

# On the determination of surface areas in activated carbons

F. Stoeckli <sup>a,\*</sup>, T.A. Centeno <sup>b</sup>

<sup>a</sup> *Institut de Chimie de l'Université, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

<sup>b</sup> *Instituto Nacional del Carbón-CSIC, Apartado 73, E-33080 Oviedo, Spain*

## Abstract

The paper examines the validity of two approaches frequently used to determine surface areas in activated carbons, namely the BET method and the use of immersion calorimetry. The study is based on 21 well characterized carbons, whose external and microporous surface areas,  $S_e$  and  $S_{mi}$ , have been determined by a variety of independent techniques. It appears clearly that  $S_{BET}$  and the real surface area  $S_{mi} + S_e$  are in agreement only for carbons with average pore widths  $L_o$  around 0.8–1.1 nm. Beyond,  $S_{BET}$  increases rapidly and  $S_{BET} - S_e$  is practically the monolayer equivalent of the micropore volume  $W_o$ . This confirms that a characterization of surface properties based on  $S_{BET}$  is, a priori, not reliable. The study of the enthalpy of immersion of the carbons into benzene at 293 K, based on Dubinin's theory, shows that  $\Delta_i H$  consists of three contributions, namely from the interactions with the micropore walls ( $-0.136 \text{ J m}^{-2}$ ), the external surface ( $-0.114 \text{ J m}^{-2}$ ), and from the volume  $W_o^*$  of liquid found between the surface layers in the micropores ( $-141 \text{ J cm}^{-3}$ ). It appears that for carbons where  $L_o > 1 \text{ nm}$ , the real surface area cannot be determined in a reliable way from the enthalpy of immersion and a specific heat of wetting alone.

*Keywords:* Activated carbons; Adsorption, BET surface area, Microcalorimetry; Microporosity

## 1. Introduction

Due to their high sorptive capacity (typically 4–6 mmol of benzene per gram of solid), activated carbons [1,2] are used extensively in filtration technology. Adsorption takes place in micropores with volumes  $W_o$  as high as  $0.8\text{--}1 \text{ cm}^3 \text{ g}^{-1}$ , if one assumes an adsorbed state similar to the liquid or the solid states at the corresponding temperature. (This hypothesis is confirmed by studies based on zeolites, with well defined cavities.) In activated carbons, micropores have accessible widths between 0.35 and 1.5–2 nm and, following Dubinin's theory [1–3], the adsorption of vapours corresponds to a volume filling process.

A number of studies, for example [1,4–7], suggest that micropores are ideally slit-shaped, at least up to widths  $L$  and extensions of 1–1.2 nm. This structure is due to the presence of aromatic (or graphitic) sheets, reminiscent of the structure of non-porous carbon blacks. Larger micropores, sometimes called supermicropores, have more complicated and cage-like structures [5–7]. The pore size distribution (PSD) depends strongly on the preparation of the carbon and it can be assessed by independent techniques: As shown by the present authors [8,9], immersion calorimetry with liquids of molecular dimensions between 0.35 and 1.5 nm provides reliable information for carbons without 'gate' effects [10]. This information is also confirmed by STM [9]. More recently, modelling of  $\text{CO}_2$  [11,12] and  $\text{H}_2\text{O}$  [13] adsorption, based on the hypothesis of slit-shaped micropores, provides an independent confirmation for the PSDs of typical microporous carbons. Fig. 1 shows

\* Corresponding author. Tel.: + 41 32 718 2400; fax: + 41 32 718 2511.

*E-mail address:* fritz.stoeckli@unine.ch (F. Stoeckli).

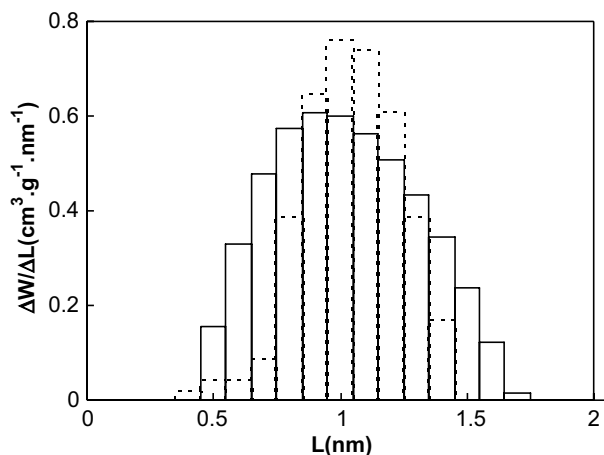


Fig. 1. The pore size distribution in activated carbons DCG-5, as obtained from immersion calorimetry (---) and from the analysis of the  $\text{CO}_2$  (273 K) adsorption isotherm (—).

the PSDs of carbon DCG-5, determined by immersion calorimetry [14] and, more recently by the deconvolution of the high pressure  $\text{CO}_2$  isotherm obtained at 273 K. There is a good agreement between the two techniques, as reported earlier for other carbons [9–12], but it appears that  $\text{CO}_2$  provides a better assessment of the smaller micropores (0.4–0.7 nm) than the liquid probes.

The approach based on modelling also provides a good estimate of  $S_{\text{mi}}$ , the cumulative surface of the micropore walls. As shown elsewhere [2,15], one observes a good agreement between this value and the monolayer capacity suggested by the adsorption of caffeine [2] and, more recently of phenol [15] from aqueous solutions, in spite of the fact that the molecular surface area may depend, to some extent, on the nature of the surface [16]. For these and other sparingly soluble molecules, the adsorption process is limited to the coating of the surface and it does not correspond to the volume filling of the micropores. This fundamental difference is revealed by the type I solution isotherm and its limiting value, as well as calorimetric studies carried out with microporous and non-porous carbons [15]. This shows clearly, that from a technological point of view activated carbons can be used separately for both properties, the micropore volume  $W_o$  in the case of vapour adsorption and the surface area  $S_{\text{mi}}$  for the adsorption of sparingly soluble species from aqueous solutions. It is therefore important to have a correct estimate of these two characteristics.

Pores of widths  $L$  beyond 2 nm correspond to classical meso- and macropores, in which capillary condensation takes place [16] and where the surface to volume ratio decreases rapidly. Due to the reduced adsorption potential, the surface of these pores may be regarded as equivalent to the surface of the corresponding non-porous material (e.g. graphitized carbon black). This

so-called external surface area,  $S_e$ , can be obtained from the comparison of the adsorption isotherm with a reference isotherm determined at the same temperature on a non-porous carbon black [16–19] (Sing's classical  $\alpha$ -plot for  $\text{N}_2$  at 77 K, also extended to other vapours).

The combination of the different techniques leads to an assessment of the micropore volume  $W_o$ , the micropore surface area  $S_{\text{mi}}$ , the external surface area  $S_e$  and the total available surface  $S_{\text{tot}} = S_{\text{mi}} + S_e$ . These concepts have well defined meanings and  $S_{\text{tot}}$  may be compared with the approach based on the classical BET theory [16], often applied to nitrogen adsorption at 77–78 K. The latter is a model describing the vapour adsorption isotherm as a gradual build-up of layers on an open and consequently non-porous surface. Although the actual molecular area  $A_m$  depends on the solid, it appears that for carbons the value of  $16.2 \times 10^{-20} \text{ m}^2$  is a reliable standard for nitrogen at 77 K [16]. As discussed below, the comparison of the total surface area  $S_{\text{tot}}$  with  $S_{\text{BET}}$  shows important deviations, in particular as the average micropore width  $L_o$  increases. This has also been pointed out by Kaneko et al. [17] and by Setoyama et al. [18], on the basis of the so-called refined  $\alpha_s$ -plot and the modelling of  $\text{N}_2$  adsorption in slit-shaped micropores. However, this work has not received sufficient attention. It is therefore important, along the lines developed earlier, to discuss these differences and to show the limitations of the approach based on the BET surface area, often used for the characterization of activated carbons.

Simultaneously, it will also be shown that  $\Delta_i H$ , the enthalpy of immersion of these carbons into liquids showing no specific interactions with surface groups (e.g. benzene [20]), can be related to contributions from  $S_{\text{mi}}$ ,  $S_e$  and, the volume  $W_o^*$  contained between the surface layers in micropores of width  $L_o > 0.9$ –1 nm. It follows, that for microporous carbons, as opposed to non-porous carbons,  $\Delta_i H$  does not provide a reliable estimate of the total surface area on the basis of a specific enthalpy of immersion.

## 2. Experimental

The study is based on 18 activated carbons and 3 microporous carbon blacks with average micropore widths  $L_o$  between 0.65 and approximately 2–2.5 nm (Table 1) [1,2,8–15,20]. The structural properties  $E_o$  (characteristic energy),  $W_o$  and  $S_e$ , were obtained by the classical treatment of various adsorption isotherms of non-specific adsorbates (benzene, nitrogen,  $\text{CO}_2$ ) within the framework of Dubinin's theory, as described in detail elsewhere [1–3]. This data was further cross-checked with the corresponding enthalpies of immersion into benzene,  $\Delta_i H(\text{C}_6\text{H}_6)$ , a thermodynamic consequence [1–3] of Dubinin's equation, as discussed below.

Table 1  
Characteristics of the microporous carbons.  $-\Delta_i H[\text{C}_6\text{H}_6]_{\text{calc}}$  is given by Eq. (7)

Carbon	Cat. A <sup>a</sup> /B	$L_o$ (nm)	$W_o$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{\text{mi}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_e$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{mi}} + S_e$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$-\Delta_i H$ [ $\text{C}_6\text{H}_6$ ] <sub>exper</sub> ( $\text{J g}^{-1}$ )	$-\Delta_i H$ [ $\text{C}_6\text{H}_6$ ] <sub>calc</sub> ( $\text{J g}^{-1}$ )	$-\Delta_i H$ [ $\text{C}_6\text{H}_6$ ]/0.114 ( $\text{m}^2 \text{g}^{-1}$ )	$-\Delta_i H$ [ $\text{C}_6\text{H}_6$ ]/0.136 ( $\text{m}^2 \text{g}^{-1}$ )	$W_o^*$ ( $\text{cm}^3 \text{g}^{-1}$ )
CAF-B	A	0.65	0.273	856	60	916	673	113.0	112.3	991	831	-0.080
CMS	A	0.73	0.250	625	20	645	660	95.1	86.5	834	699	0
AZ46-5	B	0.86	0.320	744	117	861	820	124.8	116.7	1095	918	0.015
AZ46-10	B	0.86	0.330	805	115	920	815	123.7	122.7	1085	910	0
PC-ref-92-2	B	0.86	0.450	1047	50	1097	1050	149.6	151.1	1312	1100	0.021
AZ46-3	B	0.89	0.320	719	131	850	850	114.4	116.4	1004	841	0.025
AZ46-0	B	0.96	0.330	668	140	808	914	110.0	114.8	965	809	0.050
XC-72-0	A	0.96	0.057	145	105	254	221	29.5	31.4	259	217	0
XC-72-17%	A	1.08	0.130	259	119	378	220	54.0	52.2	474	397	0.024
DCG-5	A	1.10	0.540	982	40	1022	1042	146.0	157.6	1281	1074	0.137
BV46	B	1.10	0.400	727	110	837	-	131.4	125.9	1153	966	0.102
U-103	A	1.15	0.330	631	39	670	927	99.0	100.4	868	728	0.071
U-02	B	1.26	0.450	717	105	822	1078	126.6	131.6	1111	931	0.156
BV46-Ox	B	1.29	0.420	651	112	763	-	134.0	123.0	1175	985	0.153
CE-AC-35	B	1.35	0.374	548	250	798	1062	127.9	124.2	1122	940	0.149
KF-1500	A	1.38	0.580	910	28	938	1315	149.5	156.3	1311	1099	0.207
BPL	A	1.42	0.450	633	90	723	1088	115.0	123.3	1009	846	0.190
F-02	B	1.44	0.650	775	90	865	1796	172.9	162.7	1517	1271	0.332
U-03	B	1.96	0.522	572	85	657	1194	130.0	128.1	1140	956	0.287
N-125	B	2	0.640	610	157	767	1707	160.0	156.0	1404	1176	0.390
PX-21	B	>2	1.200	1166	104	1270	1853	269.0	272.5	2360	1978	0.722

<sup>a</sup> For carbons of category A, the PSDs have been determined by at least two independent techniques.

All carbons (categories A and B in the Table) were characterized by immersion calorimetry into dilute aqueous solutions of caffeine and/or phenol, which leads to the total surface area  $S_{\text{tot}}$ . Moreover, for 8 carbons (category A), including DCG-5 (see Fig. 1), the PSDs were also characterized by two independent techniques: Firstly, by immersion calorimetry using liquids of molecular dimensions between 0.35 and 1.5 nm, as described earlier by Stoeckli and Centeno [8] and assuming that the molar volume in the adsorbed state is similar to the liquid state. Secondly, with the help of  $\text{CO}_2$  adsorption at 273 K and using model isotherms derived from molecular simulations [11,12]. However, it must be kept in mind that the actual volume of  $\text{CO}_2$  in the adsorbed state ( $43 \text{ cm}^3 \text{ mol}^{-1}$ ) is somewhat smaller than in the free liquid ( $48.2 \text{ cm}^3 \text{ mol}^{-1}$ ) [11,12]. Fig. 1 shows the type of agreement obtained by both techniques in the case of carbon DCG-5. The cumulative surface areas of the slit-shaped micropores derived from the PSDs are in good agreement with the values of  $S_{\text{mi}}$  obtained from the techniques based on phenol and caffeine adsorption.

The details of the experimental procedures can be found in the relevant references [1,2,8,21] and, in the case of multiple determinations, the values of  $S_{\text{mi}}$  and  $S_e$  given in Table 1 correspond to averages.

The correlations reported here were also tested with the data for another 23 activated carbons produced and/or investigated by the authors in earlier studies [1,2,21–25]. These solids were only characterized by

the standard techniques based on the isotherm analysis ( $E_o$ ,  $W_o$ ,  $S_e$ ) and on immersion calorimetry into benzene at 293 K. Data for  $S_{\text{mi}}$  and  $S_e$  is also found in a paper by Shi [26].

### 3. Results and discussion

#### 3.1. Surface areas from adsorption data

A first inspection of Table 1 shows that the surface area of the micropores,  $S_{\text{mi}}$ , does not exceed  $1200 \text{ m}^2 \text{ g}^{-1}$ , including PX-21 [5], a carbon with a very high micropore volume ( $1.2 \text{ cm}^3 \text{ g}^{-1}$ ). The total surface area  $S_{\text{mi}} + S_e$  shows a similar limit and it is likely, that  $1500 \text{ m}^2 \text{ g}^{-1}$  is a realistic upper-bound for carbons. On the other hand, it appears that  $S_{\text{BET}}$ , the value obtained by applying the BET treatment to the overall nitrogen isotherm in the usual domain  $0.05 < p/p_s < 0.30-0.35$ , can reach values as high as  $2400 \text{ m}^2 \text{ g}^{-1}$  [26]. The unrealistic nature of  $S_{\text{BET}}$  for carbons with wide pores is also suggested by the BET analysis of  $\text{CO}_2$  isotherms generated from model isotherms combined with PSDs of known surface areas  $S_{\text{mi}}$ .

As shown in Fig. 2, the nitrogen surface area  $S_{\text{BET}}(\text{N}_2) - S_e$  is practically a linear function of the micropore volume  $W_o$ , with a slope of approximately  $2220 \text{ m}^2 \text{ cm}^{-3}$ . (One must use the difference  $S_{\text{BET}} - S_e$  rather than  $S_{\text{BET}}$ , since the latter refers to the entire type II isotherm, whereas  $W_o$  corresponds to the micropo-

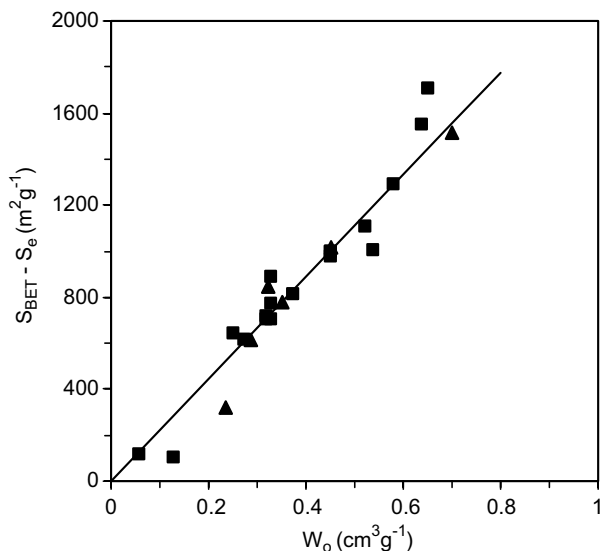


Fig. 2. Correlation between the surface area  $S_{\text{BET}} - S_e$  and the micropore volume  $W_o$  for the carbons of Table 1 (■) and 5 other well characterized carbons (▲).

rous section only.) This analysis, based on the carbons of Table 1 and on five other typical samples investigated by the present authors, indicates that  $S_{\text{BET}} - S_e$  is practically the monolayer equivalent of the micropore volume. Obviously, this formal surface area loses its meaning as soon as the micropores contain more than two layers of adsorbate, i.e.  $L_o > 0.8\text{--}1$  nm for nitrogen and benzene. As shown in Table 1, one observes a reasonable agreement between the real surface area  $S_{\text{mi}} + S_e$  and  $S_{\text{BET}}$  only for carbons where  $L_o \sim 0.8\text{--}1.1$  nm.

The present observation is also confirmed by the analysis of the data provided by Shi [26] for activated carbon fibers and microbeads with average micropore widths between 0.85 and 1.7 nm. On the basis of the nitrogen isotherm, this author determined the micropore volume,  $S_{\text{BET}}$ ,  $S_e$  and  $S_{\text{DFT}}$ , the surface obtained by the so-called DFT method. The latter surface is in principle equal or close to  $S_{\text{mi}} + S_e$ .

It is also interesting to point out that the technique outlined by Kaneko's school [17,18] and based on the analysis of a reference plot leads to an independent assessment of the surface of microporous carbons. For example, in the case of carbon DCG-5, the comparison plot for benzene adsorbed at 293 K (the reference is Vulcan 3G) leads to a total surface area of approximately  $1050 \text{ m}^2 \text{ g}^{-1}$ . This value is obtained from the slope of the line joining the origin to the point where adsorption on  $S_e$  begins, but since this point is not always clearly defined, this approach introduces a some uncertainty (approximately  $50\text{--}100 \text{ m}^2 \text{ g}^{-1}$  in the present case). On the other hand, it is obvious that the full use of a refined comparison plot based on nitrogen [16] or benzene [19], provides an independent assessment of  $S_{\text{tot}}$ ,  $S_e$ , and  $W_o$ , to be cross-checked with other techniques.

From the foregoing discussion it follows that for carbons with pore widths outside the range of 0.8–1.1 nm, it is not recommended to use  $S_{\text{BET}}$  (mainly based on nitrogen) to calculate specific surface properties (e.g. the concentration of surface oxygen in atoms per  $\text{m}^{-2}$ , or capacitances in  $\text{F m}^{-2}$  [26]). It also appears that a variety of techniques exist to provide more reliable information on the surface area of carbons.

### 3.2. Surface areas from immersion calorimetry

Following a technique proposed by Denoyel et al. [27], a number of authors (for example [28–31]) also attempted to derive surface areas from the enthalpy immersion into benzene and other liquids which have no specific interactions with surface groups. This approach is based on the determination of a surface area  $S(\text{m}^2 \text{ g}^{-1}) = \Delta_i H/h_i$ , where  $h_i$  is a specific enthalpy of immersion. In the case of benzene, it is suggested to use  $-0.114 \text{ J m}^{-2}$ , obtained for graphitized carbon blacks [2,27]. However, as shown in Table 1, this approach leads to surface areas which are higher than  $S_{\text{mi}} + S_e$  and the difference increases with the micropore width  $L_o$ . It appears that this 'calorimetric' surface area is similar to  $S_{\text{BET}}$  and also reaches unreasonable values for carbons with wide pores.

A reasonable agreement between  $\Delta_i H/h_i$ ,  $S_{\text{mi}} + S_e$  and  $S_{\text{BET}}$  is found only for carbons with average micropore widths  $L_o$  between approximately 0.8 and 1 nm. This is, for example, the case for carbon series D-8 to D-80 reported by Gonzales et al. [28] and having micropore widths between 0.7 and 1.05 nm. On the other hand, this is no longer the case for benzene and the *Nomex*-based carbons of Villar-Rodil et al. [30,31] at burn-offs above 20–25%. A closer examination of their data suggests that for a 10% burn-off,  $S_{\text{mi}}$ ,  $S_{\text{BET}}$  and the surface area  $-\Delta_i H/0.114$  are respectively 445, 560 and  $600 \text{ m}^2 \text{ g}^{-1}$ . (The external surface area  $S_e$  is small.) On the other hand, at 42% burn-off, one obtains 1000, 1329 and  $1329 \text{ m}^2 \text{ g}^{-1}$ . It is also likely, that for the carbon with 63% burn-off, the calorimetric surface area (no data provided) will exceed  $S_{\text{BET}}$  ( $1580 \text{ m}^2 \text{ g}^{-1}$ ), whereas  $S_{\text{mi}}$  is only  $1023 \text{ m}^2 \text{ g}^{-1}$ .

Further evidence for the limited use of the calorimetric approach to determine surface areas in microporous carbons is provided by earlier experiments with various carbons, following the preadsorption of *n*-nonane and/or *n*-undecane [32]. Table 2 gives the enthalpies of immersion of a carbon of series U-03 into *n*-nonane at 293 K, following degrees of prefilling  $\theta = W/W_o$  between 0 and 0.7. This quantity is determined by weighing prior to immersion. As shown by nitrogen adsorption at 78 K, preadsorption at room temperature leaves no voids in the micropore structure, the residual volume  $W(\theta)$  being close to the expected value. In separate experiments, one also determines calorimetrically  $S_{\text{tot}}(\text{caf/aaq})$ , the residual

Table 2

Accessible surface areas of carbon U-03 following the preadsorption of *n*-nonane and *n*-undecane, as suggested by immersion calorimetry and by the selective adsorption of caffeine from aqueous solutions

$\theta = W/W_o$	0	0.1	0.3	0.4	0.5	0.7	1
$-\Delta_i H(C_9H_{20}) \text{ J g}^{-1}$	120	110	95	85	70	45	12
$-\Delta_i H(C_9H_{20})/0.136 \text{ m}^2 \text{ g}^{-1}$	882	809	698	625	514	331	88
$S_{\text{tot}}(\text{caf/aq}) \text{ m}^2 \text{ g}^{-1}$	675	563	443	373	318	193	–

total surface area accessible to caffeine adsorbed from an aqueous solution (All these experiments are possible in view of the very slow desorption rate of the hydrocarbons.) As shown in Table 2, the specific enthalpy of immersion  $h_i(n\text{-C}_9\text{H}_{20}) = -0.136 \text{ J m}^{-2}$ , suggested by a non-porous reference, leads to surface areas  $-\Delta_i H(\text{J g}^{-1})/0.136 (\text{J m}^{-2})$  which are systematically higher than the surface areas obtained with caffeine. Similar results are obtained for carbons F-02 and U-02.

As shown in Table 1, the surface area corresponding to  $-\Delta_i H(\text{C}_6\text{H}_6) (\text{J g}^{-1})/0.114 (\text{J m}^{-2})$  follows the same evolution as the nitrogen surface area  $S_{\text{BET}}$  and reaches unrealistic values for the carbons with large micropores. The reason for the shortcoming of the approach based on  $\Delta_i H/h_i$  is the presence of several layers in the micropores, as well as an increase of the specific interaction with respect to the open surface. This can be shown by a closer examination of the meaning of  $\Delta_i H$  and its parameters in the case of microporous carbons.

As discussed in detail elsewhere [1–3], the enthalpy of immersion of a microporous carbon into a non-specific liquid such as benzene is a thermodynamic consequence of Dubinin's equation. It is shown, that for typical activated carbons

$$-\Delta_i H(\text{J g}^{-1}) = \beta E_o W_o (1 + \alpha T)(\pi)^{1/2} / 2V_m - h_i S_e \quad (1)$$

$\beta$  is the so-called affinity coefficient of the adsorptive [1,2] ( $\beta_{\text{C}_6\text{H}_6} = 1$ ),  $\alpha$  is the thermal expansion coefficient,  $V_m$  its molar volume at temperature  $T$  (mostly 293 K) and  $h_i$  ( $<0$ ) is the enthalpy of wetting of the external surface area  $S_e$ . From an experimental point of view, the primary information is the limiting amount adsorbed (typically 4–6 mmol  $\text{g}^{-1}$  for benzene) and  $W_o$  is calculated by assuming that  $V_m$  is close to the molar volume of the liquid. For most adsorptives, including benzene, this seems to be the case, as suggested by the comparison of several adsorbates on different carbons and by studies with large zeolites of known cage dimensions. One may therefore assume that slight differences in the packing density will not affect significantly the trends outlined in the present study.

On the basis of various techniques including modelling of adsorption [2,11,12,25], it has been shown that for ideally slit-shaped micropores of average width  $L_o$  and surface area  $S_{\text{mi}}$

$$E_o(\text{kJ mol}^{-1}) = 10.8/L_o(\text{nm}) + 11.4 \quad (2)$$

and

$$S_{\text{mi}}(\text{m}^2 \text{ g}^{-1}) = 2000W_o(\text{cm}^3 \text{ g}^{-1})/L_o(\text{nm}) \quad (3)$$

For benzene at 293 K, where  $(1 + \alpha T)(\pi)^{1/2}/2V_m = 0.0136 \text{ mol cm}^{-3}$  [2], this leads to

$$-\Delta_i H(\text{J g}^{-1}) = 0.073S_{\text{mi}} + 155W_o + 0.114S_e, \quad (4)$$

which indicates a contribution to  $\Delta_i H$  from both the surface areas  $S_{\text{mi}}$  and  $S_e$ , and the micropore volume  $W_o$ . However, Eq. (4) can be re-written in the mathematically equivalent, but physically more realistic form

$$-\Delta_i H(\text{J g}^{-1}) = c_1 S_{\text{mi}} + c_2 (W_o - c_3 S_{\text{mi}}) + c_4 S_e \quad (5)$$

The term

$$W_o - c_3 S_{\text{mi}} = W_o^* \quad (6)$$

represents the volume of the liquid found between the surface layers (see Table 1). Since the enthalpy of wetting of the external surface area  $S_e$  is known accurately ( $-0.114 \text{ J m}^{-2}$  for benzene [2,27]), the data of Table 1 can be fitted to Eq. (5) to determine parameters  $c_1$ ,  $c_2$  and  $c_3$ . (This also leads to  $W_o^*$ , see Table 1.)

For the 21 carbons of Table 1, one obtains, with a correlation coefficient of 0.9820 (see Fig. 3, ■),

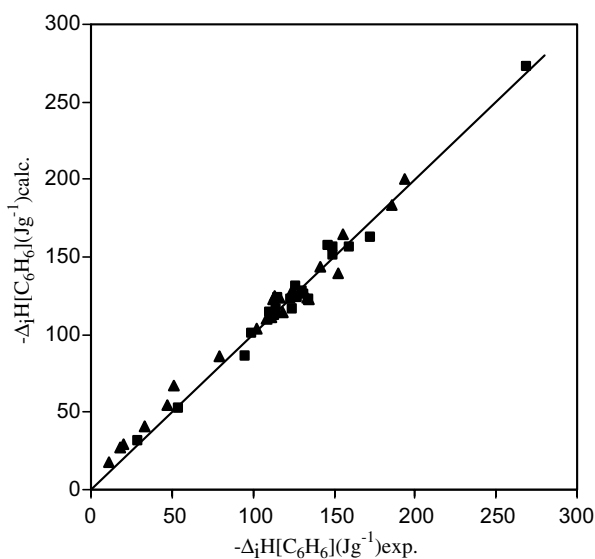


Fig. 3. Correlation between the calculated and the experimental enthalpies of immersion  $\Delta_i H(\text{C}_6\text{H}_6)$  (293 K) for the carbons of Table 1 (■) and for 20 other well characterized carbons (▲), using Eq. (7).

$$-\Delta_i H (\text{J g}^{-1}) = 0.136 S_{\text{mi}} + 141 (W_o - 4.1 \times 10^{-4} S_{\text{mi}}) + 0.114 S_e \quad (7)$$

The value  $c_3 = 4.1 \times 10^{-4}$  corresponds to a thickness of 0.41 nm for the benzene layer, which is reasonable for this molecule lying flat on a graphitic surface [16].

Eq. (7) was further tested with the data for another twenty activated carbons characterized by the authors in earlier studies [1,2,21–25], but not as extensively as the reference carbons of Table 1. As seen in Fig. 3, this data ( $\blacktriangle$ ) follows closely the predictions of Eq. (7).

Eq. (7) suggests an average specific interaction of  $-0.136 \text{ J m}^{-2}$  for the layers in contact with the walls, as opposed to  $-0.114 \text{ J m}^{-2}$  for the open surface. The higher specific enthalpy in the pores can be explained by the increased adsorption potential with respect to the open surface. It appears, that in the case of microporous carbons there are, formally, three distinct contributions to  $-\Delta_i H$ , namely two from the internal and external internal surface areas and one from the volume  $W_o^*$ . The contribution of the interlayer volume,  $141 \times W_o^* \text{ J g}^{-1}$ , is a fraction of  $-\Delta_i H$  and it is limited to micro- and supermicropores. It is likely, indeed, that  $c_2 = 141 \text{ J cm}^{-3}$ , an average value obtained by fitting the experimental data to Eq. (5), decreases with  $L_o$ . (Logically, the contribution of  $W_o^*$  should vanish for meso- and macropores.)

Dividing the experimental enthalpy of immersion  $\Delta_i H$  by a single specific enthalpy between  $-0.114$  and  $-0.136 \text{ J m}^{-2}$ , leads to an apparent surface area which is larger than  $S_{\text{mi}} + S_e$  (see Table 1) and often close to  $S_{\text{BET}}$ . It appears that, due to a compensating effect in Eq. (7), the use of the upperbound  $h_i(\text{C}_6\text{H}_6) = -0.136 \text{ J m}^{-2}$  leads to a better agreement between  $\Delta_i H/h_i$  and the total surface area  $S_{\text{mi}} + S_e$ , but only for micropore systems where  $L_o < 1.1 \text{ nm}$ . This confirms that the determination of the real surface area of a microporous carbon on the basis of  $\Delta_i H$  and a single specific enthalpy is not reliable. This shortcoming of the calorimetric approach has been recognized by some authors, but it is often overlooked.

At this stage, it is interesting to note that regrouping the terms in Eq. (7) leads to

$$-\Delta_i H (\text{J g}^{-1}) = 0.078 S_{\text{mi}} + 141 W_o + 0.114 S_e \quad (8)$$

which is very close to Eq. (4). Considering that the parameters of Eq. (7), and consequently of Eq. (8), have been obtained by a fit based directly on the independent determinations of  $S_{\text{mi}}$ ,  $S_e$  and  $W_o$ , we may conclude that there is self-consistency in the present approach.

Obviously, in the case of carbons with relatively narrow micropores ( $L_o < 0.8\text{--}1 \text{ nm}$  or approximately two layers), a good agreement may be obtained between  $S_{\text{BET}}$  and the total surface area  $S_{\text{mi}} + S_e$ . However, the present study shows that precautions must be taken in the characterization of typical industrial activated

carbons [1,5,26], where  $L_o$  is often around 1.5 nm and above (supermicropores).

#### 4. Conclusions

The present study, based on 21 well characterized carbons with average micropore sizes  $0.65 < L_o < 2\text{--}2.5 \text{ nm}$ , confirms earlier suspicions, that the BET approach (mainly based on nitrogen adsorbed at 77 K), does not provide a realistic assessment of the surface area of an activated carbon, as  $S_{\text{BET}}$  increases faster than  $S_{\text{mi}} + S_e$ . However, due to compensating effects, the two areas may agree for activated carbons with average micropore widths  $L_o$  between 0.8 and 1.1 nm, obtained at burn-offs around 25–35%. This ‘local’ agreement is probably at the origin of an incorrect generalization to carbons with higher degrees of burn-off, often used in industrial applications, or to carbons of type III in the classification of Stoeckli et al. [33].

Simultaneously, it appears that the enthalpy of immersion into benzene (and by extension into other non-specific liquids) consists of three distinct contributions, namely from  $S_{\text{mi}}$ ,  $S_e$  and the volume  $W_o^*$  found between the surface layers in the micropores and the supermicropores (However, it is likely that the contribution of  $W_o^*$  vanishes in larger pores). Consequently, as shown here, the combination of  $\Delta_i H$  with a single specific surface enthalpy  $h_i$  is unreliable for the determination of surface areas in activated carbons where  $L_o > 1 \text{ nm}$ .

These observations lead to the conclusion that the characterization of microporous carbons of medium and strong activation requires more sophisticated techniques than the nitrogen-based BET approach or immersion calorimetry into benzene with a single specific enthalpy. For example, the analysis of  $\text{CO}_2$  adsorption based on model isotherms, leading to PSDs [12,13], the selective adsorption of phenol from aqueous solutions [1,2,15], or the analysis of comparison plots [17,18]. The approaches appear to provide good estimates for the surface areas  $S_{\text{mi}}$  and  $S_e$ .

#### Acknowledgments

The authors wish to thank Drs. A. Guillot (CNRS-IMP Perpignan) and A. Slasli (Neuchatel) for the measurement and the analysis of the  $\text{CO}_2$  adsorption isotherm on carbon DCG-5.

#### References

- [1] Bansal RC, Donnet JB, Stoeckli F. Active carbon. New York: Marcel Dekker; 1988. pp. 1–14, 119–162.
- [2] Stoeckli F. In: Patrick J, editor. Porosity in carbons-characterization and applications. London: Arnold; 1995. p. 67–97.

- [3] Stoeckli F. Dubinin's theory and its contribution to adsorption science. *Russ Chem Bull Int Ed* 2001;50:2265–70.
- [4] Fryer JR. The microporous structure of disordered carbons. *Carbon* 1981;19:431–9.
- [5] Marsh H, Crowford D, O'Grady TM, Wennerberg A. Carbons of high surface area. A study by adsorption and high resolution electron microscopy. *Carbon* 1982;20:419–26.
- [6] Stoeckli F. Microporous carbons and their characterization. The present state of the art. *Carbon* 1990;28:1–6.
- [7] Py X, Guillot A, Cagnon B. Nanomorphology of activated carbon porosity: geometrical models confronted to experimental facts. *Carbon* 2004;42:1743–54.
- [8] Stoeckli F, Centeno TA. On the characterization of microporous carbons by immersion calorimetry alone. *Carbon* 1997;37:1097–100.
- [9] Stoeckli F, Hugi-Cleary D, Centeno TA. The characterization of solids by adsorption and immersion techniques and by AFM/STM. *J Eur Ceram Soc* 1998;18:1177–85.
- [10] Stoeckli F, Salsli AM, Hugi-Cleary D, Guillot A. The characterization of microporosity in carbons with molecular sieve effects. *Micropor Mesopor Mater* 2002;51:197–202.
- [11] Stoeckli F, Guillot A, Salsli AM, Hugi-Cleary D. Microporosity in carbon blacks. *Carbon* 2002;38:211–5.
- [12] Stoeckli F, Guillot A, Salsli AM, Hugi-Cleary D. The comparison of experimental and calculated pore size distributions in activated carbons. *Carbon* 2002;38:383–8.
- [13] Salsli AM, Jorge M, Stoeckli F, Seaton N. Modelling of water adsorption by activated carbons: effects of microporous structure and oxygen content. *Carbon* 2004;42:1947–52.
- [14] Stoeckli F, Currit L, Laederach A, Centeno TA. Water adsorption in activated carbons described by the Dubinin–Astakhov equation. *J Chem Soc Faraday Trans* 1994;90:3689–91.
- [15] Fernandez E, Hugi-Cleary D, López-Ramón MV, Stoeckli F. Adsorption of phenol from dilute and concentrated aqueous solutions by activated carbons. *Langmuir* 2003;19:9719–23.
- [16] Gregg SJ, Sing KSW. *Adsorption, surface area and porosity*. New York: Academic Press; 1982. p. 242.
- [17] Kaneko K, Ishii C, Ruike M, Kuwabara H. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons. *Carbon* 1992;30:1075–88.
- [18] Setoyama N, Suzuki T, Kaneko K. Simulation study of the relationship between a high-resolution  $\alpha_s$ -plot and the pore size distribution for activated carbons. *Carbon* 1998;36:1459–67.
- [19] Carrott PJM, Ribeiro-Carrott MML, Cansado IPP, Nabais JVM. Reference data for the adsorption of benzene on carbon materials. *Carbon* 2000;38:465–74.
- [20] López-Ramón MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marín F. Specific and non-specific interactions between methanol and ethanol and activated carbons. *Langmuir* 2000;16:5967–72.
- [21] Legba D, Ehrburger P, Papirer E, Donnet JB, Stoeckli F. Activation chimique des charbons par les hydroxydes, carbonates et oxydes des métaux alcalins. *Bull Soc Chim Fr* 1994;131:763–73.
- [22] Centeno TA, Stoeckli F. On the activation of Asturian anthracite following various pretreatments. *Carbon* 1994;32:1463–7.
- [23] Centeno TA, Stoeckli F. The oxidation of an Asturian bituminous coal in air and its influence on the subsequent activation by steam. *Carbon* 1995;33:581–6.
- [24] Fernandez E, Centeno TA, Stoeckli F. Chars and activated carbons derived from Asturian apple pulp. *Adsorpt Sci Technol* 2001;19:645–53.
- [25] Stoeckli F, López-Ramón MV, Hugi-Cleary D, Guillot A. Micropore sizes in activated carbons determined from the Dubinin–Radushkevich equation. *Carbon* 2001;39:1115–6.
- [26] Shi H. Activated carbons and double layer capacitance. *Electrochim Acta* 1996;41:1633–9.
- [27] Denoyel R, Fernandez-Colinas J, Grillet Y, Rouquerol J. Assessment of the surface area and microporosity of activated charcoals from immersion calorimetry and nitrogen adsorption data. *Langmuir* 1993;9:515–8.
- [28] Gonzales MT, Sepúlveda-Escribano A, Molina-Sabio M, Rodriguez-Reinoso F. Correlation between surface areas and micropore volumes of activated carbons obtained from physical adsorption and immersion calorimetry. *Langmuir* 1995;11:2151–5.
- [29] Silvestre-Albero J, Gómez de Salazar C, Sepúlveda-Escribano A, Rodriguez-Reinoso F. Characterization of microporous solids by immersion calorimetry. *Colloids Surf A* 2001;187–188:151–65.
- [30] Villar-Rodil S, Denoyel R, Rouquerol J, Martínez-Alonso A, Tascón JMD. Characterization of aramid based activated carbon fibres by adsorption and immersion techniques. *Carbon* 2002;40:1376–80.
- [31] Villar-Rodil S, Denoyel R, Rouquerol J, Martínez-Alonso A, Tascón JMD. Porous texture evolution in Nomex-derived activated carbon fibers. *J Colloid Interface Sc* 2002;252:169–76.
- [32] Stoeckli F, Huguenin D, Rebstein P. Characterization of active carbons by combined preadsorption and immersion techniques. *J Chem Soc Faraday Trans* 1991;87:1233–6.
- [33] Stoeckli F, Daguerre E, Guillot A. The development of micropore volumes and widths during physical activation of various precursors. *Carbon* 1999;37:2075–7.