

THEORETICAL WATER ISOTHERMS OF ACTIVE CARBON DERIVED FROM NITROGEN ISOTHERMS.

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Introduction

Water isotherms of microporous activated carbons play an important role in the evaluation of their possible use as an adsorbent for organic vapours and other adsorption-related applications. But only few data are found in literature. This is mainly due to the problems encountered in the experimental determination of water isotherms: one needs a specialised, expensive and very sensitive equipment, but even then the isotherms present a very high experimental error. It has also been shown that, in order to get the 'real' water isotherm, it can take as much as one week per point to reach equilibrium conditions [1]. This work focuses on an indirect method to predict water isotherms at 293K by using data obtained from N₂-isotherms at 77K.

Theoretical

It has been demonstrated that the typical shape of the water adsorption isotherm, can be described by the Dubinin-Astakhov equation (Eqn 1) [2]:

$$W = W_0 \exp \left[- \left(\frac{RT \log(p_0/p)}{\beta E_0} \right)^n \right] \quad (\text{Eqn 1})$$

- W = amount of vapour adsorbed [cm³/g]
W₀ = micropore volume of the carbon [cm³/g]
R = universal gas constant [0.008314 kJ.K⁻¹.mol⁻¹]
T = temperature [K]
p₀/p = inverse of the relative pressure of the vapour [-]
β = affinity constant (benzene = 1) [-]
n = parameter related to the pore size distribution [-]
E₀ = characteristic energy [kJ.mol⁻¹]

In earlier work [3] it was demonstrated that there exists a single value for the affinity constant: β = 0.028, for water adsorption. Both conditions being met (good fitting + single value of β), water seems to behave according to the Dubinin Theory of Volume Filling of Micropores (TVFM). As in literature it has been suggested that, except for the first and last parts, the particular shape of the water isotherm is due to condensation phenomena this assumption

seems logical. If one continues this line of thought, it should be possible to calculate the water isotherm of a particular carbon from any other isotherm measured with an adsorbate that obeys the TVFM, such as benzene or nitrogen. As pore size distribution, micropore volume and characteristic energy are all adsorbate-independent, the simple change of β would suffice to construct the water isotherm!

Experimental

Nitrogen (77K) and water (293K) isotherms were measured on several different commercially available activated carbons: BPL-HA, SCII (both CHEMVIRON), R1Extra, ROW 0.8 and C Granular (all NORIT). All these carbons are essentially microporous, except for the highly mesoporous C Granular. The N₂-isotherms were taken with an ASAP 2010 (Micromeritics). The build-in software was used to determine the values of n, E₀ and W₀. At the same time the complete pore size distribution of the carbons was determined using the DFT-, DR and BJH-methods. Water isotherms were measured gravimetrically by putting beds of activated carbon into contact with an air stream with a known relative humidity. The values of n, E₀ and W₀ derived from the nitrogen isotherms were used to calculate theoretical water isotherms (with β=0.028). These isotherms were subsequently plotted against the experimental water isotherms.

Results and Discussion

The DA-equation severely underestimates the water uptake in the first region. This was to be expected, the adsorption being the result of a chemisorption of water molecules on oxygen complexes on the pore walls. However, given the extremely low water uptake in this region, the absolute error stays very small (< 0.01 g/g). The second region is the region of 'condensation'. For water it is assumed to be a process of micropore filling due to water-water interactions (hydrogen bonding), initiated by water adsorbed on oxygen containing groups. An excellent fitting of the experimental data was obtained for the microporous carbons (Fig 1,2). When the mesoporosity of the carbon increases the model underestimates the actual water uptake (Fig 3).

In the third region of the isotherm the Dubinin-Astakhov eqn. underestimates the water uptake, similarly to the situation with other TVFM-based adsorbates. It is assumed that the micropore system is getting completely filled at these

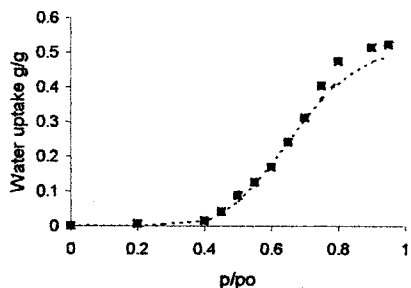


Fig 1: Fitting (---) of the experimental water isotherm (■) on BPL-HA with DA-Eqn

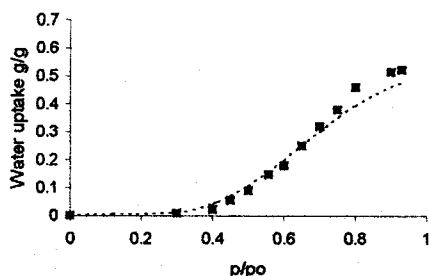


Fig 2: Fitting (---) of the experimental water isotherm (■) on R1Extra with DA-Eqn

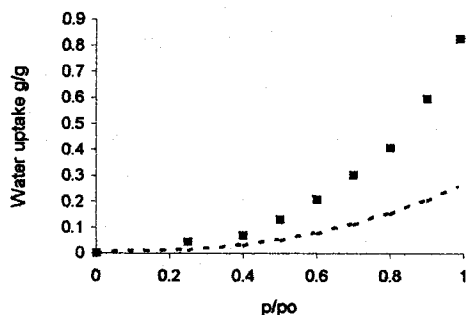


Fig 3: Fitting (---) of the experimental water isotherm (■) on C Granular with DA-Eqn

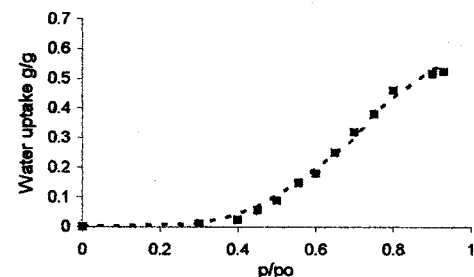


Fig 4: Fitting (---) of the experimental water isotherm (■) on R1E by DA+BJH-Eqn

high values of p/p_0 , with only a comparatively small amount of water being adsorbed on the external surface of the carbon. This is confirmed by gradually adding the BJH-mesopore volume (derived from the N_2 -isotherm) to the DA-isotherm from the point on where it starts to diverge from the experimental data (usually at $p/p_0 \approx 0.7$ for microporous carbons) (Fig 4).

As it was demonstrated that water desorption can be described by the Dubinin-Astakhov equation [4], Eqn.1 was also fitted to the water desorption isotherms (using the values of W_0 , n and E_0 derived from N_2 -desorption isotherms). This gave very poor fittings, suggesting the hysteresis in these both cases to be the result of different physical phenomena (See Figure 5).

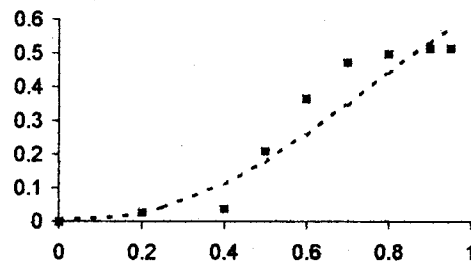


Fig 5: Fitting (---) of the experimental water desorption isotherm (■) on BPL-HA

Conclusions

- The DA-equation can be used to predict the most important part of water isotherms of microporous carbons based solely on data derived from N_2 -isotherms, i.e. there is no such thing as a “water isotherm”.
- Hysteresis in water and nitrogen desorption seem to be the effect of different physical phenomena.

References

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