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THE EXTERNAL SURFACE OF MICROPOROUS CARBONS, DERIVED FROM ADSORPTION AND IMMERSION STUDIES

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Abstract—Three typical samples of active carbons have been investigated by using immersion calorimetry and adsorption techniques (t-plot, t/F method of Dubinin and direct analysis of the adsorption isotherm before and after prefilling), in order to obtain their external surface area. The different techniques lead to consistent results.

1. INTRODUCTION

Active carbons are characterized by their micropore volume and by an external or non-microporous surface S_e, which can be as high as 200 m^2/g. This surface corresponds essentially to the walls of the meso- and macropores. Information on the micropore system is obtained from the fundamental equation of Dubinin's theory[1–3],

$$W = W_0 \exp\{-(A/\beta E_0)^n\} \quad (1)$$

where W is the volume of the adsorbate condensed in the micropores at temperature T and relative pressure p/p_0; W_0 is the total volume of the micropores, $A = \Delta G = RT \ln(p_0/p)$ and n, β and E_0 are specific parameters of the system under investigation.

When $n = 2$, eqn (1) reduces to the well-known equation of Dubinin and Radushkevich, valid for typical active carbons. It has also been shown that parameter E_0 is related to the average pore-width of the micropores[2, 3], which can provide a good estimate for the geometrical surface area of these pores[4].

Following Stoeckli and Krähenbühl[5, 6], the enthalpies of immersion of active carbons into organic liquids can be related directly to eqn (1),

$$-\Delta H_i(J/g)_{mi} = \beta E_0 W_0 (1 + \alpha T)\sqrt{\pi}/2V_m \quad (2)$$

α and V_m being the thermal expansion coefficient and the molar volume of the liquid filling the micropore system. Equation (2) can be tested directly with carbons having relatively small external surface areas, where the experimental and calculated enthalpies agree within 0.5%. In the general case, however, the experimental enthalpy also contains a contribution for the immersion of the external surface,

$$\Delta H_i(J/g)_{exp} = \Delta H_i(J/g)_{mi} + h_i \cdot S_e \quad (3)$$

where h_i is the specific enthalpy of immersion of the open surface. The second term usually represents a small fraction (10%) of the total enthalpy. Under favourable conditions, as shown below, it is possible to derive a reasonable value of S_e from eqns (2) and (3).

Traditionally, the external surface of microporous solids can be obtained by different techniques, based on the analysis of adsorption isotherms.

Comparison plots such as the t- and α_s-plots[7];

The method of Gregg and Langford[7, 8], based on the prefilling of the micropores, followed by N_2 adsorption at 78K;

The t/F method of Dubinin and Kadlec[9].

The third approach considers the experimental adsorption isotherm as a sum of contributions corresponding to the micropores, obtained from eqn (1), and to the external surface,

$$V = W + S_e \cdot t(p/p_0) \quad (4)$$

V is the total volume of adsorbate at relative pressure (p/p_0) and $t(p/p_0)$ the thickness of the adsorbed layer. By dividing both sides of eqn (4) by $F = \exp\{-(A/\beta E_0)^2\}$, one obtains

$$V/F = W_0 + S_e(t/F). \quad (5)$$

The representation of V/F vs t/F is the so-called t/F plot, which leads to W_0 and S_e.

As shown by Dubinin, the method can be applied to N_2(78K) and C_6H_6(293K) isotherms. It leads to surfaces which are in fair agreement with the cumulative surface areas of the mesopores[10]. However, in the case of carbons having large micropore volumes, with respect to the external surface, the differential method implied by eqns (4) and (5) becomes less accurate for the determination of S_e. This situation can be improved, if one applies the t/F method to a nitrogen isotherm obtained after prefilling approx. 70–80% of the micropores with n-nonane or benzene. Under these conditions, preadsorption on the external surface will also be small. This approach effectively combines the methods of Dubinin and of Gregg and Langford. However, the exact prefilling of

the whole micropore volume W_0, sometimes difficult to reach, is no longer required, since the t/F method clearly separates the adsorption on the external surface from the filling of the remaining micropore volume. The uncertainties, arising from the volume of the micropores actually prefilled or blocked, and from the direct BET analysis of the subsequent nitrogen isotherm, are therefore removed.

In the present paper, we compare the external (non-microporous) surfaces obtained by the different techniques, including immersion calorimetry.

2. EXPERIMENTAL

Three typical activated carbons (see Table 1) were selected for a detailed investigation, after preliminary work with a range of samples[6] including molecular-sieve carbons. The adsorption isotherms of N_2(78K), C_6H_6(293K) and CCl_4(293K) were determined in a standard gravimetric apparatus equipped with transducer gauges. In the case of samples N-125 and U-02, having relatively large micropore volumes, nitrogen was also adsorbed at 78K after preadsorption of nonane and benzene, at room temperature. Except in the case of the Gregg-Langford method (sample U-02), the micropores were filled to approx. 0.7–0.8 W_0.

The enthalpies of immersion at 307K, into benzene, *n*-heptane and *n*-hexadecane, were carried out as described earlier[6]. Based on earlier comparisons of adsorption and immersion experiments, the following values of the constant β were used in eqn (2): $\beta(C_6H_6) = 1$ as the usual Ref.[1], $\beta(n - C_7H_{16}) = 1.62$ and $\beta(n - C_{16}H_{34}) = 4.05$.

For h_i, the enthalpy of immersion of the external surface, typical values quoted for graphitized carbons[14] were used in eqn (3) C_6H_6: -0.114 J/m^2 [12, 13]; $n - C_7H_{16}$: -0.123[13]; $n - C_{16}H_{34}$: -0.148 J/m^2.

As confirmed by studies on a number of different activated carbons, carbon tetrachloride does not lead to reliable and coherent results, the enthalpies of immersion being sometimes unexpectedly large. Discrepancies of 20–30% with the predictions of eqn (2) have been observed in some cases.

Prior to adsorption and immersion experiments, 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 10–12 hr. This procedure, also applied in the case of water adsorption and immersion[11], ensures a standard treatment.

Table 1. Adsorption characteristics of the solids and average external surfaces derived from Tables 2 and 3

Carbon	E_0(kJ/mole)	W_0(cm^3/g)	S_e(m^2/g)
N - 125	16.6	0.64	157 ± 20
U - 02	20.0	0.43	105 ± 16
FA	20.0	0.29	112 ± 6

Table 2. External surface areas obtained from enthalpies of immersion at 307K and eqns (2) and (3)

Carbon / liquid		ΔH_i (307K) (J/g) exp	ΔH_i (307K) (J/g) calc eqn(2)	S_e(m^2/g)
N-125	C_6H_6	160.2	143.8	144
	n-C_7H_{16}	166.0	142.4	194
	n-$C_{16}H_{34}$	192.4	166.4	176
U-02	C_6H_6	126.1	116.2	88
	n-C_7H_{16}	129.1	115.0	115
	n-$C_{16}H_{34}$	146.5	134.4	82
FA	C_6H_6	91.9	77.9	123
	n-C_7H_{16}	90.8	77.1	112
	n-$C_{16}H_{34}$	105.8	90.1	106

3. RESULTS AND DISCUSSION

From the linear sections of the Dubinin–Radushkevich plots[1], one obtains parameters W_0 and E_0 (Table 1). These values can be used safely for different adsorbates, with their β values, provided that no molecular-sieve effects occur. The combination of the experimental enthalpies of immersion with eqns (2) and (3) leads to the external surface areas given in Table 2.

The adsorption isotherms of C_6H_6(293K), and of N_2(78K) with and without preadsorption of *n*-nonane or benzene, were analyzed by the different techniques described above. Table 3 gives the various surface areas derived from the *t*-plots[7], the t/F method[9] given by eqn (5), and by the direct BET analysis of the residual isotherm obtained by substracting the D–R contribution from the experimental isotherm. The BET c values (10–15) obtained for N_2 in the latter method were smaller than for Dubinin's *t*-plot ($c = 88$). They may be compared with the values of 20–30 found by Gregg and Langford[8] for Mogul II, and possibly reflect the adsorption of N_2 vapours on nitrogen having filled the micropores.

In the case of samples N-125 and U-02, the cumulative surface area of these pores was also calculated from the desorption branch of the nitrogen isotherm at 78K, as described in Ref.[7]. As shown by Tables 2 and 3, the values of S_e obtained by the various techniques are fairly consistent and lead to the averages given in Table 1. The overall scatter of 10–15% is not too surprising, in view of the possible errors inherent to the individual techniques[7]. The calorimetric technique may be used either as a complementary test of self-consistency, including W_0, E_0 and S_e, or to determine S_e if the analysis of the isotherms is not satisfactory.

The present study and previous investigations deal-

Table 3. External surface areas S_e obtained from the analysis of adsorption isotherms, by different methods

Carbon	Isotherm and	method	$S_e(m^2/g)$
N - 125	C_6H_6 (293K)	t/F method	175
	N_2 (78K)	Kelvin (mesopores)	145
	N_2 (78K)	t-plot	128
	N_2 (78K)	preadsorbed C_6H_6 decomposition and BET	155
	N_2 (78K)	preadsorbed n-C_9H_{20} decomposition and BET	141
U - 02	N_2 (78K)	t/F method	115
		Kelvin (mesopores)	96
	N_2 (78K)	preadsorbed n-C_9H_{20} to W_0; Gregg-Langford	93
	N_2 (78K)	preadsorbed C_6H_6 t-plot	115
		t/F method	108
		decomposition and BET	131
FA	C_6H_6 (293K)	t-plot	106
		t/F method	111
		decomposition and BET	118
	N_2 (78K)	t-plot	109
		t/F method	105
		decomposition and BET	114

ing with enthalpies of immersion [6, 11] show that this technique provides useful information on the physics and the chemistry of microporous carbons.

At the present time these techniques are used in our laboratory for the characterization of series of carbons.

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REFERENCES

1. M. M. Dubinin, *Progr. Surface Membrane Sci.* **9**, 1 (1979).
2. M. M. Dubinin and H. F. Stoeckli, *J. Colloid Interface Sci.* **75**, 34 (1980).
3. M. M. Dubinin, *Carbon* **20**, 195 (1982).
4. M. M. Dubinin, *Carbon* **18**, 355 (1980).
5. H. F. Stoeckli (Festschrift M. M. Dubinin), *Izvesv. AN SSSR, Ser. khim* 65 (1981).
6. H. F. Stoeckli and F. Krähenbühl, *Carbon* **19**, 353 (1981).
7. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*. Academic Press, London (1982).
8. S. J. Gregg and J. F. Langford, *Trans. Faraday Soc.* **65**, 1394 (1969).
9. M. M. Dubinin and O. Kadlec, *Carbon* **13**, 263 (1975).
10. M. M. Dubinin and L. I. Kataeva, *Izvest. AN SSSR, Ser. khim.* **1980**, 498.
11. H. F. Stoeckli, F. Krähenbühl and D. Morel, *Carbon* **21**, 589 (1983).
12. F. E. Bartell and R. M. Suggitt, *J. Phys. Chem.* **58**, 36 (1954).
13. L. Robert, *Bull. Soc. Chim. France* **1967**, 147.
14. W. H. Wade, M. L. Deviney, W. A. Brown, M. H. Hnoosh and D. R. Wallace, *Rubber Chem. Tech.* **45**, 117 (1972).