

INFLUENCE OF THE DYNAMICS OF ADSORPTION ON THE WATER ISOTHERM FOR ACTIVATED CARBONS.

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Introduction

The authors have recently been involved [1,2,3] in the study of the adsorption of water vapour on activated carbon. These studies included measuring water isotherms and the dynamics of water adsorption. The measurement techniques employed in these studies produced different results; the principle reason for this appears to be the length of time allowed for the equilibration of the sample during the determination of the isotherms. This research attempts to quantify this phenomenon and to explain it in terms of pore size distribution of the carbons.

Experimental

Static water adsorption isotherms for four different commercial carbons, BPL HA 12x30, SC II 12x30 (both Chemviron Carbon), R1 Extra and C Granular (both Norit), were measured gravimetrically at 296K using two different methods.

In method 1, the isotherms were determined automatically using a HIDEN Analytical IGAsorp. The carbon samples (approx. 100 mg) were outgassed at 120 C until no further weight loss was observed (2 hours, 10^{-4} mbar), and were cooled under vacuum to 23 C. The samples were exposed to a constant partial pressure of water vapour until equilibrium was attained. The partial pressure was then altered and the process repeated to obtain a full isotherm. Attainment of equilibrium was achieved when the mass uptake of the sample did not fluctuate by more than 1% during 5 minutes. This led to short equilibrium times of between 4-10 hours. The resulting isotherms will be referred to as "fast isotherms".

In the second method (method 2), the isotherms were determined manually. Carbon samples (ca. 10 g) were placed in a glass container (after outgassing) and were weighed accurately (10^{-6} g). The samples were then placed in a climatic chamber (WEISS type 305 SB/+10 IU/ 80

DU) at 296 K and exposed to a constant partial pressure of water vapour until equilibrium was attained. The partial pressure was then altered and the process repeated to obtain a full isotherm. Regular weighing of the samples showed equilibrium conditions to be established only after 4-6 days; although after a few hours a pseudo-equilibrium was reached. The dynamics of adsorption in the first 4-10 hours can be described rather accurately by a semi-empirical equation [3], which suggests surface diffusion being the rate controlling step. After this first, rather steep rise, the weight of the carbon samples continues to increase, at a much slower rate, for several days until real equilibrium is reached. The isotherms measured with this method will be referred to as "slow isotherms".

These findings were confirmed by two more independent methods: using the IGAsorb without any pre-set equilibrium criteria, and pre-humidifying individual gas mask canisters filled with the same carbon at an air flow of 30 l/min with a known relative humidity. The same phenomenon was observed in both cases.

Results and Discussion

The isotherms for BPL HA obtained using both methods (fast and slow) are shown in Figure 1, the results for the other carbons used in this study were similar.

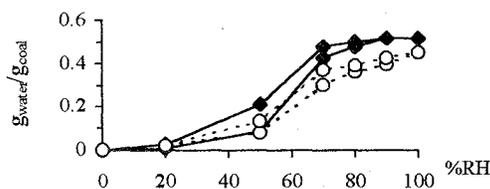


Figure 1 : Comparison of water isotherms on Chemviron BPL HA at 23°C: Slow (closed diamonds) vs Fast (open circles) isotherms

Qualitatively the isotherm obtained with the slow method gives a higher total water uptake. The hysteresis effect in the region of capillary condensation is comparable to the isotherm obtained with the fast method, but the desorption branch is displaced to higher RH's until 20% RH is reached.

The adsorption branch of the isotherms was quantitatively evaluated using the Dubinin-Astakhov equation [4]. The results for the water isotherms on BPL HA, depicted in Figure 1, are given in Table 1.

Parameter	Slow isotherm	Fast isotherm
W_0 (cm ³ /g)	0.52	0.40
n	3.0	2.6
βE_0 (kJ/mol)	1.5	1.4

Table 1: Fitted parameters of the Dubinin-Astakhov eqn. for the water isotherms on BPL HA at 23°C

The value of βE_0 is nearly identical for both isotherms. This could be expected as this energy is linked to the proportion of hydrophilic sites on the carbon, and hence on the inflection point of the isotherms, which should be independent of the adsorption kinetics. But the micropore volume W_0 and the parameter n (related to the gradient of the adsorption branch of the isotherm after the inflection point) are significantly greater in the case of the slow isotherm. The difference, for this carbon (BPL HA), is about 20%.

The value of the micropore volume W_0 , as calculated from N₂-adsorption at 77K, varies between 0.48 cm³/g (Dubinin-Radushkevich) and 0.43 cm³/g (Density Functional Theory). The value of 0.40 cm³/g obtained from the fast isotherm is acceptable since it is generally agreed in the literature that the micropore volume W_0 is underestimated when calculated from water adsorption data.

The higher value of W_0 for the slow isotherm could be explained by adsorption of water in ultra-micropores. The smaller size of the water molecule compared to N₂ (2.3 Å versus 3.5 Å), should enable water to penetrate in pores with pore entrances well below the lower limit of N₂-porosimetry (5 to 7 Å).

This process would be very slow as the thermal energy of the water molecule, even at the relatively high temperature of 296K, will only allow a very slow diffusion through the energy barrier at the pore entrances. It would also hamper desorption: the very small pores would only be vacated at very low partial pressures (requiring very long equilibrium times). These two features, a higher value of W_0 and difficult desorption, can be found in the water isotherms of all carbons examined.

Conclusions

If one allows extremely long equilibrium times when measuring water vapour isotherms on activated carbon the water uptake exceeds the expected values by up to 20%. This could be attributed to the slow diffusion of water molecules into ultra-micropores or into pores with very small pore openings. Further investigations, including MAS-NMR [1], will be carried out in order to prove the validity of this theory.

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