

On the determination of the total surface area of carbons by the selective adsorption of caffeine from aqueous solutions

Key Words - Adsorption, surface area, carbons, immersion, caffeine

At the present time, the characterization of the external (i.e. nonmicroporous) surface area  $S_e$  of carbonaceous materials can be carried out by standard adsorption and immersion techniques, using simple organic molecules.

On the other hand, if micropores are present, the true surface area of their walls,  $S_{mi}$ , can be determined indirectly from the parameters of Dubinin's theory [1], from the adsorption of simple gases such as He or  $CO_2$ , or from the small-angle scattering of X-rays (SAXS), for example [2]. For carbons with pore widths  $L < 0.8$  nm, the use of molecules of various sizes can also give information on the total surface of the ideally slit-shaped pores. However, these techniques are time consuming and not always available.

We wish to describe a simple technique, developed in our laboratory and based on the selective adsorption of caffeine (1:3:7 trimethyl 2:6 dihydroxy purine) [3] from nearly saturated aqueous solutions. A comparative study, carried out with non-porous and porous carbons shows that a good assessment of the total surface area (external + micropore walls) can be obtained on the basis of an enthalpy change of  $113 \pm 15$  mJ/m<sup>2</sup> when the carbons are immersed into these solutions at 298.15 K. This technique is, however, limited to micropores larger than approximately 0.6 nm.

The non-porous carbon blacks (Table 1) and the active carbons (Table 2) were characterized by gravimetric adsorption of benzene vapours at 298.15 K and by immersion techniques described elsewhere [1,4]. In the case of immersion into the caffeine/water solutions, caffeine was always present in excess, so that its concentration  $c$  did not decrease below one tenth of the saturation concentration  $c_0$ .

The apparent adsorption isotherm of caffeine on sample M-25, determined by UV photospectroscopy of the solution showed that a plateau was reached for  $c/c_0 \cong 0.1$ . The limiting value corresponds to a

molecular surface area of approximately  $135 \cdot 10^{-20}$  m<sup>2</sup> for caffeine, if one assumes a monolayer. This value represents 3 to 4 times the area of a flat benzene molecule ( $40 \cdot 10^{-20}$  m<sup>2</sup>), in agreement with the relative dimensions of these molecules given by X-ray crystallography [3].

The strong and selective adsorption of caffeine may be ascribed to the hydrophobic character of carbon and to the limited solubility of caffeine into water (2 g into 100 cm<sup>3</sup> of water near 298.15 K).

On the basis of the BET surface areas, the average specific enthalpy of immersion of the non-porous carbon blacks into benzene is

$$-\Delta H_i (C_6H_6) = 120 \pm 12 \text{ mJ/m}^2$$

and for the aqueous solutions of caffeine

$$-\Delta H_i (\text{caffeine}/H_2O) = 113 \pm 15 \text{ mJ/m}^2$$

The comparison of the individual values of  $\Delta H_i$  with constant  $c$  of the BET model and with the specific enthalpy of immersion into water shows no definite trends. Moreover, the dispersion observed for benzene is similar to that reported in the literature [5-7], with values ranging from 107 to 120 mJ/m<sup>2</sup>. The overall average for carbon blacks is therefore near 115 mJ/m<sup>2</sup>. In the case of microporous carbons [1], immersion into benzene corresponds to the filling of the micropore volume  $W_0$  and to the wetting of  $S_e$ . The fundamental equation is [1,4]

$$-\Delta H_i (J/g) = E_0 W_0 (1 + \alpha T) \sqrt{\pi} / 2 V_m + 0.115 \cdot S_e \quad (1)$$

On the other hand, if preferential adsorption of caffeine also takes place on the walls of the micropores, the

Table 1  
 Experimental data for the carbon blacks, from adsorption and immersion techniques

Carbon Black	V-3	L-100	L-400	L-800	M-100	M-400	M-800
$S_{BET}$ (m <sup>2</sup> /g)	71.3	75.4	83.3	81.6	89	77	76
C (BET)	77	79	99	93	93	78	83
$\Delta H_i (C_6H_6)$ (J/m <sup>2</sup> )	0.114	0.139	0.124	0.121	0.122	0.132	0.109
$\Delta H_i (\text{caf}/H_2O)$ (J/m <sup>2</sup> )	0.116	0.119	0.110	0.098	0.108	0.129	0.113
$\Delta H_i (H_2O)$ (J/m <sup>2</sup> )	0.030	0.055	0.051	0.042	0.053	0.043	0.038

Table 2  
Experimental data for strongly activated carbons and the comparison of the total surface areas obtained from different techniques

Active Carbon	V-72	U-02	N-125	F-02
$E_o$ (kJ/mol)	22.0	20.0	16.6	18.7
$W_o$ (cm <sup>3</sup> /g)	0.059	0.43	0.64	0.64
$S_e$ (m <sup>2</sup> /g)	114 ± 10	115 ± 16	157 ± 20	80 ± 10
$S_t$ (m <sup>2</sup> /g)				
caffeine	232 ± 25	558 ± 60	982 ± 100	707 ± 70
other technique	220	684/620	715	752
	eqn(1), ref[8]	(SAX/He)	(He)	(SAXS)

following equation should apply, instead of eqn (1),

$$-\Delta H_i(\text{J/g}) = 0.113 (S_e + S_{mi}) \quad (2)$$

A slightly larger enthalpy may be expected, owing to a higher adsorption potential in the pores, as observed for gas adsorption, but eqn (2) seems to remain valid as a good approximation. As shown in table 2, the total surface areas  $S_t = S_e + S_{mi}$  obtained from different techniques show a reasonable agreement with the values obtained from eqn (2). This suggests that the simple technique, based on immersion calorimetry with aqueous solutions of caffeine, can be used to provide a satisfactory and quick assessment of the total surface area of active carbons and consequently of their internal surface. It must be stressed, however, that owing to molecular sieve effects, this technique will only apply to strongly activated carbons with characteristic energies  $E_o$  usually smaller than 22-24 kJ/mole. This approach will also provide much needed data to establish a firm correlation between  $E_o$  and  $L$  above 1.0-1.2 nm, the two parameters being related [1,8]. Further details will be published later.

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