Water adsorption in activated carbons of various degrees of oxidation described by the Dubinin equation

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The purpose of this Letter is to outline a description of water adsorption isotherms based on Dubinin’s theory [1] and on immersion calorimetry. It considers specific and non-specific interactions, as well as the structural characteristics of the solids.

Water adsorption isotherms are of types IV or V and lead to single characteristic curves, as shown by plots of the relative amounts adsorbed, \( N_s/N_{\text{el}} \) versus \( A = RT \ln(p/p) \) [2,3]. Consequently, as suggested by Stoeckli et al. [2–4], these isotherms can be described with the help of the Dubinin–Astakhov (DA) equation,

\[
N_s = N_{\text{el}} \exp\left[-(A/E)^n\right]
\] (1)

\( N_s \) is the amount adsorbed at relative pressure \( p/p \) and temperature \( T \); \( N_{\text{el}} \) is the limiting amount filling the micropore volume \( W = V_n N_{\text{el}} \) and \( E \) is the so-called characteristic energy of the system. The latter can be written as \( E = \beta E_c \), where \( \beta \) is the affinity coefficient of the adsorptive. Benzene is the reference and \( \beta_{\text{C,B}} = 1 \).

A thermodynamic consequence of Eq. (1), based on the temperature invariance of \( E \) and \( n \), is the relation for the enthalpy of immersion of the carbon into the corresponding liquid [1],

\[
\Delta H (J/g)_{\text{exp}} = -N_{el} E (1 + \alpha T) F(1 + 1/n) + hS_s
\] (2)

\( \alpha \) is the thermal expansion coefficient of the liquid, \( F(1 + 1/n) \) the ‘Gamma’ function and the last term represents the wetting of the external surface \( S_s \) (\( h \) and \( \Delta H < 0 \)).

With increasing oxidation, the initial type V water isotherm changes to type IV and it can be described by a sum of type I and V DA isotherms [3,4],

\[
N_s = N_{\text{el}}(I) \exp\left[-(A/E_{\text{H}_2\text{O}}(I))^{n_1}\right]
\]

\[
+ N_{\text{el}}(V) \exp\left[-(A/E_{\text{H}_2\text{O}}(V))^{n_2}\right]
\] (3)

\( E_{\text{H}_2\text{O}}(I) \) and \( E_{\text{H}_2\text{O}}(V) \) are typically 5–7 kJ mol\(^{-1}\) and 1–3 kJ mol\(^{-1}\), 1.5 < \( n_1 \) < 2 and 2 < \( n_2 \) < 4. Parameter \( n_2 \) probably reflects the pore-size distribution (slope of the type V isotherm).

More data has become available, in particular from combined studies of water adsorption, immersion calorimetry and the determination of surface oxygen [O] and basic groups [HCl], determined by TPD and by HCl titration. (To a first approximation, one may assume that the basic groups are mainly oxygen-free [5]). Their sum is \([O+\text{HCl}]_{\text{TPD}} \) (mmol or meq g\(^{-1}\)). Table 1 shows combined results for 13 carbons, as received and/or oxidized with \( \text{H}_2\text{O}_2 \), \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \) and \( \text{HNO}_3 \).

Recently [5,6], for 21 carbons the following correlations has been established between \([O+\text{HCl}]_{\text{TPD}} \) and the

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enthalpies of immersion into water and benzene,

$$\Delta_h(H_2O) = 0.21 \Delta_h(C,H)$$

$$- 10 (J \text{ mmol}^{-1})[O + HCl]_{TPD} \ (4)$$

This suggests that a number of hydrophilic sites \([O + HCl]_{a,h}\) can be estimated from \(\Delta_h(H_2O)\) and \(\Delta_h(C,H)\) alone,

$$[O + HCl]_{a,h} = [0.21 \Delta_h(C,H)]$$

$$- \Delta_h(H_2O)]/(10 J \text{ mmol}^{-1}) \ (5)$$

Table 1 shows a good agreement between \(N_{a,w}(I)\) and the surface groups \([O + HCl]_{TPD}\) or \([O + HCl]_{a,h}\). This confirms that the type I contribution reflects a strong interaction between water and the sites, in a 1:1 ratio. It also appears that \(E_{H_2O}(V)) = 0.29 \pm 0.02\) (standard error), which corresponds to the affinity coefficient \(\beta_{H_2O}(V)\) for the type I contribution. It is in good agreement with the value of 0.26 derived from the ratio of the parachors of H$_2$O and C,H, an approach often used to calculate $\beta$.

It appears that \(E_{H_2O}(V)\) depends on both the structural properties of the carbon and the surface sites. This is suggested by the fact that in series AZ-46 and CMS, the characteristic energies for benzene, \(E_{a,w}\), are practically constant, whereas \(E_{H_2O}(V)\) increases with oxidation. By analogy with a recent study [7] on the specific interactions of methanol and ethanol with activated carbons with different degrees of oxidation, one may introduce an affinity coefficient for water in the type V isotherm,

$$\beta_{H_2O}(V) = E_{H_2O}(V)/E_a \ (6)$$

The data of Table 1 leads to the overall correlation (standard deviations, $\sigma$)

$$\beta_{H_2O}(V) = 0.069 (\pm 0.010) - 1.11(\pm 0.15)$$

$$\times [(O + HCl)_{TPD}]/\Delta_h(C,H)_{exp} \ (7)$$

where 0.069 is the affinity coefficient for water in the absence of sites, $\beta(H_2O)$. If one uses \([O + HCl]_{a,h}\) given by Eq. (5), with additional $\beta_{H_2O}(V)$ values for 6 carbons not investigated by TPD, the correlation is practically the same. The energy of \(-1.11\) kJ mol$^{-1}$ (or J mmol$^{-1}$) reflects long-range specific interactions between water and the sites. Following Eq. (2), the substitution of $\Delta_h(C,H)$ and $N_{a,w}(C,H)$ leads to

$$\beta_{H_2O}(V) = 0.069 + (5.4 \text{ kJ mol}^{-1})$$

$$\times [(O + HCl)_{TPD}]/E_a N_{a,w}(H_2O) \ (8)$$

On the basis of the foregoing observations, we suggest the following expression for the combined (or generalized) water adsorption isotherm on activated carbons,

$$N_a = [O + HCl] \exp[-(A/\beta_{H_2O}(V))^{n}] + (N_{a,w}(H_2O))$$

$$- [O + HCl] \exp[-(A/\beta_{H_2O}(V))^{n}] \ (9)$$

where $\beta_{H_2O}(I) = 0.29$, $\beta_{H_2O}(V)$ is given by Eqs. (7) or (8), and exponents $1.5 < n_i < 2$, $2 < n_2 < 4$. The sites can be either $[O + HCl]_{TPD}$ or $[O + HCl]_{a,h}$. Water isotherms can be estimated on the basis of structural data ($N_{a,w}(H_2O)$, $E_a$) combined with TPD and/or immersion calorimetry ($\Delta_h(C,H)$) and $\Delta_h(H_2O)$. Fig. 1 illustrates the case of carbon CMS-ox at 293 K, using $[O + HCl]_{a,h}$ and $n_2 = 3$ (narrow pore distribution), but this type of agreement has to be confirmed by a more detailed study, to be reported later.

Eq. (9) also gives an indication for the mechanism of water adsorption by activated carbons, by distinguishing the specific and the non-specific interactions. The type I contribution correspond exclusively to primary adsorption.

### Table 1

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$E_{H_2O}(I)$ (kJ mol$^{-1}$)</th>
<th>$N_{a,w}(I)$ (mmol g$^{-1}$)</th>
<th>$[O + HCl]_{TPD}$ (meq g$^{-1}$)</th>
<th>$[O + HCl]_{a,h}$ (meq g$^{-1}$)</th>
<th>$\beta_{H_2O}(V)$</th>
<th>$\Delta_h(C,H)$ (J g$^{-1}$)</th>
<th>$N_{a,w}(H_2O)$ (mmol g$^{-1}$)</th>
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<tbody>
<tr>
<td>AZ46-0</td>
<td>22.6</td>
<td>7.54</td>
<td>5.25</td>
<td>2.3</td>
<td>0.075</td>
<td>110</td>
<td>21.6</td>
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<td>AZ46-1</td>
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<td>4.18</td>
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<td>0.111</td>
<td>114</td>
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<td>4.90</td>
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<td>0.119</td>
<td>114</td>
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<td>5.30</td>
<td>5.0</td>
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<td>114</td>
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<td>5.95</td>
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<tr>
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</table>
term, \(-1.11 E_n[O + HCl]/\Delta H (C_nH_o)_{exp}\) or \((5.4 \text{ kJ mol}^{-1})([O + HCl]_{TPD})/N_m(H_2O)\), reflects the weaker specific interactions, which depend essentially on the ratio \(([O + HCl])/N_m(H_2O)\).

Eq. (9) suggests a new quantitative and relatively simple approach for the description of water adsorption by microporous carbons, based on structural and chemical properties and where immersion calorimetry plays an important role.

It is likely that the present approach can be extended to other specific interactions in oxidized or chemically modified microporous carbons. This will be reported later.

References


Fig. 1. Experimental (■) and calculated (+) water adsorption isotherm on carbon CMS-ox at 293 K. The calculations are based on Eqs. (5), (7) and (9).