The adsorption of water by active carbons, in relation to their chemical and structural properties

F. Stoeckli\textsuperscript{a,*}, A. Lavanchy\textsuperscript{b}

\textsuperscript{a}Chemistry Department of the University, Avenue de Bellevaux 51, Ch-2000 Neuchâtel Switzerland
\textsuperscript{b}NBC Laboratory, 3700 Spiez, Switzerland

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An interesting letter has recently been published in this Journal by Lodewyckx and Vansant [1], introducing the idea of an affinity coefficient for water with respect to benzene, the usual reference in Dubinin’s theory. This concept is valid for carbons with relatively low oxygen contents, where the water adsorption isotherm is of type V and corresponds to a Dubinin-Astakhov equation, as shown earlier [2,3].

We wish to show that Lodewyckx’s idea can be included in a more general approach based essentially on the comparison of the enthalpies of immersion of carbons into water and benzene and taking into account the chemistry of the surface through an excess enthalpy of immersion. Our approach follows two recent studies dealing with the interaction of water [4] and of methanol and ethanol [5] with active carbons containing variable amounts of oxygen and basic groups. The starting point is the DA equation [3,6]

\[ N_a = N_{aw} \exp \left(-\frac{A}{E} \right) \]  

(1)

where \( N_a \) is the amount adsorbed at relative pressure \( p/p_c \) and temperature \( T \); \( N_{aw} \) is the limiting amount filling the micropore volume; \( A = RT \ln(p_c/p) \) and \( E \) is the so-called characteristic energy of the system. The latter can be written as \( E = \beta E_{\omega} \), where \( \beta \) is the affinity coefficient of the adsorbate. Benzene is the reference and by definition \( \beta(C,H_\omega) = 1 \).

As shown elsewhere [3], the enthalpy of immersion of a microporous carbon into a liquid whose vapour is adsorbed according to Eq. (1), is given by

\[ \Delta h_a(J/g)_{mi} = -W_c \beta E_{\omega}(1 + \alpha T) I(1 + 1/n)/V_m \]  

(2)

The quantities \( W_c = N_{aw} V_m \), \( \alpha \) and \( V_m \) are respectively the total micropore volume of the solid, the thermal expansion coefficient of the adsorptive and its molar volume in the liquid state. \( I(1 + 1/n) \) is tabulated ‘Gamma’ function, which takes values between 0.89 and 0.92 when \( n \) varies from 1.5 to 5. This means that the enthalpy of immersion depends essentially on the characteristic energy \( E = \beta E_{\omega} \).

Since active carbons also possess an external (non-microporous) surface \( S_e \), the experimental enthalpy of immersion, \( \Delta h_a(J/g)_{exp} \) is

\[ \Delta h_a(J/g)_{exp} = \Delta h_a(J/g)_{mi} + h S_e \]  

(3)

where \( h \), a negative quantity, represents the wetting of the surface. For benzene and water at 293 K, \( -h \) corresponds to 0.114 and 0.030 J/m\(^2\) [3–5] and the last term of Eq. (3) is only a fraction of the total enthalpy of immersion.

From Eqs. (2) and (3), it follows that the enthalpy of immersion of a given adsorbate can be calculated from the parameters of the DA isotherm. A good agreement has been found for a variety of liquids [2,3].

Since Dubinin’s theory only considers non-specific (dispersive) interactions, an extra term must be added to Eq. (3) when specific interactions are present and

\[ \Delta h_a(J/g)_{exp} = \Delta h_a(J/g)_{mi} + h S_e + \Delta h_{spec} \]  

(4)

Carbons contain variable amounts of surface oxygen and basic centres interacting with water [4] and therefore \( \Delta h_{spec} \) will be a function of these groups. (This enthalpy may also be regarded as an excess enthalpy of immersion with respect to the contribution arising from the non-specific interactions, as used previously [5].)

Adsorptives with no specific interactions can be used as references and benzene is a suitable candidate, since it is not affected by changes in the oxygen content of the surface. As shown recently [5] and illustrated in Table 1, the oxidation of active carbon AZ46-0 with \((\text{NH}_4)_2\text{S}_2\text{O}_8\),

\[ *Corresponding author. \]
increases the oxygen content from 0.3 to 7 mmol/g, but the enthalpy of immersion of benzene at 293 K remains virtually constant. According to Eq. (2), in the absence of specific interactions the enthalpies of immersion of a given carbon into liquids 1 and 2 are related by

$$
\Delta h_i (1)_{m} / \Delta h_i (2)_{m} = \beta_i (1 + \alpha_i T) V_m / \beta_i (1 + \alpha_i T) V_m
$$

(5)

For benzene and water at 293 K one obtains

$$
\Delta h_i^s (H_2O)_{m} / \Delta h_i (C_{6}H_{6})_{m} = 3.84 x \beta_i (H_2O)
$$

(6)

where $\Delta h_i^s (H_2O)_{m}$ represents the enthalpy of immersion due to the non-specific interactions only and the factor $3.84 = (1 + \alpha_{i,O} T) V_m (C_{6}H_{6}) / (1 + \alpha_{i,O} T) V_m (H_2O)$.

From the combination of Eqs. (3) and (6) it follows that

$$
\Delta h_i (H_2O)_{exp} + 0.030 S_p = 3.84 \beta_i (H_2O) [\Delta h_i (C_{6}H_{6})_{exp} + 0.114 S_p] + \Delta h_i (H_2O)_{spec}
$$

and

$$
\Delta h_i (H_2O)_{exp} = 3.84 \beta_i (H_2O) [\Delta h_i (C_{6}H_{6})_{exp} + S_p [0.44x\beta_i (H_2O) - 0.030] + \Delta h_i (H_2O)_{spec}
$$

(7)

Since $\beta_i (H_2O)$ is close to 0.05 (see below), it appears that the term in square brackets is equal to $-0.011 S_p$ and therefore relatively small. Calculations based on the data of Table 1 show that $-0.011 S_p / 3.84 \beta_i (H_2O) x \Delta h_i (C_{6}H_{6})_{exp} = 0.05 \pm 0.01$ and consequently Eq. (7) becomes, to a very good approximation,

$$
\Delta h_i (H_2O)_{exp} = 4.03 \beta_i (H_2O) [\Delta h_i (C_{6}H_{6})_{exp} + \Delta h_i (H_2O)_{spec}
$$

(8)

Although Eq. (7) is formally correct, Eq. (8) has the advantage that it uses only the experimental enthalpies of immersions and it does not require the knowledge of $\Delta_i$. Eq. (8) holds for carbons where adsorption in the micro pores is larger than on the external surface area.

As discussed in detail elsewhere [4], water interacts with the oxygen atoms of the different surface complexes and with the basic centres. (The latter are characterized by their equivalents of HCl and it appears that most of them do not contain oxygen). The concentration of the basic sites does not exceed 0.8 milliequivalents of HCl/g, whereas the oxygen content [O] of the surface can be as high as 7 mmol/g. It was also found that the specific interactions, reflected by $\Delta h_i (H_2O)_{spec}$, is due to interactions with oxygen atoms. It was also found that the specific interactions between water and the surface oxygen ($-12.1 J / $mmol) and the basic groups ($-10.3 J / $meq HCl) are close. Therefore, and by analogy with the case of methanol and ethanol, it is reasonable to postulate, as a first approximation, that $\Delta h_i (H_2O)_{spec}$ is a linear function of [O + HCl], the sum of the surface oxygen (mmol/g) and the HCl milliequivalents of basic sites ($meq/g$). Consequently, Eq. (8) becomes

$$
\Delta h_i (H_2O)_{exp} = c_i \Delta h_i (C_{6}H_{6})_{exp} + c_j [O + HCl]
$$

(9)

where $c_i = 4.03 x \beta_i (H_2O)$.

In order to test the present model, the data given in Table 1 has been fitted to Eq. (9), as shown in Fig. 1. The data corresponds to 15 carbons of different origins [7–10], used in earlier investigations [4,5,7]. The best fit (correlation coefficient 0.9704) leads to

$$
\Delta h_i (H_2O)_{exp} / (J/g) = 0.210 \Delta h_i (C_{6}H_{6})_{exp} - 9.9 [O + HCl]
$$

(10)
These results suggest an affinity coefficient $\beta(H_2O)$ of 0.210/4.03 = 0.052, with a standard deviation of ±0.007. The average specific interaction is −9.9±0.7 Joules per mmol of oxygen or milliequivalent HCl.

The affinity coefficient of water found here is in good agreement with the value of 0.060 given by Lodewyckx and Vansant [1]. On the other hand, the average specific interaction energy is somewhat smaller than the earlier estimates. It should also be pointed out, that no reliable results could be obtained from an equation of the type

$$\Delta h_i(H_2O)_{exp} (J/g) = c_i \Delta h_i (C_xH_y)_{exp} + c_x[O] + c_{\beta}[\text{basic}]$$

(11)

This suggests that it is reasonable to postulate a unique interaction energy of approximately −10 $J$/mmol of oxygen or $J$/meq HCl. The correlation given by Eq. (10) is shown in Fig. 1.

As indicated by Eq. (10), the non-specific interaction of microporous carbons with water is only 12% of the enthalpy into benzene and $\Delta h_i(H_2O)_{spec}$ increases rapidly with the surface groups. On the other hand, in the case of methanol and ethanol interacting with the same carbons, the non-specific interactions arising from the organic part of the molecules represent the largest contribution to the enthalpy of immersion.

An interesting consequence of Eq. (10) is the possibility to estimate the number of surface groups (predominantly oxygen atoms) from the experimental enthalpies of immersion of pure active carbons into water and into benzene at 293 K. One obtains, to a good approximation,

$$[O + HCl] (\text{mmol/g}) = [-\Delta h_i(H_2O)]_{exp} + 0.210/\Delta h_i(C_xH_y)_{exp}]/10$$

In agreement with Lodewyckx and Vansant, in the case of carbons with low oxygen contents the type V water adsorption isotherm can be approximated by Eq. (1), using a characteristic energy $E(H_2O) = \beta(H_2O)xE_o$ and an arbitrary exponent $n$ around 4 (The latter is suggested by experience [2]). Since $E_o$ depends on the average micropore width [3], the corresponding water isotherm also reflects the structural properties of the carbon. However, when the oxygen content increases (typically beyond 2.5 to 3 mmol/g for industrial carbons), the isotherm is gradually modified by the appearance of an initial section of type 1 [11, 12]. This change and the increase in the enthalpy of immersion reflect the strong influence of the specific interactions in the case of water, as opposed to the case of short alcohols [5].

Eq. (10), which is based on the enthalpies of immersion, has the advantage that it provides a reasonable estimate for the affinity coefficient of water $\beta(H_2O)$ and the specific interactions. Moreover, no particular model is required, except, that in the absence of specific interactions, the limiting enthalpy of immersion into water is related to the enthalpy of immersion into benzene by Eq. (6). However, when the oxygen content increases, the water adsorption isotherm is modified under the influence of the specific interactions, which are reflected in the experimental enthalpy of immersion. The exact correlation between Eq. (10) and the isotherm is being investigated and results will be presented in due course.

References