

The Relationship between Immersion Calorimetry and the Parameters of the Water Adsorption Isotherm on Active Carbons

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It is shown that for active carbons with a single type of hydrophilic adsorption sites, the enthalpy of immersion into water is related to the number of sites, a_0 , and to a parameter, c , both of which appear in the Dubinin-Serpinskii equation for the water adsorption isotherm. The correlation was established on the basis of data for 13 different active carbons whose sites were either acidic or of the carbonyl type. It follows that the adsorption branch of the water isotherm can be calculated from data based on the enthalpy of immersion and the micropore volume.

It is well known that carbonaceous surfaces are essentially hydrophobic, owing to the relatively low dispersion energies which exist between water molecules and aromatic sheets. Water can, however, be adsorbed preferentially on oxygen-containing centres which usually cover a small fraction of the total surface area. The mechanism of water adsorption has been discussed by Dubinin *et al.*¹ in the fifties, and more recently by Dubinin and Serpinskii,² who postulated the following relation for the adsorption of water by active carbons:

$$p/p_0 = a/[c(a_0 + a)(1 - ka)]. \quad (1)$$

In this equation a represents the amount of water adsorbed at relative pressure p/p_0 and a_0 is the number of so-called primary centres (usually expressed in mmol g⁻¹ of solid); c is the ratio between the rate constants of adsorption and desorption and k is a constant whose magnitude is fixed by the condition that for $p/p_0 = 1$ the total amount of water adsorbed in the micropores is a_s . Implicitly eqn (1) is valid for a given type of primary sites and in the case of sites with different energies, parameters a_0 and c become apparent quantities. Note also that eqn (1) applies to the adsorption branch of the water isotherm and there exists no model for the description of the hysteresis loop associated with the desorption of water from the micropores.

It has been shown recently by Stoeckli *et al.*³ that the number of primary sites a_0 is directly related to the enthalpy of immersion of active carbons into water. For typical industrial carbons, treated *in vacuo* at 400–600 °C and containing a uniform type of hydrophilic sites (probably of the carbonyl type since their high desorption temperature leads to carbon monoxide⁴), the relation is

$$\Delta h_i = -25a_0 - 0.6(a_s - a_0) \quad (2)$$

where Δh_i is in J g⁻¹ and a_0 and a_s are in mmol g⁻¹. The quantity Δh_i represents the change in enthalpy associated with the transfer of a_s mmol of water at room temperature, from the liquid state into 1 g of active carbon. Eqn (2) shows that the excess enthalpy can be divided into contributions from the primary sites and from the bulk of the micropores. The latter, arising from dispersion forces, are relatively small, but since $a_s \gg a_0$, the two contributions are of the same order of magnitude. The energies appearing in eqn (1) can be compared with the data from *ab initio* calculations by

Water Adsorption on Active Carbon

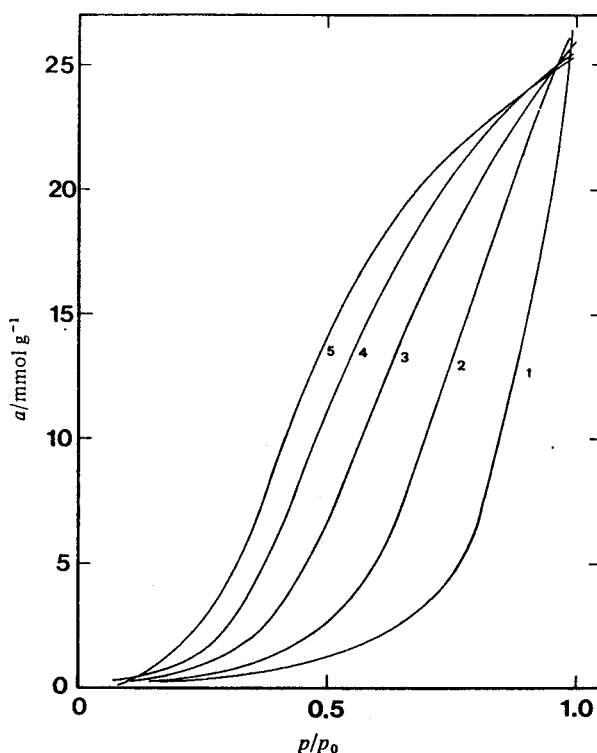


Fig. 1. The influence of the parameter c of eqn (1) on the shape of the water adsorption isotherm. (1) $c = 1.0$, (2) $c = 1.5$, (3) $c = 2.0$, (4) $c = 2.5$ and (5) $c = 3.0$. In all cases $a_0 = 1.00 \text{ mmol g}^{-1}$.

Malenkov and Dubinin⁵ for the interaction of water with carbon surfaces containing carbonyl sites.

As suggested by Barton and Koresh,⁶ the adsorption of water vapour by active carbons depends on the amount of surface oxides, reflected by a_0 , and on the size of the micropores. The former parameter plays a major role at relative pressures $p/p_0 < 0.3$, whereas the pore dimensions manifest themselves in the region $0.3 < p/p_0 < 0.5$.

Mathematical modelling (see fig. 1) and the analysis of experimental data show that parameter c of eqn (1) also plays an important role in the description of water adsorption by active carbons. A better understanding can therefore be gained by relating this parameter to other properties of the system under investigation. Dubinin *et al.*⁷ have recently shown that for a given series of carbons with increasing degrees of burn-off, c decreases as the average micropore width increases. These authors had also shown earlier⁸ that in the case of an active carbon subjected to heat treatment in argon at temperatures ranging from 1000 to 1600 °C, there exists a linear relation between constant c and the total surface area S of the micropores, which both decrease with increasing heat treatment. However, in this case a closer examination shows that the relation between c and the pore width does not hold, an indication that c probably depends on different variables. In the present paper we therefore wish to show that there exist a relatively simple relation between c and the enthalpy of immersion into water, as suggested by the analysis of eqn (1) within the framework of thermodynamics.

Table 1. Parameters of the water adsorption isotherms and the enthalpies of immersion of 13 different active carbons into water^a

solid	$-\Delta h_1$ /J g ⁻¹	a_s /mmol g ⁻¹	$-\Delta H_1$ /J mol ⁻¹	$a_0(1)$ /mmol g ⁻¹	$a_0(2)$ /mmol g ⁻¹	$a_0(3)$ /mmol g ⁻¹	c	c_0
UO2-1	27.9	26.1	1069	0.35	0.50	—	1.79	1.15
UO2-2	40.7	26.1	1559	0.95	1.03	—	1.85	0.98
UO2-3	70.0	26.3	2662	2.01	2.22	—	2.49	0.84
UO2-4	51.2	28.0	1829	0.59 ^b	0.63 ^b	0.52 ^b	1.92	0.91
UO2-5	56.2	31.0	1813	0.70 ^b	0.69 ^b	0.70 ^b	2.04	0.97
UO3-1	31.2	31.0	1006	0.22 ^b	0.23 ^b	—	1.63	1.08
FO2	47.0	32.6	1442	1.49	1.12	—	1.62	0.90
N-125	31.6	31.5	1003	0.49	0.52	—	1.66	1.10
MSC5-1	23.3	9.5	2453	0.74	0.72	—	2.35	0.86
MSC5-2	14.4	9.5	1516	0.38	0.36	—	2.05	1.10
SP ¹²	17.1	7.0	2443	0.58	0.53	—	3.10	1.14
AU-1	40.4	22.0	1836	1.18	1.61	—	1.98	0.96
AU-2	49.4	35.0	1411	0.95	1.16	—	1.80	1.02

^a $a_0(1)$ values obtained from the isotherm and eqn (1); $a_0(2)$ values obtained from the enthalpy of immersion and eqn (2) and (12); $a_0(3)$ values obtained by back-titration with HCl after neutralization with NaOH in excess. ^b Acidic sites.

Experimental

Water adsorption isotherms were determined at 293 K, and in some cases at 263 K, on a series of well defined active carbons, characterized as described elsewhere.⁹ The equipment was of the McBain type, fitted with transducer pressure gauges.

The enthalpies of immersion were measured in a calorimeter of the Calvet type with 180 copper-constantan thermocouples, corresponding to a sensitivity of 9.5 mV K⁻¹. The equipment, calibrated electrically and with standard systems, has a reproducibility of 1%.

In order to extend the range of hydrophilic centres, carbons with carboxylic groups (UO2-4 and UO3-1) were prepared by treating solids UO2 and UO3, outgassed at 400 °C, with hydrogen peroxide: 2 dm³ of H₂O₂ (10% by volume) were added slowly to 60 g of active carbon, and the mixture was stirred gently for 20 h. The carbons, filtered off, were subsequently washed with water in a Soxhlet for 3 days and finally dried for 6 h at 120 °C in an oven. Sample UO2-5 was prepared in a similar fashion starting with solid U-O2 but with a 30% solution of H₂O₂. Prior to adsorption and immersion experiments, these solids were outgassed for 12 h under vacuum at a temperature of only 120 °C (*cf.* 400 °C for the other carbons, with sites of the carbonyl type).

In order to assess quantitatively the number of acidic sites, samples of carbons UO2-4 and UO2-5, previously outgassed at room temperature, were immersed into solutions of NaOH in excess and stirred for 48 h in PVC containers, to avoid base consumption by glass. From the back-titration with HCl the number of primary sites, a_0 , could be obtained. As shown in table 1, this was found to be in good agreement with the value derived from the adsorption isotherm, eqn (1). The reproducibility of the titration method was $\pm 1\%$.

The other solids of the UO2 and MSC5 series were prepared by treating the initial solids at various temperatures between 473 and 873 K.

Theory

Starting from the definition of the isosteric heat of adsorption, q^{st} ,¹⁰

$$\left(\frac{\delta \ln p}{\delta T}\right)_a = \frac{q^{\text{st}}}{RT^2} \quad (3)$$

and using the water adsorption isotherm, eqn (1), written in the form

$$p = p_0 a / [c(a_0 + a)(1 - ka)] \quad (4)$$

one obtains

$$\left(\frac{\delta \ln p_0}{\delta T} - \frac{\delta}{\delta T} \ln [c(a_0 + a)(1 - ka)/a]\right)_a = \frac{q^{\text{st}}}{RT^2}. \quad (5)$$

Assuming that k does not depend too much on T , an assumption supported by experimental evidence, it follows that

$$\frac{\delta \ln c}{\delta T} = -(q^{\text{st}} - \Delta H_{\text{vap}}) / RT^2 \quad (6)$$

where q^{st} is a function of the temperature and of the filling of the micropores, $\theta = a/a_s$.

As shown elsewhere,¹¹ in the case of a microporous solid the isosteric heat of adsorption is related to the enthalpy of immersion into the corresponding liquid and

$$-\Delta H_i(T) = \int_0^1 q^{\text{st}}(T; \theta) d\theta - \Delta H_{\text{vap}}(T) \quad (7)$$

all energies being expressed in J mol^{-1} or kJ mol^{-1} of adsorptive (water in the present case).

With eqn (7), eqn (6) becomes

$$\frac{\Delta H_i}{RT^2} = \int_0^1 \frac{\delta \ln c}{\delta T} d\theta \quad (8)$$

and since c does not depend on θ for a given system, it follows that

$$\frac{\delta \ln c}{\delta T} = \frac{\Delta H_i(T)}{RT^2}. \quad (9)$$

If the enthalpy of immersion does not vary significantly within a given domain of temperature, as suggested by typical experiments between 293 and 307 K, eqn (9) leads finally to

$$c = c_0 \exp(-\Delta H_i/RT). \quad (10)$$

The enthalpy of immersion, expressed in J mol^{-1} of water filling the micropores, is obtained by the simple relation

$$\Delta H_i = \Delta h_i / a_s \quad (11)$$

where Δh_i is in J g^{-1} and a_s is in mol g^{-1} . Eqn (10) establishes a direct relation between constant c of the water adsorption isotherm and the enthalpy of immersion of the microporous carbon, a quantity which can be measured easily and quickly. Moreover, through eqn (2) and (10) the influence of the primary centres a_0 on c becomes obvious, provided that these centres are of the same type.

Results and Discussion

Table 1 summarizes the data obtained from water adsorption and immersion experiments at 293 K with 13 different samples. For sample SP all the data was found in the literature,¹² and in the case of samples AU-1 and AU-2 the adsorption isotherms were provided by Dubinin.¹³ As a typical example, fig. 2 shows the water adsorption isotherm

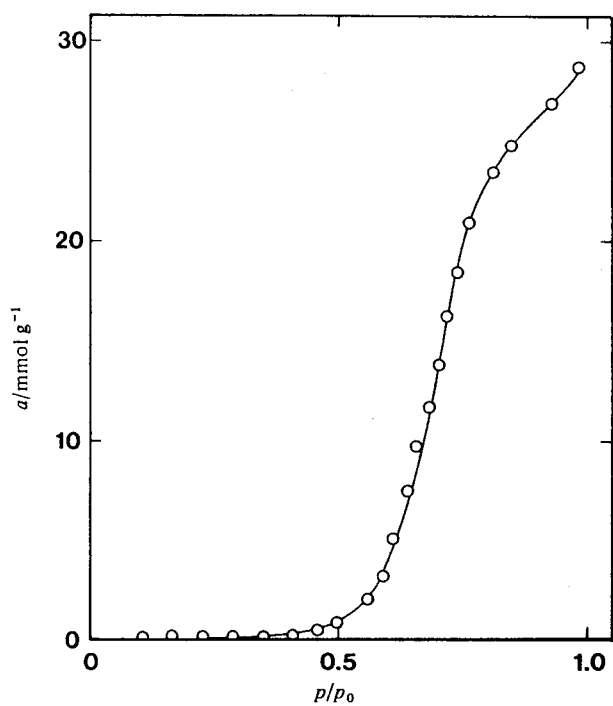


Fig. 2. The adsorption of water vapour by carbon UO3-1 at 293 K (hysteresis loop not shown).

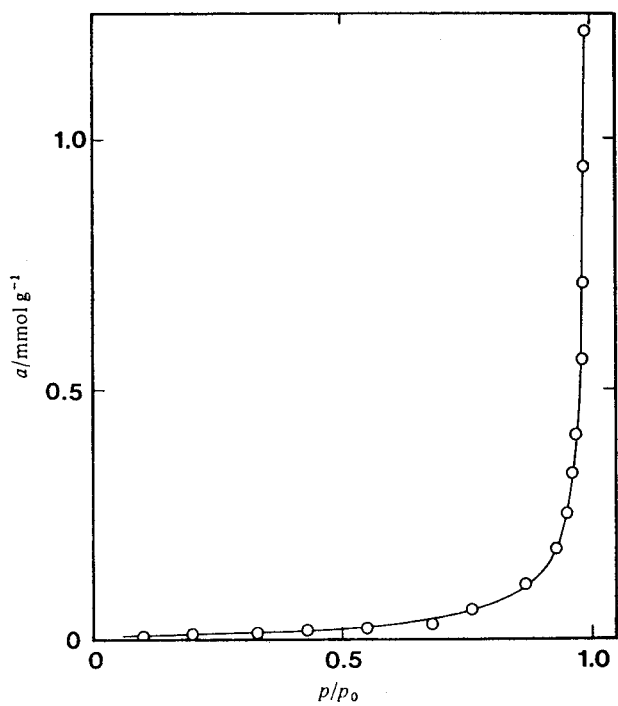


Fig. 3. The adsorption of water vapour by graphitized carbon black Vulcan-3G at 293 K (desorption points not shown).

for sample UO3-1 at 293 K. The constants a_0 and c were obtained from a best fit of the adsorption data to eqn (1), as discussed elsewhere.^{3, 14} The multiple linear regression was preferred to the graphical method proposed earlier by Dubinin,² but in both cases the value of c depends, to some extent, on the number of points and on the pressure range.

In the case of samples UO2-4 and UO2-5, containing only acidic sites, the values of a_0 obtained from the isotherm are in good agreement with the direct titration. It also appears that the corresponding enthalpies of immersion can be fitted to an equation similar to eqn (1), but with higher specific interactions:

$$\Delta h_i = -55a_0 - 0.6(a_s - a_0). \quad (12)$$

The specific interaction is twice as large as observed for the carbonyl groups described by eqn (2), which underlines their different nature. It has also been found that the enthalpy of immersion does not change between 293 and 307 K.

As illustrated by table 1, the best fit of c and ΔH_i to eqn (10) leads to the average value $c_0 = 1.00 \pm 0.11$. A similar value is obtained for the adsorption of water by the graphitized carbon black Vulcan-3G at 293 K (fig. 3), where $c = 0.99$. In the case of sample UO3-1, the analysis of the water adsorption isotherms for 263 and 293 K has led to identical values of a_0 (0.22 mmol g^{-1}) and to $c = 1.715$ and 1.633 , respectively. From eqn (9) it follows that $\Delta H_i = -1048 \text{ J mol}^{-1}$, in good agreement with the experimental result, $-1006 \pm 15 \text{ J mol}^{-1}$.

Since the individual values of c derived from the isotherms are relatively inaccurate (up to $\pm 10\%$ in some cases), it seems justified to calculate them by using the corresponding enthalpies of immersion in eqn (10) with $c_0 = 1$. For active carbons with a known micropore volume and containing only one type of primary centre, parameters a_0 and c can be derived from the enthalpies of immersion by using eqn (2) or (12) and (10). It follows that the water adsorption isotherm, given by eqn (1), can also be calculated *a priori* for a range of temperatures.

If the two types of sites mentioned above are present simultaneously, the enthalpy of immersion into water is a linear combination of eqn (2) and (12):

$$-\Delta h_i = 25a_{01} + 55a_{02} + 0.6(a_s - a_{01} - a_{02}) \quad (13)$$

where a_{01} and a_{02} (in $\text{mmol H}_2\text{O g}^{-1}$) represent the corresponding sites. The back-titration of the acidic sites leads to a_{02} , and a_{01} can be calculated from eqn (13). By using a_{01} , a_{02} and the corresponding values of c_1 and c_2 given by eqn (10), it is possible to calculate, in principle, an overall adsorption isotherm resulting from the combination of the individual isotherms, eqn (1).

Since immersion calorimetry is an accurate and relatively fast technique (1–2 days for the preparation of the solid and the measure of its enthalpy of immersion, as opposed to 2–3 weeks for the determination of a water adsorption isotherm), much time can be saved using the approach outlined in this paper in order to predict the interaction between water vapours and a pure active carbon.

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