor counts, and corrected for detector dark current, pixel sensitivity and background scattering from the quartz cell. The quartz cuvettes of thickness 2 mm, mounted in the humidity chamber, were used for SANS measurements. The diameter of sample aperture, i.e., the beam size of neutrons on the sample was 10 mm. Thus, the total sample volume irradiated was ~0.16 $cm^3$. Bulk density can be determined by weighing powder loaded sample holder with the known internal volume. The bulk density in present case is estimated to be 0.25 g/$cm^3$. Thus, the total weight of the sample exposed to neutron beam is approximately 0.04 gm. The SANS profiles are normalized by the amount of carbon in neutron beam for all measurements.

### 2.3. In-situ SANS experiment on UMC under controlled environment

Water adsorption on UMC was monitored by in-situ SANS using a humidity chamber in the neutron flux placed at a 6.83 m sample-to-detector distance, to cover Q-range of 0.04 $Å^{-1}$ to 0.5 $Å^{-1}$. Humidified air was generated by using a relative humidity (RH) generator (Model RH-200, L&C Science, Hialeah, FL). The control RH sensor in the RH generator was positioned close to the sample position and another RH sensor (SHT75, Sensirion, Switzerland) was employed for simultaneous, independent RH measurement for consistency in the sample cell. The water reservoir of the RH generator was filled with 99.96% $D_2O$ (Cambridge Isotope Laboratories, Tewksbury, MA). $D_2O$ was used instead of $H_2O$ to achieve the desired humidity in the humidity chamber to avoid the incoherent scattering from hydrogen.

Two types of adsorption experiments were performed. First, water adsorption kinetics on the as-received UMC sample (vacuum-dried at 200 °C of physisorbed water but having unaltered all inventory of oxygen-containing groups) was measured at 50% RH by recording SANS data every 5 min for up to 9 h in total. A similar