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THE ADSORPTION OF WATER BY ACTIVE CARBONS, IN RELATION TO THE ENTHALPY OF IMMERSION

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Abstract—It is shown that there exists a simple relation between the enthalpy of immersion of pure active carbons into water, and the number of so-called primary adsorption sites a_0 derived from the water adsorption isotherm by using the new Dubinin–Serpinsky equation. The adsorption sites left on the surface after outgassing near 400°C, probably of the carbonyl type, contribute to the enthalpy of immersion by -25 kJ/mole, vs -0.6 kJ/mole for the bulk of the water filling the micropores at 307 K.

1. INTRODUCTION

An equation describing the adsorption of water by active carbons has been proposed by Dubinin and Serpinsky[1], and used in a series of investigations [2–5]. This equation is the improved version of an earlier description[6], and it reads

$$p/p_0 = a/c(a_0 + a)(1 - ka) \qquad (1)$$

a is the amount adsorbed at relative pressure p/p_0, a_0 characterizes the so-called primary centres through the amount of water adsorbed on them, and c is the ratio between the rates of adsorption and desorption. For active carbons, the latter varies between 1.6 and 2.5, as shown in the table. Term $(1 - ka)$ takes into account the decrease in acting adsorption centers with increasing micropore filling. Parameter k itself can be calculated from the condition that at $p/p_0 = 1$, the limiting amount adsorbed is $a = a_s$. Typical water adsorption isotherms are shown in Figs. 1–2.

The quantity a_0 can be obtained from eqn (1) either by the approximate graphical procedure described by Dubinin and Serpinsky[1, 4], or by using straightforward curve fitting with a desk computer. The latter technique was used in the present study and it was found that a better fit to eqn (1), than in Dubinin's method, could be obtained from adsorption data between $p/p_0 = 0.05$–0.1 and the inflexion point of the ascending branch of the isotherm. The bad fit at low relative pressures can be explained by the Langmuir type of adsorption observed in the very early stages of adsorption and recently investigated by Dubinin *et al.*[6]. On the other hand, at high degrees of micropore filling, a_0 represents only a few per cent of the amount of water adsorbed and the influence of the primary centres becomes less important. As a consequence, the primary centres are important in the type III part of the isotherm and in the actual position of the steep rise, as illustrated in Fig. 1–2.

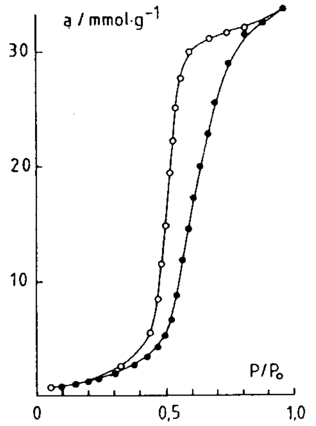

Fig. 1. The adsorption (●) and desorption (○) of water by sample 3, at 293 K.

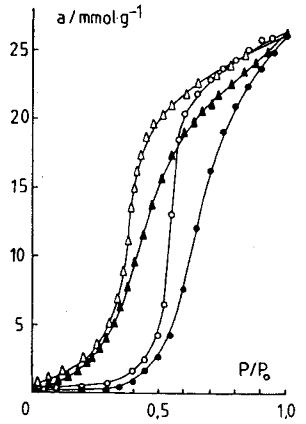

Fig. 2. The adsorption of water by samples 1 (● ○) and 2 (▲ △) at 293 K, containing respectively 4.6 and 26.5% of primary centres. Open symbols refer to desorption data.

The upper part, as p/p_0 tends to unity, reflects the limited filling capacity of the micropore system, as opposed to graphitized carbon blacks, and it is not related to a_0.

Independently, it is also found that the primary centres play a significant role in the enthalpy of immersion ΔH_i of active carbons into water[7–10]. As shown recently by Stoeckli and Kraehenbuehl[9], ΔH_i (H_2O; 307 K) can drop from -140 to -90 J/cm^3 of micropores for an MSC-5 carbon reduced in hydrogen, whereas in the case of benzene and other non-specific liquids, ΔH_i remains virtually unchanged. Immersion calorimetry is therefore a useful technique in dealing with the chemistry of the surface, and complementary to the analysis of the water adsorption isotherm.

The present study establishes the relation which exists between the two approaches, thus providing a complementary method for the study of water adsorption in microporous carbons.

EXPERIMENTAL

Eight typical active carbons derived from anthracite (1–2), vegetable materials (3) and polymers (4–8) were used in the present study. Their micropore volumes W_0 and characteristic energies E_0 were derived from the Dubinin equation[11] applied to the N_2(77 K) and C_6H_6(293 K) adsorption isotherms. Samples 4 and 5 correspond to the MSC-V carbon described previously[9]. The water adsorption isotherms were determined at 293 K, in a standard gravimetric apparatus equipped with quartz springs and pressure sensors. Prior to adsorption, the samples were outgassed *in vacuo* (10^{-5}–10^{-6} Torr), the temperature being raised over 12 hr to 400°C and kept there for another 12 hr. This procedure ensured a standard treatment for the various samples, with respect to the elimination of oxygen-containing species. In agreement with Barton *et al.*[10], our experiments showed a decrease of 10-20 J/g in the enthalpies of immersion into water, for outgassing between 150 and 400–420°C. This stresses the need for a standard treatment prior to adsorption and immersion experiments. Barton *et al.*, investigating the desorption of surface complexes from a PVC carbon, also showed that the bulk of CO_2 was desorbed before 400–420°C, as opposed to CO for which temperatures up to 800–1000°C are required. The work of Puri[7] leads to similar conclusions.

In the present case, the hydrophilic centres left after the standard treatment should be mostly of the type leading to CO desorption (probably carbonyl groups on the surface, following Ref.[10]).

The enthalpies of immersion into water at 307 K were carried out as described earlier[9], and the samples were subjected to the same treatment as for the corresponding adsorption experiments.

3. RESULTS AND DISCUSSION

The results derived from the adsorption isotherms at 293 K and from immersion calorimetry at 307 K are shown in Table 1. They also include the data for an untreated sugar charcoal, outgassed at 600°C and described by Puri[7]. For this sample, the water adsorption isotherm and ΔH_i were also given.

As suggested by Dubinin[2], $a_{0.6}$, the amount of water adsorbed near $p/p_0 = 0.6$ corresponds in many cases to the monolayer covering the walls of the micropores. Since $a_{0.6}$ is close to the true surface of these pores (not to be confused with their total volume W_0), the ratio $a_0/a_{0.6}$ represents the fraction of the surface occupied by the primary centres. This ratio, rather than a_0 alone, is a useful quantity for the characterization and the comparison of different active carbons. As shown by Dubinin[2], the surface of the micropore walls can also be derived from constants E_0 and W_0 of the Dubinin-Radushkevich equation, E_0 being related to the width of slit-shaped micropores[11]. Ideally, the surfaces obtained from the two methods should be the same. However, as found by the present authors, for active carbons having micropore widths above 0.6–0.7 nm, a good agreement can be found only if the primary centres represent less than 5–7% of the surface. For higher ratios, all other structural properties remaining unchanged, the adsorption isotherm will be shifted gradually to the left and $a_{0.6}$ becomes too high.

This is illustrated in Fig. 2, an extreme case. Sample 2 was obtained from 1 by treatment with Ce^{4+}, in order to increase a_0, and carefully washed and checked for impurities. As shown by adsorption isotherms and immersion calorimetry with organic liquids, the two solids are structurally identical, but the shape of the water adsorption isotherm is modified significantly.

For carbons with small micropores, on the other hand, like samples 4–5, the micropores can accommodate only two layers of water and $a_{0.6}$ is always found on the r.h.s. of the steep rise in the isotherm[9].

The analysis of the data given in the table leads to the relation

$$\Delta H_i(\mathrm{J/g}) = -25.0(\mathrm{J/mmol\ H_2O})\cdot a_0 - 0.6(\mathrm{J/mmol\ H_2O})\cdot(a_s - a_0) \quad (2)$$

a_s and a_0 being expressed in mmol of water per *g* of active carbon.

In the case of samples 4 and 5, a_s is virtually unchanged by hydrogenation[9] and corresponds to 0.17 cm^3/g, vs 0.16 and 0.19 cm^3/g from the benzene adsorption isotherms. The difference reflects molecular-sieve effects.

The table also shows the satisfactory correlation which exists between a_0 derived from the isotherms and values recalculated through eqn (2) from the enthalpies of immersion.

Experiments carried out with other samples show that the enthalpy of immersion is sensitive to mineral impurities, whose hydration or dissolution can affect ΔH_i. Equation (2) therefore applies strictly to pure microporous carbons.

The contribution of -25 kJ/mole of water ad-

Table 1. Specific parameters derived from water adsorption (293 K) and immersion (307 K) experiments, for various microporous carbons. The amounts a_s, $a_{0.6}$ and a_0 are given in mmole H_2O/g. The data for sample 9 are taken from Ref.[7]

sample	c	a_s	$a_{0.6}$	a_0(exp)	a_0(calc)	$a_0/a_{0.6}$	$-\Delta H_i/(J/g)$
1	1.79	26.1	7.6	0.35	0.50	0.046	27.9
2	2.49	26.3	-	2.01	2.22	0.265*	70.0
3	1.62	32.6	16.6	1.49	1.12	0.090	47.0
4	2.35	9.5	8.3	0.74	0.72	0.089	23.3
5	2.02	9.5	8.0	0.37	0.36	0.046	14.4
6	2.00	20.5	17.0	0.15	0.10	0.009	14.7
7	2.20	30.0	16.5	0.50	0.56	0.026	31.6
8	2.26	23.5	12.9	0.31	0.46	0.024	25.4
9 [7]	3.10	6.9	5.2	0.58	0.53	0.111	17.1

* calculated with $a_{0.6} = 7.6$

sorbed on the primary sites, left after outgassing near 400°C, can be correlated with other observations [8, 10, 12]. The study of Barton *et al.*[10] shows that the enthalpy of immersion of a PVC charcoal into water decreases rapidly with the amount of preadsorbed water. A value of -23.8 kJ/mole H_2O is found for the early stages, corresponding to the interaction with the primary sites.

These authors also found a linear decrease in ΔH_i (H_2O) with the amount of oxygen desorbed as CO at various temperatures, corresponding to -30 kJ/mole of atomic oxygen. A similar study with graphite[12] leads to 20 kJ/mole of atomic oxygen on the surface, desorbed as CO and CO_2. For the sugar charcoal of Puri[7], included in out table, further outgassing at 900 and 1200°C shows that this sample contained 10.2 mg of oxygen/g of solid, desorbed as CO. This corresponds to 0.64 mmole of atomic oxygen/g, in good agreement with $a_0 = 0.58$ mmole/g obtained from the water adsorption isotherm, through eqn (1). These observations, combined with eqn (2), clearly establish the correspondence between the oxygen atoms on the surface and the number a_0 of molecules of water adsorbed on the primary centres, the contribution of these interactions to the enthalpy of immersion being near -25 kJ/mole. This also supports the model on which the Dubinin–Serpinsky eqn (1) is based.

Following the treatment of our carbons prior to the adsorption and immersion experiments, it appears that eqn (2) applies mainly to the centres desorbed as CO from the surface. An extension of this equation, including the weaker centres will be considered later.

4. CONCLUSION

It appears from the present study, and from an earlier investigation[9] relating the enthalpy of immersion to the Dubinin–Radushkevich equation, that this technique can be very useful for the characterization of microporous carbons. When combined with a minimum of adsorption data, such as C_6H_6(293 K) for example, enthalpies of immersion into organic liquids will provide complementary information on the structure (i.e. the physics) of the micropore system. Enthalpies of immersion into water, on the other hand, will provide quick information on the chemistry of the micropores. The combination of these techniques can be very useful in the case of a series of related carbons.

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