

COMPARISON OF DUBININ-RADUSHKEVICH MICROPORE VOLUMES OBTAINED FROM N₂, CO₂ AND H₂O-ADSORPTION ISOTHERMS.

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Introduction

Adsorption isotherms are one of the most important tools in the characterisation of the micropore volume of activated carbons. Many different adsorbates have been used over the last decades. Some are very specific (e.g. Kr for carbons with extremely low surface areas) [1], others have been discarded by most laboratories due to their (eco-)toxicity (e.g. benzene). This has resulted in the generalised use of only two adsorbates: nitrogen (at 77K) and carbon dioxide (at 273 or 293K). However, both of these substances present several disadvantages. Nitrogen at 77K requires cryogenic circumstances, involving a difficult and sensitive temperature control system. Hence, most apparatus are designed for measurements of small quantities of adsorbent, thus giving way to a high experimental uncertainty. Finally, the size of the N₂-molecule does prevent it from entering into the smallest micropores, resulting in a possible underestimation of the total micropore volume calculated from these isotherms [2,3]. Even when the N₂-molecules enter into the ultramicropore system, this process is very slow due to the molecule's low energy at this temperature, resulting in extremely long equilibrium times for low relative pressures (up to several days per point). Mainly to overcome these last problems, several researchers have preferred to use CO₂ at (near) room temperature over N₂ at 77K [2,3]. The smaller size of the molecule and its higher energy (at room temperature !) allow it to enter quickly into the ultramicropore system. But working at room temperature restrains the upper relative pressure limit to $p/p_0 \approx 0.03$, i.e. well below the upper limit of microporosity [4,5]. In other words, one needs to compare both CO₂- and N₂-isotherms of an adsorbent to get a clear view of the microporosity in general and of the total micropore volume. Recently it has been demonstrated [6,7] that the adsorption of water at room temperature in the micropore system of activated carbons obeys the volume filling theory of Polanyi [8]. In consequence, it must be possible to calculate the micropore volume of an activated carbon from its water isotherm. This presents several advantages: no cryogenic circumstances, no toxic compounds, a very small molecule [9] with a high energy and, last but not least, the possibility

to measure the isotherm on rather high amounts of carbon, reducing the relative error of the measurements. On the downside we can note long equilibration times, resulting in a limited number of data points.

Theoretical

The most common way of deriving the total micropore volume of an activated carbon from any isotherm is by means of the Dubinin-Radushkevich equation (Eq. 1) [8].

$$\frac{W}{W_0} = \exp \left[- \frac{BT^2}{\beta^2} \ln^2 (p_0 / p) \right] \quad (\text{Eq 1})$$

Where W = volume of the pores that has been filled at p/p_0 [cm³/g]
 W_0 = total volume of the micropore system [cm³/g]
 B = structural constant related to the width of the Gaussian pore distribution [K⁻²]
 T = temperature at which the isotherm has been taken [K]
 β = similarity constant, depending solely on the adsorbate ($\beta=1$ for benzene) [-]
 p_0/p = inverse of the relative pressure of the adsorbate [-]

The validity of this equation for a given adsorption process is established by testing the temperature invariance from plots of $\ln^2(p_0/p)$ versus $\ln(W)$ at different temperatures. These plots should yield straight lines (for at least some part of the plot) with a common intercept $\ln(W_0)$. This has been tested, and validated, for water isotherms [10]. Of course, this implies that no other type of adsorption is preceding nor overlapping the volume filling of the micropores. Otherwise, the value of W_0 obtained from the DR-plot would be a combination of this kind of adsorption and micropore filling, i.e. an overestimation of the total micropore volume. As it is well known that the adsorption

of water is initiated by specific interactions between surface oxygen complexes [11] and water molecules, this last assumption could jeopardise the use of the DR equation in the case of water vapour. However, as most of these active sites are situated inside the micropore system [12,13], the total volume obtained from the DR plot (i.e. the amount of water adsorbed through specific bonding inside the micropores plus the amount of water adsorbed through micropore filling of the remaining micropore volume) should correspond to the real total micropore volume of the carbon. And, given the size of the water molecule, the isotherm temperature and the partial pressures at which microfilling occurs (approx. $p/p_o = 0.4 - 0.7$) this volume should be equal to, or even slightly higher, than the micropore volume obtained through nitrogen adsorption.

A supplementary information is given by the slope of the straight line from the plot of $\ln^2(p_o/p)$ versus $\ln(W)$: $-BT^2/\beta^2$. As the structural parameter B is linked to the adsorbent rather than to the adsorbate it can be derived from another isotherm, e.g. with nitrogen at 77K. In reality B, being related to the width of the Gaussian pore distribution, will be influenced by the nature of the adsorbate as different adsorbates will 'see' different pore size distributions due to differences in molecular diameter, polarizability, etc.... However, as the micropore size distribution 'seen' by water molecules will be only slightly broader than the one obtained through the nitrogen isotherm (due to the smallest micropores), the two values of B should only differ slightly. This makes it possible to calculate the value of the similarity constant β for water, and to compare this value with previously published data [6,7].

Experimental

H₂O (293K)- and N₂ (77K)-isotherms were taken from six different commercially available activated carbons: BPL-HA, SCII, ASC-T (all Chemviron), R1Extra, RB1, ROW0.8 and C Granular (all Norit). These carbons vary in pore structure, surface activity and impregnation with metal salts: ASC-T is impregnated with Cu- and Cr-salts as well as Tri-Ethylene-Di-Amine. Some of their relevant parameters are given in Table I, including impregnation and Dubinin-Serpinsky amount of primary adsorption sites a_o (as a measure for the amount of surface oxygen complexes).

The N₂-isotherms were measured with a Micromeritics ASAP 2010M, after outgassing at 250°C and ≈ 0.5 Pa for 96 hours. Water isotherms were measured on a standard test rig for filter testing according to EN 141 [14]. This implies manufacturing rather large carbon beds (i.e. filters containing typically 40g of carbon) and putting them in an

air stream of a known relative humidity (= set-point of a Humidity sensor/ controller). At regular intervals the filter is taken out of the installation and the weight gain is checked. If no significant weight change is detected (i.e. less than 1% difference between the three last measurements) the total weight gain per gram of carbon is considered to be the relevant point of the water isotherm at this relative humidity. This technique is more tedious than using an automated gravimetric apparatus, but presents two advantages: the high amount of carbon reduces significantly the experimental error and, thanks to the dynamic conditions, the equilibrium is reached within a few days where as in an automated apparatus this could take up to several weeks per point if real equilibrium is ever reached [9,15]. A major set-back of this method is the accuracy of the Humidity sensor/controller: even though it is quite possible to maintain a fixed relative humidity over a prolonged period of time it is not obvious to set a precise value on beforehand – small variations in the set-point can cause rather large variations in relative humidity. This feature is responsible for the limited number of measured points of the water isotherms presented further in this study.

Results

Figures 1 and 2 show some of the results of the application of the Dubinin-Radushkevich equation on the water adsorption isotherms. These figures demonstrate the applicability of the DR plot but show some significant differences with the usual (N₂-)DR-plots.

The first deviation of the DR plot, in the region of bigger pores (i.e. lower values of $\ln^2[p_o/p]$) is usually attributed to capillary condensation in the mesopores. The thesis of the authors [16] that, in the case of water adsorption, capillary condensation is also responsible for an enhanced uptake in the mesopore region, seems to be confirmed. However, this enhancement is less pronounced than in the case of nitrogen adsorption, especially for the biggest mesopores (i.e. $\ln^2[p_o/p]$ tending towards 0). This can be attributed to the differences in the parameters of the Kelvin equation (Eq 2) [17] for water and nitrogen:

$$\ln\left(\frac{p}{p_o}\right) = -\frac{2\gamma V_L}{RT} \left(\frac{1}{r_m}\right) \quad (\text{Eq. 2})$$

Where p/p_o = relative pressure of the adsorbate [-]
 γ = surface tension of the liquid adsorptive [N/m]

- V_L = molar volume of the liquid adsorptive
 [m³/mol]
 R = universal gas constant [N.m/mol.K]
 T = temperature of the isotherm [K]
 r_m = radius of the 'cone' filled in a pore at
 pressure p
 (assuming contact angle $\theta = 0^\circ$)

The value of the term $\gamma V_L/T$ is significantly higher for water than for nitrogen. This implies that for very high values of p/p_0 (>0.9) the radius of the pores that should be filled by the water exceeds the upper range of capillary condensation, where as for nitrogen the phenomenon of capillary condensation extends till $p/p_0 \approx 1$. This suggests that, as can be seen from the general type V shape of the water isotherms, there is hardly any water adsorption at these high values of relative pressure, which accounts for the limited deviation of the H₂O-DR-plots when approaching $\ln^2(p_0/p) = 0$.

The second deviation is to be found for the adsorption in very small pores, i.e. for high values of $\ln^2(p_0/p)$. In the case of N₂-isotherms this deviation is (nearly) always negative: the uptake is less than could be expected from the Polanyi theory of volume filling of micropores (TVFM). This has been attributed to a number of different phenomena, ranging from diffusion through energetic barriers to completely different adsorption mechanisms. However, in the case of H₂O-isotherms the explanation is straightforward: as the deviation is positive, it indicates an enhancement of the uptake compared to the TVFM, due to the specific interactions between H₂O-molecules and the surface oxygen complexes. This chemisorption of water molecules is particularly situated in the first part of the isotherm (low p/p_0) as the oxygen complexes become less accessible once the micropore system starts getting filled up by the TVFM-mechanism [12,13]. A comparison between the micropore volumes (W_0) obtained from the DR-plots of, respectively, N₂, CO₂ and H₂O can be found in table I.

In five out of seven cases the micropore volumes are nearly identical for nitrogen and water, the W_0 obtained from the water isotherm being slightly higher. This can be ascribed to a contribution of the ultramicropores to the total micropore volume due to their increased accessibility for the smaller water molecule (vs. nitrogen) [9]. In one case (RB1), the W_0 derived from the water isotherm is actually smaller. Repeated measurements have shown this to be no experimental error. A possible explanation is provided by the pore size distribution of this carbon. This can be found in Fig 3.

This distribution (Density Functional Theory-plot of N₂-isotherm) shows a rather narrow micropore size distribution and suggests the absence of any pores smaller

than 0.5 nm (5Å), i.e. no ultramicroporosity. Combining this with the previous observations leads us to the idea that the DR-plot of the water isotherm provides information about a pore range that extends beyond the N₂-region on the side of the smaller pores, and is slightly smaller towards the higher micropore diameters. In other words, there seems to be an analogy between the DR-plot of the H₂O-isotherm and the CO₂-isotherm when comparing them to DR-plots of the N₂-isotherm. With this difference that the range covered by the water isotherm extends to higher pore sizes than for CO₂. This is schematically presented in Fig 4.

In only one case the DR-plot of the H₂O-isotherm is totally different from the N₂-data is for C Granular. This carbon is the most mesoporous and presents the most surface oxygen complexes (see Table I). Mesoporosity should not directly influence the apparent micropore volume: it is clearly distinguishable in the DR-plot and other carbons (BPL-HA,...) also present a fair amount of mesoporosity without any influence on $W_0(\text{H}_2\text{O})$. But if the difference is due to the high amount of active sites, the same phenomenon should be apparent for ASC-T: for this carbon, the impregnation seems to form chemical bonds with the water molecules (cfr the high value of a_0 in Table I). A possible explanation lies in an indirect influence of the mesoporosity of C Granular. If the active sites for chemical water bonding are (nearly) exclusively present in the micropores, their contribution will not influence W_0 : in the first part of the isotherm, the uptake will be enhanced (= upwards deviation vs. the DR-plot). But the total amount of water that can be adsorbed in the micropores is not affected as the volume filling process will take up the available space and the chemically bound water just shifts the straight line of DR-plot in order to obtain a $W_0(\text{H}_2\text{O}) = W_0(\text{real})$. If, on the other hand, many active sites are situated on the external surface of the carbon (meso- and macropores), then the total adsorbed volume given by the DR-plot will not represent the micropore volume but a sum of $W_0(\text{real})$ and the amount of water that was chemically adsorbed on the external surface before the process of micropore filling. Throughout the micropore filling, there seems to be no specific interaction with the water molecules as the DR-plot of C Granular presents a straight line in the same region as the other carbons: $p/p_0 \in [0.45 - 0.60]$. If there would be a chemical adsorption process in this pressure region, it would influence the data of the DR-plot. Hence the evidence presented by the DR-plots suggests three distinct stages in the water adsorption process: chemical interaction with the carbon surface, volume filling of the micropores and capillary condensation in the mesopores.

These findings are, partially, contradicted by the calculated values of β (see Table I). The values for the two carbons

with the highest amount of active sites (ASC-T and C Granular) are significantly higher than those of the five other carbons, even though they are of the same order of magnitude. This suggests an influence of the specific interactions on the DR-plot. A possible explanation is to be found in the rather large micropore size distribution of activated carbons: all carbons involved in this study exhibit a continuous distribution of pores between 0.5 and 2 nm. These pores will not be filled by the TVFM at the same pressure – smaller micropores will be filled before the larger ones. As, presumably, all these pores contain surface oxygen complexes the two physical phenomena (pore filling and specific interactions in the larger micropores) will co-exist. For carbons with high amounts of surface oxygen complexes, it seems necessary to subtract the amount adsorbed due to the specific interactions from the total amount adsorbed throughout the entire DR-plot (e.g. by subtracting a fit of the first isotherm points by means of the Dubinin-Serpinsky equation). If the oxygen complexes are situated exclusively inside the micropore system this will only influence the value of β and not the micropore volume W_0 , as the slope of the straight line will change but not the intercept (see table I for ASC-T). The values of β for the other carbons are sufficiently close to the value of 0.06 obtained by fitting the complete isotherms [6] and the experimentally derived value of 0.05 obtained by Stoeckli et al [7].

Conclusions

Water isotherms have always been regarded as a "special case" of adsorption onto activated carbon. Over the last few years it has become apparent that at least some stages in the water adsorption process are of a more general nature. The aim of this work was to show the applicability of the very general Dubinin-Radushkevich-plot to the water isotherms and to verify the structural parameters of the activated carbons obtained by these plots by comparing them to nitrogen and carbon dioxide data.

The results show that water isotherms contain important information about the micropore volume and micropore size distribution of activated carbons. In the case of carbons with a low content of surface oxygen complexes, a direct application of the DR-plot will yield the micropore volume. The static physical adsorption behaviour of a carbon can also be derived from the data obtained from the water isotherm as the value of $\beta(\text{H}_2\text{O}) = 0.06$ has been confirmed.

For carbons with high amounts of surface oxygen complexes, the determination of the "true" micropore volume is less straightforward. However, in this case a comparison between nitrogen and water data can reveal

important information about the exact location of the surface oxygen complexes inside the overall pore structure of the carbons.

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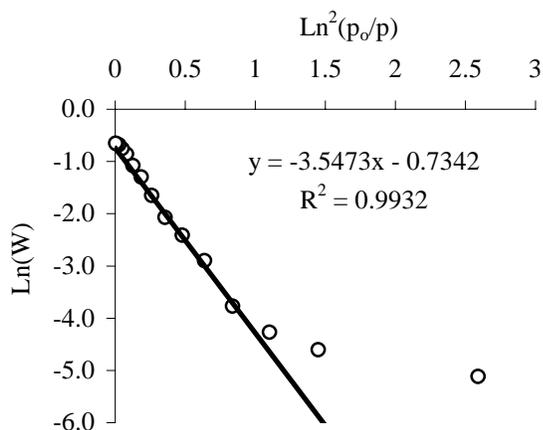


Fig 1: DR plot of the water adsorption isotherm of Norit R1Extra at 296K

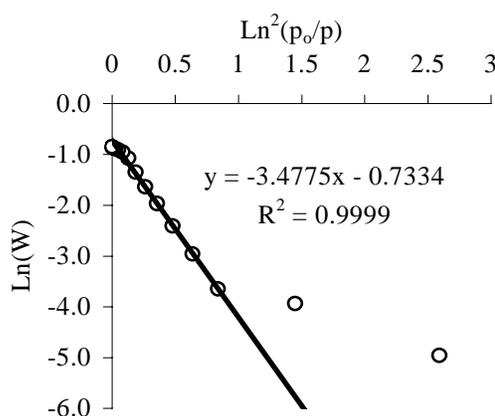


Fig 2: DR plot of the water adsorption isotherm of Chemviron SCII at 296K

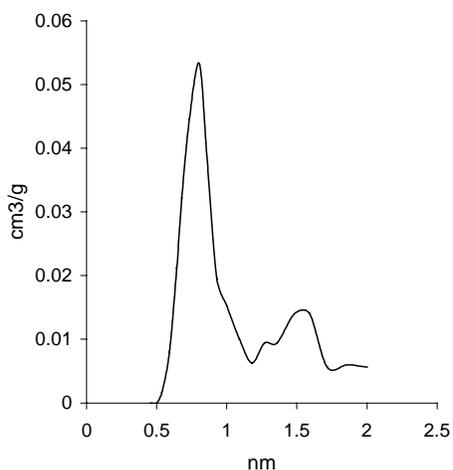


Figure 3: Micropore distribution of RB1

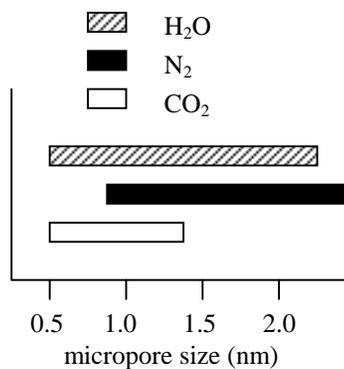


Figure 4: Schematic comparison of the range of micropores "seen" by different adsorbates

Table I: Significant parameters of the activated carbons used in this study

| Carbon | Dubinin-Serpinsky (H ₂ O) a ₀ [mmol/g] | Impregnation? | Dubinin-Radushkevich (N ₂) | | DR (CO ₂) | Dubinin-Radushkevich (H ₂ O) | |
|------------|--|---------------|--|--|--|---|--------------|
| | | | B [10 ⁻⁷ K ⁻²] | W ₀ [cm ³ /g] | W ₀ [cm ³ /g] | W ₀ [cm ³ /g] | β [-] |
| BPL-HA | 0.5 | no | 2.3 | 0.46 | 0.27 | 0.48 | 0.072 |
| R1 Extra | 0.5 | no | 1.4 | 0.47 | 0.30 | 0.48 | 0.059 |
| SC II | 1.0 | no | 2.0 | 0.45 | 0.29 | 0.48 | 0.071 |
| RB1 | 0.4 | no | 1.2 | 0.38 | 0.28 | 0.35 | 0.063 |
| ROW 0.8 | 0.9 | no | 1.2 | 0.39 | 0.31 | 0.40 | 0.059 |
| C Granular | 3.6 | no | 2.2 | 0.23 | 0.21 | 0.34 | 0.101 |
| ASC-T | 3.3 | Yes | 1.4 | 0.30 | 0.21 | 0.31 | 0.094 |