

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_a/N_{ao} versus $A = RT \ln(p_s/p)$ [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,

$$N_a = N_{ao} \exp[-(A/E)^n] \quad (1)$$

N_a is the amount adsorbed at relative pressure p/p_s and temperature T ; N_{ao} is the limiting amount filling the micropore volume $W_o = V_m N_{ao}$ and E is the so-called characteristic energy of the system. The latter can be written as $E = \beta E_o$, where β is the affinity coefficient of the adsorptive. Benzene is the reference and $\beta_{C_6H_6} = 1$.

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],

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$$\Delta_i H \text{ (J/g)}_{\text{exp}} = -N_{ao} E (1 + \alpha T) \Gamma(1 + 1/n) + h_i S_e \quad (2)$$

α is the thermal expansion coefficient of the liquid, $\Gamma(1 + 1/n)$ the 'Gamma' function and the last term represents the wetting of the external surface S_e (h_i and $\Delta_i H < 0$).

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],

$$N_a = N_{ao}(I) \exp[-(A/E_{H_2O}(I))^{n_1}] + N_{ao}(V) \exp[-(A/E_{H_2O}(V))^{n_2}] \quad (3)$$

$E_{H_2O}(I)$ and $E_{H_2O}(V)$ 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+HCl]_{TPD} (mmol or meq g⁻¹). Table 1 shows combined results for 13 carbons, as received and/or oxidized with H₂O₂, (NH₄)₂S₂O₈ and HNO₃.

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

Table 1

Main characteristics of the carbons and their water adsorption isotherms at 293 K. $\beta_{\text{H}_2\text{O}}(\text{V})=E_{\text{H}_2\text{O}}(\text{V})/E_o$

Carbon	E_o (kJ mol ⁻¹)	$E_{\text{H}_2\text{O}}(\text{I})$ (kJ mol ⁻¹)	$N_{\text{ao}}(\text{I})$ (mmol g ⁻¹)	$[\text{O} + \text{HCl}]_{\text{TPD}}$ (meq g ⁻¹)	$[\text{O} + \text{HCl}]_{\Delta_i H}$ (meq g ⁻¹)	$\beta_{\text{H}_2\text{O}}(\text{V})$ -	$-\Delta_i H(\text{C}_6\text{H}_6)$ (J g ⁻¹)	$N_{\text{ao}}(\text{H}_2\text{O})$ (mmol g ⁻¹)
AZ46-0	22.6	7.54	2.52	1.52	2.3	0.075	110	21.6
AZ46-1	23.0	7.58	4.18	4.08	4.0	0.111	114	21.8
AZ46-3	23.5	6.80	4.90	4.93	5.6	0.119	114	22.2
AZ46-4	23.9	6.48	5.30	5.35	5.0	0.129	114	22.2
AZ46-5	23.9	6.81	5.95	5.92	5.5	0.129	114	22.6
AZ46-10	24.7	6.68	7.27	6.70	5.7	0.123	112	21.5
AZ46-24	24.7	6.91	9.55	7.21	7.1	0.136	113	20.0
CMS-0	26.2	7.16	0.9	1.64	0.8	0.080	95	13.5
CMS-ox	27.0	6.9	6.71	6.40	6.2	0.150	93	14.1
U02-ox	20.0	7.38	2.90	2.79	2.8	0.114	122	25.2
U03	17.7	7.38	1.0	1.50	1.1	0.067	129	28.9
P-92-2	23.9	5.8	3.2	2.79	2.4	0.092	162	25.6
N-125	16.8	4.0	1.51	1.75	1.1	0.071	160	44.8

enthalpies of immersion into water and benzene,

$$\Delta_i H(\text{H}_2\text{O}) = 0.21 \Delta_i H(\text{C}_6\text{H}_6) - 10 (\text{J mmol}^{-1}) [\text{O} + \text{HCl}]_{\text{TPD}} \quad (4)$$

This suggests that that a number of hydrophilic sites $[\text{O} + \text{HCl}]_{\Delta_i H}$ can be estimated from $\Delta_i H(\text{H}_2\text{O})$ and $\Delta_i H(\text{C}_6\text{H}_6)$ alone,

$$[\text{O} + \text{HCl}]_{\Delta_i H} = [0.21 \Delta_i H(\text{C}_6\text{H}_6) - \Delta_i H(\text{H}_2\text{O})] / (10 \text{ J mmol}^{-1}) \quad (5)$$

Table 1 shows a good agreement between $N_{\text{ao}}(\text{I})$ and the surface groups $[\text{O} + \text{HCl}]_{\text{TPD}}$ or $[\text{O} + \text{HCl}]_{\Delta_i H}$. 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 $E_{\text{H}_2\text{O}}(\text{I})/E_o = 0.29 \pm 0.02$ (standard error), which corresponds to the affinity coefficient $\beta_{\text{H}_2\text{O}}(\text{I})$ 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_2O and C_6H_6 , an approach often used to calculate β .

It appears that $E_{\text{H}_2\text{O}}(\text{V})$ 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_o , are practically constant, whereas $E_{\text{H}_2\text{O}}(\text{V})$ 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,

$$\beta_{\text{H}_2\text{O}}(\text{V}) = E_{\text{H}_2\text{O}}(\text{V})/E_o \quad (6)$$

The data of Table 1 leads to the overall correlation (standard deviations, σ)

$$\beta_{\text{H}_2\text{O}}(\text{V}) = 0.069 (\pm 0.010) - 1.11 (\pm 0.15) \times ([\text{O} + \text{HCl}]_{\text{TPD}}) / \Delta_i H(\text{C}_6\text{H}_6)_{\text{exp}} \quad (7)$$

where 0.069 is the affinity coefficient for water in the absence of sites, $\beta_o(\text{H}_2\text{O})$. If one uses $[\text{O} + \text{HCl}]_{\Delta_i H}$ given by Eq. (5), with additional $\beta_{\text{H}_2\text{O}}(\text{V})$ values for 6 carbons not investigated by TPD, the correlation is practically the same. The energy of $-1.11 \text{ kJ mol}^{-1}$ (or J mmol^{-1}) reflects long-range specific interactions between water and the sites. Following Eq. (2), the substitution of $\Delta_i H(\text{C}_6\text{H}_6)$ and $N_{\text{ao}}(\text{C}_6\text{H}_6)$ leads to

$$\beta_{\text{H}_2\text{O}}(\text{V}) = 0.069 + (5.4 \text{ kJ mol}^{-1}) \times ([\text{O} + \text{HCl}]_{\text{TPD}}) / E_o N_{\text{ao}}(\text{H}_2\text{O}) \quad (8)$$

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

$$N_a = [\text{O} + \text{HCl}] \exp[-(A/\beta_{\text{H}_2\text{O}}(\text{I})E_o)^{n_1}] + (N_{\text{ao}}(\text{H}_2\text{O}) - [\text{O} + \text{HCl}]) \exp[-(A/\beta_{\text{H}_2\text{O}}(\text{V})E_o)^{n_2}] \quad (9)$$

where $\beta_{\text{H}_2\text{O}}(\text{I})=0.29$, $\beta_{\text{H}_2\text{O}}(\text{V})$ is given by Eqs. (7) or (8), and exponents $1.5 < n_1 < 2$, $2 < n_2 < 4$. The sites can be either $[\text{O} + \text{HCl}]_{\text{TPD}}$ or $[\text{O} + \text{HCl}]_{\Delta_i H}$. Water isotherms can be estimated on the basis of structural data ($N_{\text{ao}}(\text{H}_2\text{O})$, E_o) combined with TPD and/or immersion calorimetry ($\Delta_i H(\text{C}_6\text{H}_6)$ and $\Delta_i H(\text{H}_2\text{O})$). Fig. 1 illustrates the case of carbon CMS-ox at 293 K, using $[\text{O} + \text{HCl}]_{\Delta_i H}$ 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

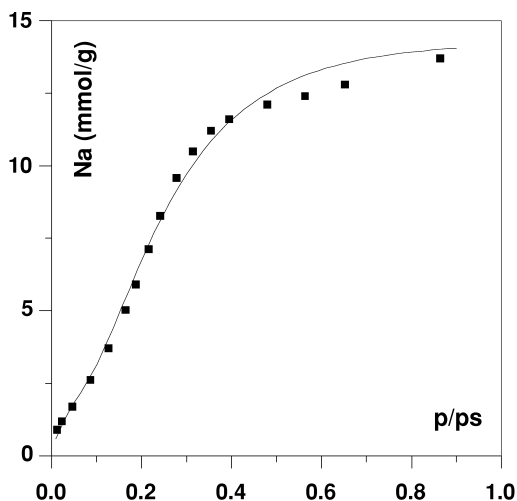


Fig. 1. Experimental (■) and calculated (→) water adsorption isotherm on carbon CMS-ox at 293 K. The calculations are based on Eqs. (5), (7) and (9).

on the oxygen atoms and the basic groups, practically in 1:1 ratio, and $\beta_{\text{H}_2\text{O}}(\text{I})=0.29$. On the other hand, the type V contribution to the overall isotherm is governed by both non-specific and specific interactions, as indicated by $\beta_{\text{H}_2\text{O}}(\text{V})E_o$. The first term, $0.069E_o$, reflects the non-specific micropore filling by water, whereas the second

term, $-1.11E_o[\text{O}+\text{HCl}]/\Delta_i H (\text{C}_6\text{H}_6)_{\text{exp}}$ or $(5.4 \text{ kJ mol}^{-1})([\text{O}+\text{HCl}]_{\text{TPD}})/N_{\text{ao}}(\text{H}_2\text{O})$, reflects the weaker specific interactions, which depend essentially on the ratio $([\text{O}+\text{HCl}])/N_{\text{ao}}(\text{H}_2\text{O})$.

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.

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