On the Characterization of Microporous Carbon Blacks by Various Techniques

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Abstract. It is shown that the combination of different techniques, based on the adsorption of vapors and on calorimetry, can lead to the unambiguous characterization of carbonaceous materials. The case of a microporous carbon black, with pores in the range 0.35–1.2 nm, is used as an example.

1. Introduction

Carbonaceous materials exist in a variety of forms, ranging from highly porous active carbons and active carbon fibers, to virtually nonporous graphitized carbon blacks. However, a number of carbon blacks present some degree of microporosity, which can be characterized by adsorption and calorimetric techniques used and developed in our laboratory [1–4]. The differential heat of adsorption of vapors, measured with a calorimeter of the *Tian-Calvet* type, appears to be a very useful technique [4]. The standard approach, based on the BET method alone is not sufficient and in some cases it can be misleading. This point is illustrated by the study of sample XC-72, a microporous carbon black of industrial origin which has been studied extensively in our laboratory.

2. Theoretical

Adsorption by microporous carbons is described by the equation of *Dubinin* and *Astakhov* [1]

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

where W represents the volume filled at temperature T and relative pressure p/p_0; W_0 is the total volume of the micropo-

res, $A = RT\ln(p_0/p)$ and n, E_0 and β are specific parameters of the system under investigation. For a variety of active carbons, $n = 2$ and *Eqn. 1* becomes the classical expression of *Dubinin* and *Radushkevich*. A plot of $\ln(W)$ *vs.* $(A/\beta)^2$ leads to parameters W_0 and E_0.

It has been shown [2], that parameter E_0, the so-called characteristic energy of the micropore system given in kJ/mol, is related to the average micropore-size L of the system by

$$L \text{ [nm]} = 10.8/(E_0 - 11.4) \qquad (2)$$

If one assumes slit-shaped micropores, the surface area of their walls S_{mi}, is

$$S_{mi} \text{ [m}^2\text{/g]} = 2 \cdot 10^3 W_0 \text{[cm}^3\text{/g]}/L \text{ [nm]} \qquad (3)$$

Microporous carbons often contain a non-microporous or external surface area S_e. It can be obtained either from the decomposition of the overall isotherm, by substracting the contribution of the micropores, or from the enthalpy of immersion into an organic liquid (*e.g.* CH_2Cl_2, whose vapour can be used for the adsorption isotherm). From *Eqn. 1*, one can derive an expression for the enthalpy of immersion [1],

$$\Delta h_i \text{ [J/g]} = -\beta E_0 W_0 \pi^{1/2} (1+\alpha T)/2 \, V_m + h_i S_e \qquad (4)$$

where a and V_m are the thermal expansion coefficient and the molar volume of the liquid, and Δh_i is the enthalpy of wetting of the surface by the liquid. The two techniques are usually in good agreement [1]. *Eqn. 4 can* also be used to determine the micropore distribution from the limiting volumes W_0 filled by liquid molecular probes in the range of 0.35 to 1.5 nm [1][2]. *Fig. 1* shows the distribution obtained for sample XC-72. The cummulative surface area leads to $S_{mi} = 120 \text{ m}^2\text{/g}$ if one postulates slit-shaped micropores.

As shown recently, the total surface of a microporous carbon, $S_t = S_{mi} + S_e$, can also be obtained from the enthalpies of immersion into aqueous solutions of caffeine [2] or ammonia [4]. In the case of caffeine, however, the technique is limited to pores larger than 0.6–0.7 nm, approximately.
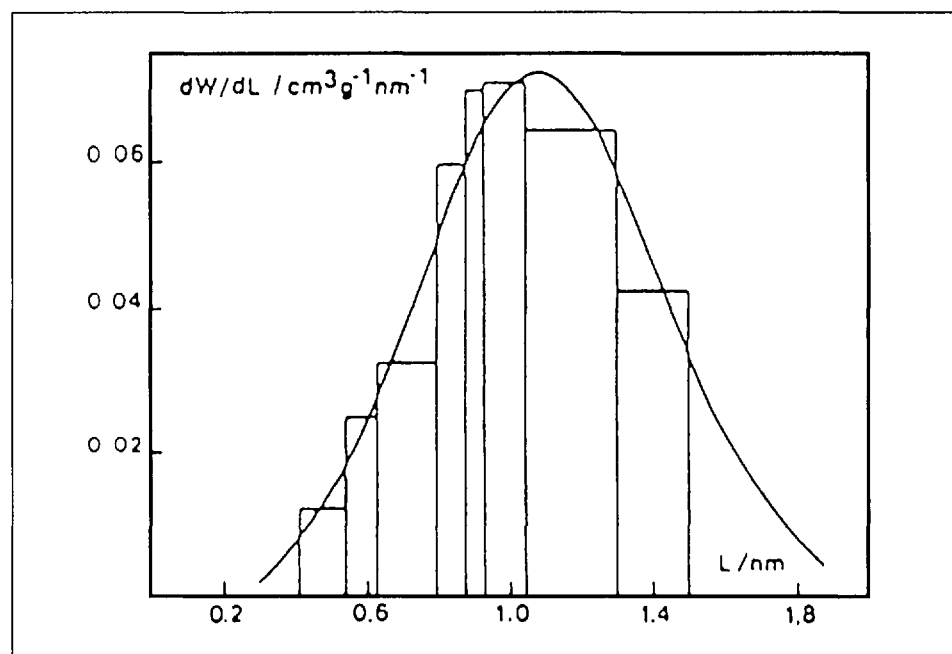
A complementary picture is also pro-

Fig. 1. *The micropore distribution of carbon black XC-72, obtained from adsorption and immersion experiments.* The continuous curve corresponds to a theoretical model [2].

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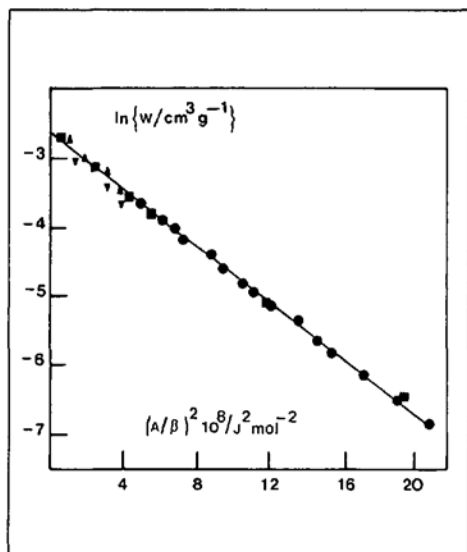Avenue Bellevaux 51
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Fig. 2. *The* Dubinin-Astakhov *plot of* Eqn. 1 *with n = 2 for the adsorption of* N_2 *(77 K)* (▲), N_2O *(293 K)* (●), C_6H_6 *(293 K)* (▼), *and* CH_2Cl_2 *(293 K)* (■)
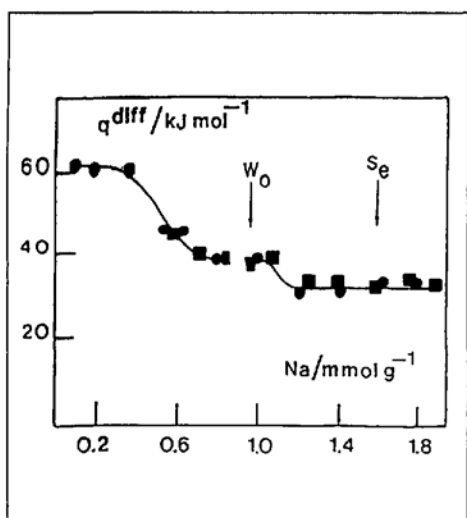

Fig. 3. *The differential heats of adsorption of* CH_2Cl_2 *(293 K) on carbon black XC-72, as a function of the amount adsorbed.* The amounts equivalent to the filling of the micropores and to coating of the external surface area are also shown. Experiments 1 (●) and 2 (■).

vided by q^{diff}, the differential heat of adsorption of a vapor such as CH_2Cl_2, measured calorimetrically at 293 K. In the case of active carbons, experience shows [5] that for small micropores ($L < 0.8$ nm), q^{diff} (CH_2Cl_2; 293 K) is around 60 kJ/mol. In very large micropores ($L > 1.5$ nm), on the other hand, one observes first the coating of the walls, corresponding to 40–45 kJ/mol, followed by their filling in the range of 35–40 kJ/mol. For the intermediate micropores (1–1.5 nm), these two processes occur almost simultaneously. Finally, adsorption takes place on the external surface, near 30–35 kJ/mol. This shows that the calorimetric approach distinguishes clearly the various stages of adsorption by carbonaceous materials.

3. Results and Discussion

The different techniques, and in particular calorimetry from the vapor phase, were applied to sample XC-72, a microporous carbon black of industrial origin. This solid has already been investigated extensively and the results were part of a study leading to *Eqn. 2* [1–3].

Prior to adsorption and calorimetric experiments, the solid was prepared following standard procedures [1–3]. For the adsorption from the gas phase, we used N_2 at 77 K and C_6H_6, N_2O, and CH_2Cl_2 at 293 K. Their respective affinity coefficients β are 0.38, 1.00, 0.46, and 0.66 [1]. As shown in *Fig. 2*, one obtains practically a single linear logarithmic plot of *Eqn. 1* and, with the exception of the nitrogen similar limiting volumes W_0 given in the *Table*. This is not too surprising, in view of the dimensions of these molecules (0.35–0.40 nm) and the width of the micropore distribution shown in *Fig. 1*.

The enthalpies of immersion into various liquids at 293 K and *Eqn. 4* lead to an average external surface area $S_e = 121 \pm 20$ m²/g. It is in good agreement with the value of 120 ± 30 m²/g obtained from the analysis of the N_2, C_6H_6, and CH_2Cl_2 adsorption isotherms (decomposition and/or t-plot). The α_s plot technique for N_2 (77 K), using the data of *Carrott* and *Sing* [6], leads to $S_e = 127 \pm 10$ m²/g. On the other hand, the micropore volume of 0.044 cm³/g is too small. The discrepancies observed for nitrogen are not understood yet.

The solid has, therefore, a total micropore volume W_0 close to 0.060 cm³/g ($L > 0.35$–0.4 nm) and a total surface area of *ca.* 240 m²/g. As shown recently [4], the technique based on the immersion of carbons into aqueous solutions of NH_3 leads to a total surface area of 234 m²/g (uncertainty of 10–15%).

The combination of the cummulative surface area $S_{mi} = 120$ m²/g (derived form the histogram of *Fig. 1*) with W_0, through *Eqn. 3*, leads to $L = 1$ nm for the average micropore width. This data has been used to derive *Eqn. 2*, on the basis of results obtained with various samples [1][2].

The classical BET treatment [7] of the N_2 (77 K) and C_6H_6 (293 K) isotherms leads to 195 and 214 m²/g. This information is relatively limited, since no distinction is made between the internal and external surface areas of the solid.

The variation of the differential heat of adsorption of CH_2Cl_2 at 293 K, obtained from gas-phase calorimetry, confirms the general picture derived from adsorption and immersion experiments. As seen in *Fig. 3*, the process begins with the filling of the smaller micropores where q^{diff} is around 60 kJ/mol, as observed for active carbon CAF-B [5]. In the present case, the amount of 0.4 mmol/g would correspond to the micropores having width $L < 0.8$ nm, approximately.

The decrease in the heat of adsorption and the plateau near 38 kJ/mol correspond to the coating of the walls and the filling of the larger micropores. In view of the pore-size distribution shown in *Fig. 1*, the two processes overlap to some extent. In the region of $N_a = 1$ mmol/g, corresponding to W_0, one observes a final drop in q^{diff}. Beyond this stage, adsorption occurs exclusively on the external surface.

The present study shows that the combination of adsorption and calorimetric techniques provides complementary information for the study of microporous carbon blacks, along the same lines as for active carbons.

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Table. *The Main Characteristics of Carbon Black XC-72*

Vapor	N_2	N_2O	C_6H_6	CH_2Cl_2
W_0 [cm³/g]	0.089	0.07	0.059	0.060
E_0 [kJ/mol]	19.0	22.4	22.0	23.5
S_e [m²/g]	120 ± 20	120 ± 30		127 ± 10
	(*Eqn. 4*)	(isotherm analysis)		(N_2 α_s-plot)