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Characterization of industrial activated carbons by adsorption and immersion techniques and by STM

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The results obtained from a variety of techniques (vapour adsorption, selective adsorption of caffeine and immersion calorimetry) used to characterize activated carbons of industrial origin are compared. It is shown that gate effects due to constrictions, and often overlooked, can be revealed by simple experiments with larger molecular probes. Immersion calorimetry appears to be a simple and efficient technique, as illustrated by an activation series. Complementary information is also provided by scanning tunnelling microscopy (STM).

Activated carbons are widely used in filtration technology and in heterogeneous catalysis, where their microporous structure (pore sizes and volume) as well as the external surface area play an important role. It has been known for a long time that the sorptive capacity generally increases with the degree of burnoff (mass loss) resulting from the physical or the chemical activation of the precursor. However, depending on its origin and on the treatment, various types of activated carbons can be obtained[1]. It is therefore essential to be able to characterize them in a reliable fashion, in order to assess the influence of the various factors leading to the final material. This approach provides the information needed in the various applications of activated carbons.

The present paper illustrates this approach, by describing a variety of techniques available for full characterization of microporous carbons. The study is based on two series of industrial activated carbons, obtained from different precursors and by different methods (physical activation of coconut shells at ~ 900°C and chemical activation of hardwood by H_3PO_4 at ~ 450°C).

It is shown how the main structural properties of the carbons can be determined to various degrees of sophistication, depending on the techniques used, and how these properties depend on the history of the material. Emphasis is also put on the comparison of various techniques and on the convergence of overlapping techniques. It is therefore left to the reader to decide which approach might be most suitable for specific needs.

THEORETICAL

The study is based on the adsorption from the vapour and liquid phases, on immersion calorimetry and on scanning tunnelling microscopy (STM), a technique which has been applied only recently—but successfully—to active carbons.

The various techniques have been described separately elsewhere and therefore only their essential characteristics are recalled here. Basically, for microporous carbons, the gas–solid and liquid–solid interactions (adsorption and calorimetry) are based on the theory of Dubinin and its developments[2]. The fundamental expression is the equation of Dubinin and Astakhov:

$$N_a = N_{ao} \exp[-(A/\beta E_o)^n] \qquad (1)$$

where N_a represents the amount (in mmol g^{-1}) adsorbed at temperature T and relative pressure P/P_o, N_{ao} is the limiting amount adsorbed in the micropores, $A = RT \ln(P_o/P)$, and n, E_o and β are temperature-invariant parameters depending on the system under investigation. For activated carbons, n varies typically between 1.5 (very heterogeneous micropore distributions) and 3 (narrow distributions), the average being ~ 2. This value corresponds to the classical equation of Dubinin and Radushkevich (D–R), which is used to describe adsorption by most industrial activated carbons.

Parameter β is an empirical scaling factor called the affinity coefficient, which depends on the adsorbate. By convention, benzene is the reference vapour and $\beta(C_6H_6) = 1$.

Parameter E_o (kJ mol^{-1}), called the characteristic energy of the system, is related to the average micropore width L. Various techniques have suggested the approximate relation[3]

$$L = 10.8/(E_o - 11.4)\,\mathrm{nm} \qquad (2)$$

which is of fundamental importance in the characterization of microporous carbons. If it is assumed, to a good first approximation, that the molar volume in the adsorbed state is close to that of the liquid state, V_m, it follows that the micropore volume is $W_o = N_{ao} \cdot V_m$. It is the volume filled as P/P_o tends to unity and may vary, depending on molecular sieve effects (see below, *Figures 4* and *6*). Usually an activated carbon is characterized by the volume W_o filled by a small molecular probe such as CH_2Cl_2 or C_6H_6 near room temperature. (These molecules are preferred to nitrogen and CO_2, which may lead to problems.)

The combination of W_o and L leads to the approximate area of slit-shaped micropores[1,3]:

$$S_{mi} = 2 \cdot 10^3 W_o/L\,\mathrm{m^2 g^{-1}} \qquad (3)$$

with W_o in $\mathrm{cm^3 g^{-1}}$ and L in nm. The external surface area S_e, found in meso and macropores, can be determined from isotherm analysis[4,5] or immersion calorimetry[2], with an overall accuracy of ~ 10 – 15%. The total surface area of the carbonaceous material, derived from adsorption data, is therefore $S_{tot[isoth]} = S_{mi} + S_e$.

Pore size distributions and molecular sieve properties, on the other hand, can be derived from adsorption experiments with molecules of different sizes. However, owing to experimental difficulties, it is preferable to use immersion calorimetry with liquids having molecular sizes between 0.4 and 1.5 nm. In this case, the fundamental equation[1,2] is

$$\Delta h_i = \beta E_o W_o (1 + \alpha T)\pi^{1/2}/2V_m + h_i S_e\ \mathrm{J\,g^{-1}} \qquad (4)$$

where α is the thermal expansion coefficient of the liquid. The term $h_i S_e$ takes into account the wetting of the external surface by the liquid, h_i being obtained from experiments with non-porous carbons of known surface areas. As shown elsewhere[1,2], Equation (4) is a thermodynamic consequence of Equation (1).

On the other hand, immersion calorimetry in water provides information on the hydrophilic/hydrophobic character of the surface, depending on the number of primary centres a_o. The relation between $\Delta h_i(H_2O)$ and the parameters of the water adsorption isotherm is discussed in detail elsewhere[1,6–8].

It has been observed[9] that adsorption from aqueous solutions by activated carbons often follows an expression similar to Equation (1):

$$N_a = N_{ao} \exp[-D \log^2(c_o/c)] \qquad (5)$$

where c is the equilibrium concentration and c_o is the saturation concentration of the adsorbate. Strictly speaking, the affinity coefficient of the solute should also be taken into account, but its influence is small, in view of the logarithmic relation between c and N_a. As shown below, this relation applies also to the selective adsorption of caffeine on to carbons. This molecule has a limited solubility in water and a high affinity for carbonaceous surfaces. As shown elsewhere[10], its net enthalpy of adsorption from aqueous solutions is $0.112 \pm 0.015\,\mathrm{J\,m^{-2}}$, as opposed to typical values of 0.035–$0.060\,\mathrm{J\,m^{-2}}$ for water. This provides a means to assess rapidly the area accessible to this molecule in industrial activated carbons (the external surface and the area of the pores wider than ~ 0.7 nm).

EXPERIMENTAL

The equipment and the techniques used in the present study have been described in detail elsewhere[1–3]. The properties of the main adsorbates are given in *Table 1*.

In caffeine adsorption, the initial and equilibrium concentrations were determined by u.v. spectroscopy (maximum at 273 nm), using an internal calibration. A reference isotherm was also determined for a graphitized carbon black (N-326), which has an N_2(77K) surface area of $83\,\mathrm{m^2 g^{-1}}$. Some earlier data on caffeine adsorption by carbon black M-100 and active carbons N-125 and F-02 were also included, to obtain a better overall assessment of this technique.

The activated carbons of series DE resulted from the physical activation of coconut shells by steam at ~ 900–1000°C after carbonization at 600–800°C. Sample DE-60 was reactivated in the laboratory to a weight loss of 69%, to investigate the evolution of gate effects described below. Samples BTH and CBH resulted from the activation of pinewood. BTH was obtained from the same physical activation as in series DE. BCH, on the other hand, was carbonized and activated in one step at 450–500°C with phosphoric acid.

Scanning tunnelling microscopy (STM), developed by Binnig and Rohrer in 1982, has become a powerful tool for the exploration of carbon surfaces. Most interesting results have been obtained so far on well-oriented carbons (graphite), carbon fibres[11], and more recently also on small-particle carbon blacks[12]. However, to the authors' knowledge, activated carbons have not hitherto been examined extensively by STM[13]. Surface-activated carbon fibres have already been observed in the laboratory[14].

STM observations were carried out with a Nanoscope II microscope (Digital Instruments), using a commercially available 80/20 Pt–Ir tip. The STM images were obtained in the constant-current mode, at room temperature and in air, with a setpoint current varying from 1 to 5 nA and a positive bias voltage of 20–100 mV, depending on the scan size and on the tunnel current applied.

One of the major limitations of STM is the fact that it is applicable only to conducting materials, since the imaging mechanism depends on a tunnelling current. Activated carbons are considered to be bad conductors and therefore it has been generally assumed that a study by STM would prove difficult. The present paper shows that such a study is indeed possible, provided that a number of precautions are taken. To remove surface oxidation by-products, which are poor conductors of electricity, the samples are subjected to toluene extraction for 2 d. They are then dried in vacuum at 110°C and a small particle of carbon to be examined by STM is fixed to a glass plate by a conducting glue (based on silver) which ensures electrical conductivity. The reproducibility of images is good at low and high (atomic) resolutions. About 80 raw

Table 1 Main properties of the adsorbates

	L_c(nm)	α(10^{-3}K^{-1})	V_m(cm^{3}mol^{-1})	β	$-h_i$(J m^{-2})
Dichloromethane	0.33	1.34	64.02	0.66	0.152
Benzene	0.41	1.24	88.91	1.00	0.114
Cyclohexane	0.54	0.96	108.10	1.04	0.101
Carbon tetrachloride	0.63	1.22	96.50	1.05	0.115
Cyclododeca-1,5,9-triene (CDDT)	0.76	0.76	182.02	1.90	0.103
Tetrabutylurea (TBU)	0.93	0.85	283.34	3.50	0.118
Tri-2,4-xylylphosphate (TXP)	1.50	0.66	360.04	4.05	0.160

Table 2 Structural parameters of the carbons

Carbon	DE-60	DE-69	DE-80	DE-150	BTH	BCH	N-326
W_o(cm^3/g^{-1})	0.42	–	0.57	0.80	0.48	0.49	–
E_o(kJ mol^{-1})	20.6	–	17.4	15.2	18.1	16.5	–
L(nm)	1.17	–	1.80	2.84	1.61	2.12	–
S_{mi}(m^2/g^{-1})	718	–	633	521	596	462	–
$S_{e[imm.]}$(m^2/g^{-1})	118	–	86	263	81	831	–
$S_{tot[isoth]}$(m^2/g^{-1})	836	–	719	784	677	1293	–
$N_{ao[caff.]}$(mmol g^{-1})	2.03	–	2.75	3.86	2.39	2.64	–
$-\Delta h_{i[caff.]}$(J g^{-1})	50.0	52.5	69.4	76.6	67.0	164.1	9.2
$-\Delta h_{i[H_2O]}$(J g^{-1})	42.9	30.8	40.6	50.7	39.7	139.7	0.3
$-\Delta h_{i[H_2O]}/S_{tot}$(J m^{-2})	0.051	–	0.056	0.065	0.059	0.108	–

Table 3 Molecular sieve properties of the carbons

	W_o(cm^{3}g^{-1})							$-\Delta h_i$(J g^{-1})						
Adsorbate	Ar	C_6H_6	C_6H_8	CCl_4	CDDT	TBU	TXP	CH_2Cl_2	C_6H_6	C_6H_8	CCl_4	CDDT	TBU	TXP
DE-60	0.42	0.40	0.35	0.36	0.16	0.11	0.00	128.1	124.0	91.3	109.6	49.2	44.0	19.0
DE-69	–	–	–	–	–	–	–	147.6	144.8	113.0	131.4	102.2	–	45.9
DE-80	0.57	0.60	–	0.59	–	0.60	0.33	139.3	152.2	–	143.7	–	151.9	82.5
DE-150	0.80	0.76	–	0.81	–	0.88	0.88	194.6	186.1	–	191.4	–	213.4	200.7
BTH	0.48	0.43	–	0.38	–	0.33	0.17	122.8	115.9	–	100.1	–	91.5	49.4
BCH	0.49	0.44	–	0.43	–	–	0.32	229.1	193.4	–	187.8	–	–	195.0

images were collected for each sample, and the most typical are presented here.

RESULTS AND DISCUSSION

The results of the adsorption and immersion experiments are summarised in *Tables 2* and *3*. *Figures 1* and *2* show the logarithmic plots of Equation (5) for the selective adsorption of caffeine from aqueous solutions at 293 K. These plots are linear and lead to the limiting values N_{ao} corresponding, in principle, to the monolayer capacity of the accessible surface area of the carbons (the isotherms are practically of type I). These values were compared with the surface areas derived from the selective adsorption of caffeine, measured by immersion calorimetry, $S_{(immers)} = \Delta h_{i(caff)}/0.112\,\mathrm{J\,m^{-2}}$, or by other techniques. It appears, that the comparison of N_{ao} with the surface area derived from immersion calorimetry is subject to a certain scatter, although the two should be proportional. On the other hand, the surface area derived from the enthalpy of immersion into aqueous solution of caffeine is in good agreement with the total surface area, $S_{tot} = S_{mi} + S_e$, derived from independent adsorption data (see *Figure 3*), provided that no molecular sieve effects are present (such an effect is observed in sample DE-60). An overall assessment of the data in *Table 2* and *Figure 3* suggests an average molecular surface area of $\sim 65 \cdot 10^{-20}\mathrm{m}^2$ for caffeine, but the values range from 40 to $100 \cdot 10^{-20}\mathrm{m}^2$. It appears that the calorimetric technique leads to better results than the caffeine isotherm. The latter is also more time-consuming.

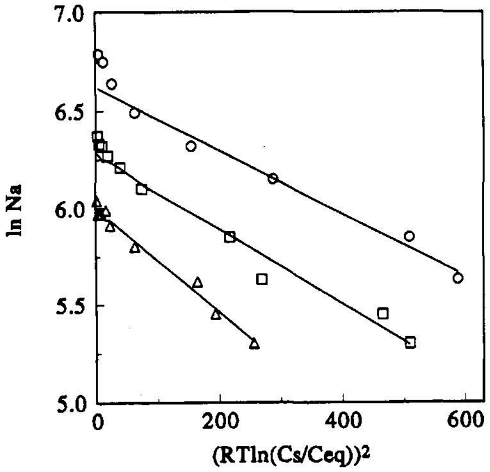

Figure 1 D–R plot for the selective adsorption of caffeine from aqueous solutions at 293 K by carbons DE-150 (○), DE-80 (□) and DE-60 (△)

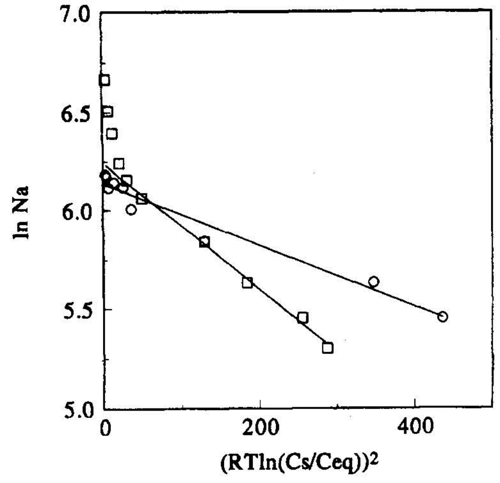

Figure 2 D–R plot for the selective adsorption of caffeine from aqueous solutions at 293 K by carbons BTH (○) and BCH (□)

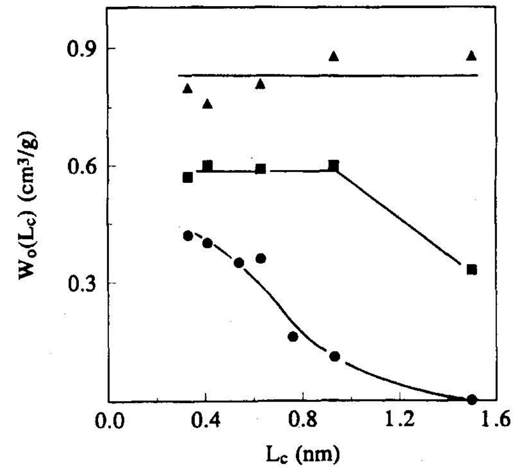

Figure 4 Micropore volume $W_0(L_c)$ filled by liquids with average molecular sizes L_c for carbons DE-60 (●), DE-80 (■) and DE-150 (▲)

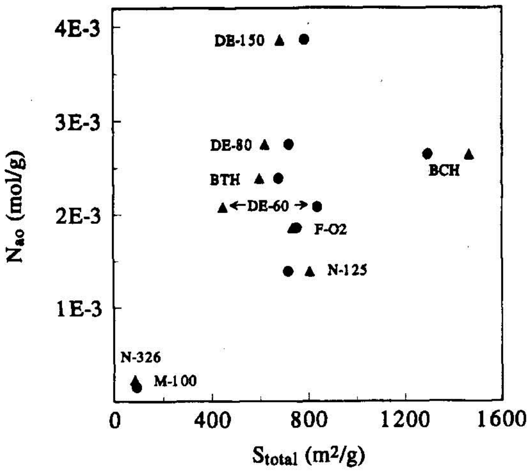

Figure 3 Comparison of the limiting amount of caffeine adsorbed by various activated carbons with the total surface areas $S_{tot[isoth]}$ obtained from $S_{mi} + S_e$ (●) and from the enthalpy of immersion into aqueous solutions of caffeine, $\Delta h_i/(0.112\,J\,m^{-2})$ (▲)

In the case of series DE, the vapour adsorption of a small molecule (Ar at 77 K) shows that the micropore volume W_0 increases with activation, as expected[1]. The average micropore size, on the other hand, is relatively large in all samples. This behaviour, which has been observed previously[15,16], reflects the origin and history of the material. The adsorption data, combined with the determination of the external surface area S_e, lead to the total surface areas $S_{tot[isoth]}$, which can be compared with the values obtained from caffeine adsorption and immersion.

On the basis of the data obtained from small molecular probes, such as CH_2Cl_2 at 293 K, it might be concluded that the activated carbons of series DE have large micropores and that sample DE-80 should be very similar to N-125, a carbon described in detail elsewhere[17] ($W_0 = 0.64\,cm^3\,g^{-1}$, $E_0 = 16.6\,kJ\,mol^{-1}$ and $S_e = 157 \pm 20\,m^2 g^{-1}$). As found experimentally, the micropore system of this solid is equally accessible to molecules of different sizes.

However, for carbons DE-60, DE-69 and DE-80, immersion calorimetry with molecules of different sizes reveals a limited accessibility of the micropore systems. *Figure 4* shows the volumes $W_0(L_c)$ accessible to the molecules of critical dimension L_c, as calculated from Δh_i (*Table 3*). It appears that the largest molecule, TXP (1.5 nm) is completely excluded from the micropore volume of solid DE-60, although its average pore size is ~ 1.2 nm. This behaviour reflects a gate effect, probably due to constrictions at the entrance of the pores. As seen in *Figure 4*, this effect disappears with increasing burnoff. In sample DE-80 a volume of $0.33\,cm^3 g^{-1}$ becomes accessible to TXP, whereas the overall micropore volume is only $0.15\,cm^3$ greater than that of DE-60. This is a clear indication of the presence of constrictions in solid DE-60 which also exclude to some extent caffeine. As a consequence, a smaller surface area is obtained than is predicted by $S_{tot[isoth]}$ (446 against $836\,m^2 g^{-1}$).

It appears that the total accessibility of the pore system is achieved only for sample DE-150. For this carbon, immersion calorimetry with caffeine solutions leads to a total surface area of ~ $700\,m^2 g^{-1}$, in reasonable agreement with $S_{tot[isoth]} = 734\,m^2 g^{-1}$.

For the carbons of series DE, the specific enthalpies of immersion into water $h_i(H_2O) = \Delta h_i / S_{tot}$ vary between 0.050 and $0.065\,J\,m^{-2}$ and are typical for this type of activated carbon. This suggests that within an activation series, the enthalpy of immersion into water can already provide an estimate of the total surface area of the solid.

The STM images shown in *Figure 5* were obtained in the constant-current mode. The tip was rastered across the surface, while the tunnelling current was kept constant by a feedback circuit. The STM images describe the surface relief, which is expressed by different shades of colour. This relief reflects the surface topography. At high magnifications (full scale < 20 nm), the very rugous aspect of the surface is apparent. Micrograph 5a (sample DE-150), covering an area of 15×15 nm, shows a central region of < 5 nm with slits converging towards it. The overall structure is similar to that described to Stoeckli[17].

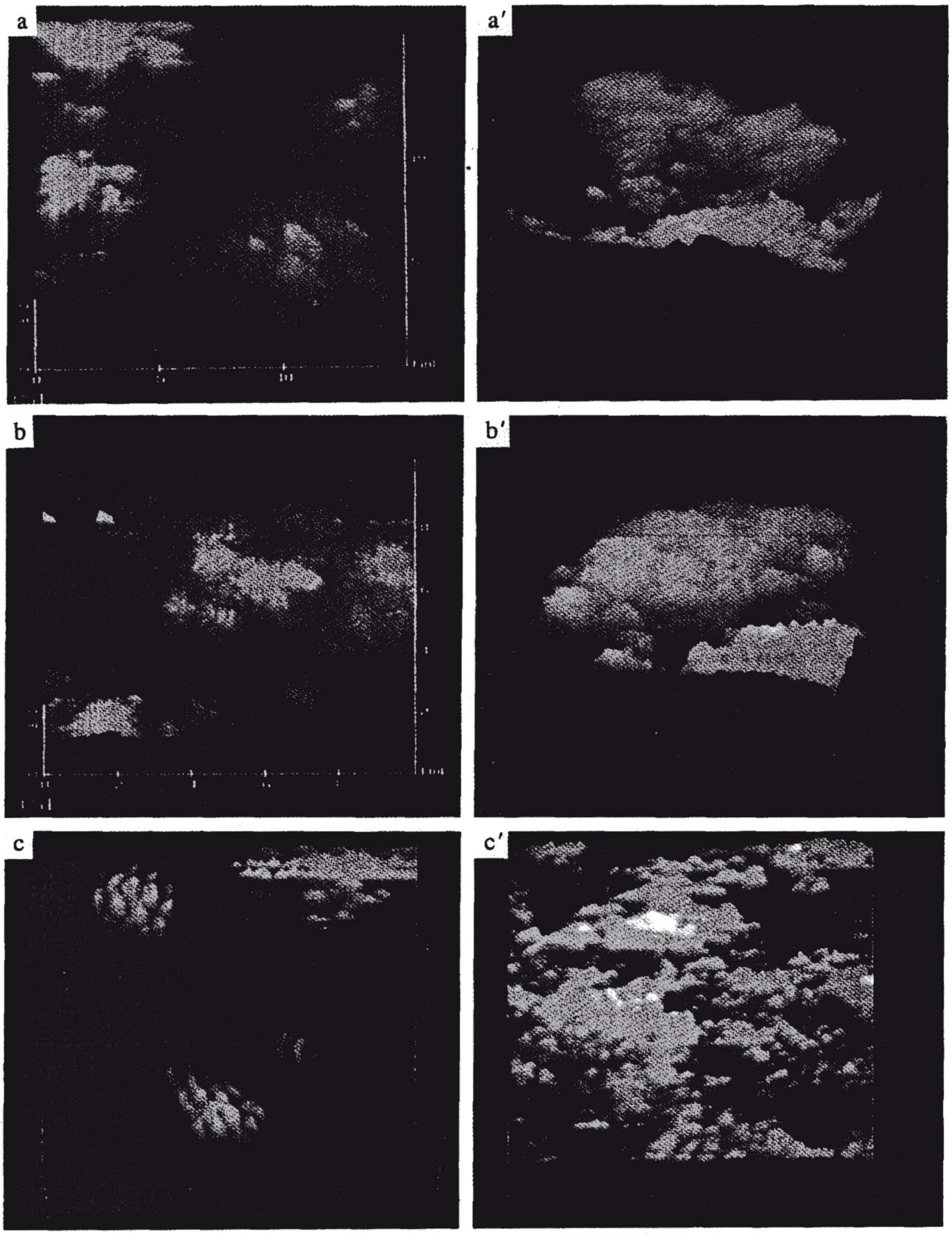

Figure 5 Typical STM micrographs of samples DE-150 (a, b, c) and DE-60 (a′, b′, c′)

Such slits appear more clearly on micrographs 5b and 5c with corresponding areas of observation equal to 10×10 nm and 5×5 nm. The width of these slits is ~ 2 nm, which corresponds to supermicropores. The quantitative analysis of STM micrographs is difficult because of the small areas observed, but as suggested by micrographs 5a–c, the microporosity of sample DE-60 is less important than that of DE-150.

In the case of adsorption by samples BTH and BCH, a similar pattern is observed as illustrated by *Figure 6*. The larger molecules are still excluded to some extent, but the gate effect becomes important only beyond 1 nm. Therefore, as shown in *Table 2*, the bulk of the structure becomes accessible to caffeine and the total surface areas obtained from the isotherm and from immersion calorimetry are in good agreement with the

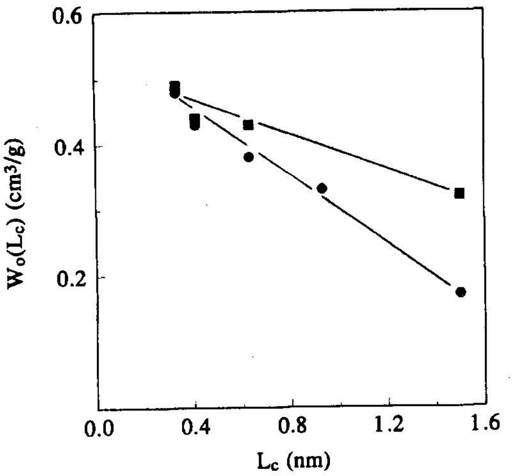

Figure 6 Micropore volume $W_0(L_c)$ filled by liquids with average molecular sizes L_c for carbons BTH (●) and BCH (■)

values based on the adsorption isotherms of the small probes.

It is also worth pointing out the very large external surface area of sample BCH, ~ 850 m^2g^{-1}. This solid has essentially supermicropores, with a theoretical width of 2 nm. These pores are equally accessible to the various molecular probes, as indicated by the values of Δh_i given in *Table 3* and illustrated by *Figure 6*. Moreover, the high specific enthalpy of immersion into water (0.108 $J m^{-2}$), unchanged by washing with aqueous HCl, suggests a larger ratio than usual between edges and basal planes, since the oxygen-containing groups are located on the edges.

For sample BTH, the micrographs 7a and b show slit-shaped micropores with a width of < 1 nm. Since the average micropore width is ~ 1.6 nm, as suggested by small molecular probes (*Table 2*), the micrographs probably show the constrictions indicated by *Figure 6*. It will therefore be interesting to correlate their modification with the increasing accessibility of the micropore system, after further activation of sample BTH. This combination of STM and adsorption techniques will be reported in due course.

CONCLUSIONS

The exhaustive physical characterization of the carbons of series DE and BH illustrates the possibilities currently available. The techniques based on gas adsorption and on immersion calorimetry can already provide useful information, in particular within a given series of carbons. Scanning tunnelling electron microscopy on the other hand is still in its early stages as far as activated carbons are concerned, but it is likely that it will become a useful tool for the characterization of this type of solid.

It appears that the adsorption of small molecules such as CH_2Cl_2 or benzene at 293 K, combined with immersion into the corresponding liquids, provides a first set of data (W_0, E_0, L, S_e, S_{mi}). This approach is probably more reliable than the use of N_2 at 77 K (where activated diffusion can play a role) and of CO_2 at ~ 273 K. However, the presence of a gate effect, often overlooked at this stage, requires additional but simple experiments based on immersion calorimetry. The use of larger molecular probes and the selective adsorption of caffeine from aqueous solutions (0.112 ± 0.015 $J m^{-2}$) provide rapid information on the accessibility of the micropore volume. This is particularly important for the subsequent use of the carbons in filtration technology, where other molecules are involved.

Standard tests, as described here, can also be used in the study of series of carbons, where immersion calorimetry provides a shortcut for the standard characterization, usually based on adsorption isotherms.

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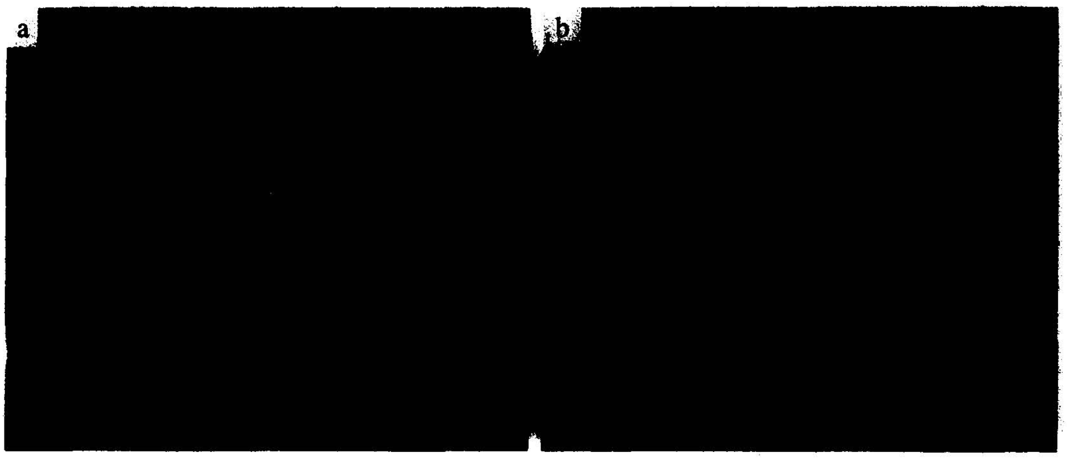

Figure 7 Typical STM micrographs of sample BTH

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