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Towards a better understanding of water adsorption hysteresis in activated carbons by scanning isotherms

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ABSTRACT

The occurrence of water sorption hysteresis associated with the filling of micro and narrow mesopores (particularly for pores of widths smaller than ca. 3 nm, where nitrogen and argon isotherms at their boiling temperatures, i.e. 77 K and 87 K, respectively, are known to be reversible) provides additional opportunities for textural characterization. In this work systematic water scanning desorption isotherms within the hysteresis loop were carried out on well-characterized activated carbons with varied textural features and surface chemistry. Accurate micro-mesopore analysis was obtained by means of nitrogen, argon and carbon dioxide adsorption experiments coupled with advanced density functional theory methods (i.e., NLDFT, QSDFT). The obtained results indicated that water adsorption/desorption phenomena for pores of different sizes take place independently from each other. This investigation constitutes a starting point for the interpretation of water adsorption hysteresis by means of scanning desorption measurements.

1. Introduction

Although the potential use of water as a probe for surface chemistry and pore structure characterization of porous carbon materials has led to a lot of interest in the last years [1–9], much remains to be done to improve our understanding of the involved mechanisms. In fact, and even though several theories have been proposed to describe the adsorption isotherm of water on activated carbons, still none can be used satisfactorily for all types of activated carbons and in the whole range of relative pressure [2].

The use of water adsorption is attractive because: i) it can be performed at room temperature, ii) water has a very small kinetic diameter (0.28 nm) [6] which allows it to enter pores even smaller than the ones accessible to carbon dioxide [10] and iii) it is sensitive to surface chemistry. Currently, the most accepted mechanism that can better describe the adsorption of water on activated carbons claims that water molecules are first adsorbed on primary active sites on the surface of the carbon. Then the adsorbed water molecules act as secondary sites for further adsorption of water to form a cluster and as the relative pressure increases these clusters grow and finally merge to fill the micropores [11]. So although at low relative pressures the controlling factor in water adsorption is the surface chemistry of the carbon, at higher relative pressures both surface chemistry and pore structure play an important role for the water adsorption/desorption mechanism [2,12]. Bearing this in mind, it is clear that adsorption of water on activated carbons is quite different from that of non-associating simple fluids, such as nitrogen, carbon dioxide, or hydrocarbons [13]. The main underlying differences arise from the strong water–water interactions, the weak water–carbon interactions, and the formation of hydrogen bonds with oxygen and nitrogen groups on the surface of the material. Hence, the models developed to describe the behaviour of simple fluids in confined spaces cannot be applied to water in porous carbons [1].

Moreover, water adsorption in activated carbons exhibits a hysteresis loop that cannot be explained by capillary condensation theory. The hysteresis indicates that during the adsorption and/or desorption process the water molecules form different molecular structures [14]. The properties of the carbon material, such as pore shape, pore connectivity and surface chemistry, but also

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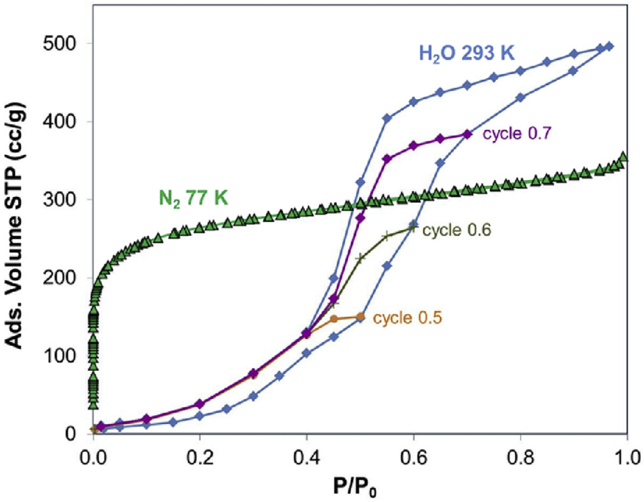

Fig. 1. Comparison between the water (273 K) and the nitrogen (77 K) isotherms obtained for the same activated carbon (BPL).

operational variables like temperature or equilibration time, influence the position, the extension and width of the water hysteresis loop [12,15–17].

Nowadays, there is a lack of methods to perform a complete and integrated characterization of the textural and surface properties of activated carbons in the micropore region (pore size < 2 nm). In fact nitrogen and argon adsorption at their boiling temperatures (77 and 87 K, respectively) are reversible up to pore diameters of ca. 3 nm [18], whereas water is one of the few adsorbents to exhibit hysteresis even in micropores. Hence, it is worthwhile to investigate the potential of water hysteresis scanning isotherms for obtaining more information about the textural and surface features of these materials (this can be visualized in Fig. 1 and will be further discussed in the results section). Hysteresis scanning isotherms are measured by reversing the direction of the gas pressure variation in the adsorption or desorption process only in the relative pressure range where hysteresis occurs, and once the initial hysteretic adsorption/desorption curve (the so-called boundary adsorption/desorption isotherm) has been obtained.

Scanning hysteresis behaviour within the context of typical capillary condensation into mesopores was already studied for the first time by Van Bemmelen in 1897 [19], and a few decades later by Everett and others (ref [20] and references therein), who pointed out that the description of the scanning curves cannot only be achieved based on the models of adsorption in individual pores and that it is necessary to consider a cooperative nature of capillary condensation/evaporation, including pore network effects. Although for some years this methodology seems to have been set aside, very recently it has gained the attention of the adsorption scientific community because of the availability of ordered mesoporous molecular sieves which serve as model substances. Specifically, this methodology was applied to N$_2$, Ar and Xe isotherms in order to obtain new useful information about the pore network geometry, including its connectivity and pore size distribution, of porous materials with different structures, which cannot be revealed from the main adsorption and desorption isotherms [21]. In the case of water adsorption, the study of the scanning curves within the hysteresis loop has been limited to theoretical studies [22] or to isolated experiments on very specific samples [6,23].

Therefore, it seemed necessary to carry out a systematic study by water scanning desorption isotherms of well-characterized activated carbons and thus investigate the potential of this technique to get new useful information regarding the textural and surface characterization of this kind of materials.

To attain this goal, and in order to have a complete picture of the process, three commercial activated carbons with different textural properties and hydrophilicity were fully characterized and then submitted to water desorption scanning measurements, as described in the experimental section. The varied features of these materials, especially their different surface oxygen content, made it possible to distinguish between the influence of the pore structure and the surface chemistry on the observed water scanning desorption performance.

Summing up, this work constitutes a first systematic approach to explore the usefulness of water desorption scanning isotherms for (i) investigating the underlying mechanisms that govern the water sorption processes in carbon micropores, (ii) the potential of water desorption hysteresis scanning as a complimentary tool for the pore structure and surface chemistry characterization of activated carbons.

2. Experimental

The selected activated carbons were manufactured by Blücher GmbH (Blücher), Cabot Norit (110362) and Calgon Carbon (BPL) and a comparison between their textural properties and oxygen content is presented in Table 1. The choice of these three activated carbons allowed us to perform the following sequential study: i) first of all, a highly hydrophobic activated carbon with a highly developed porosity (Blücher) was studied in order to isolate the effect of the textural properties of the material on its water scanning behaviour, and ii) the contribution of the surface chemistry was evaluated by the comparison of the results obtained with two activated carbons (Norit and BPL) with similar textural properties and different (high) oxygen contents.

Complete and scanning water desorption isotherms were carried out at 293 K using a gravimetric water sorption analyser (Aquadyne DVS, Quantachrome Instruments). Scanning isotherms are normally performed by repeatedly loading and unloading the adsorbent in the relative pressure range where hysteresis occurs. However, in the case of water sorption on surfaces with polar surface functionality, irreversible changes to the surface chemistry cannot be ruled out and, therefore, we used a fresh sample from the same homogeneous batch to carry out each water sorption measurement. Thus, after the initial adsorption/desorption isotherm was obtained, another fresh sample was taken and the adsorption branch was measured only up to a relative pressure which is smaller than the saturation pressure. Consequently only a portion of the pore system was filled with the probe molecule before the

Table 1
Textural parameters, calculated from the N$_2$ adsorption isotherms at 77 K, and oxygen content, measured by XPS, of the selected activated carbons.

Activated carbon	S_{BET} (m^2/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g) NLDFT	Oxygen content (wt. %)
Blücher	2317	1.61	0.47	1.9
110362	1076	0.12	0.39	16.9
BPL	1002	0.15	0.37	13.4