

Microporosity in carbon blacks

F. Stoeckli^{a,*}, A. Guillot^b, A.M. Slasli^a, D. Hugi-Cleary^a

^aChemistry Department of the University, Avenue de Bellevaux 51, CH-2007 Neuchâtel, Switzerland

^bCNRS-IMP, Université de Perpignan, Avenue de Villeneuve, F-66806 Perpignan, France

Abstract

Microporous carbon blacks can be characterized by the same techniques as activated carbons, using the classical DR equation and comparison plots based on non-porous materials. The CO₂ adsorption isotherm at 273 K, combined with computer modelling, also leads to an assessment of microporosity. The results agree with independent techniques such as immersion calorimetry into liquids of variable molecular dimensions and a modified Dubinin equation. The study also confirms that the comparison plots based on N₂ (77 K), CO₂ (273 K) and C₆H₆ (293 K) do not necessarily lead to overlapping results for the total micropore volume and the external surface area of the carbons.

Keywords: A. Carbon black; C. Adsorption, Modelling; D. Porosity

1. Introduction

Carbon blacks [1] and activated carbons [2] both contain graphitic sheets as building blocks, the difference being the extent of order. In the case of carbon blacks, high temperature treatments may also improve the graphitic structure. On the other hand, activated carbons will remain disordered, the extent of the graphitic domains being limited to approximately 2–3 nm and 2–4 layers. These structural similarities are sufficient to ensure, locally at least, similarities in the microporosity of the two types of carbons. It has been shown by the dark-field technique developed by Oberlin et al. [3–5] and, more recently by STM [6–9], that the micropores of activated carbons are locally slit-shaped, at least up to a width of 1 nm. The micropore system may therefore be regarded as a three-dimensional collection of interconnected slits, the difference with carbon blacks being, to a first approximation, the extent of regularity.

The microporosity of carbon blacks and of other materials can be assessed by techniques such as neutron or X-ray scattering, but it appears that the classical techniques are still appropriate for a reasonable characterization. Since the introduction of the method based on nitrogen comparison plots by de Boer [10,11] and later by Sing [12,13],

progress has been made. This includes the use of other vapours such as benzene at 293 K [14] and, more recently, of CO₂ between 253 and 353 K and at pressures up to 5 MPa [15–18]. Like CH₄ [9], CO₂ is a relatively simple molecule and its adsorption isotherm can be modelled by computer simulations [19–23].

The present study re-examines the assessment of microporosity in carbon blacks, as described earlier [24–27] and based on comparison plots, isotherms, immersion calorimetry into liquids of variable molecular dimensions and on differential heats of adsorption. As a novelty, we include the use CO₂ isotherms at 273 K and pressures up to 3 MPa, as well as the recent reference isotherm on Vulcan 3-G [26]. The CO₂ isotherms are also analysed with the help of model isotherms resulting from computer simulations, which leads to the corresponding micropore distributions [9,23].

2. Theoretical background

Adsorption of vapours by microporous carbons is described by Dubinin's theory [2,28–30] and its fundamental equation is the so-called Dubinin–Astakhov equation,

$$N_a = N_{ao} \exp[-(A/E)^n] \quad (1)$$

N_a represents the amount adsorbed at relative pressure p/p_s , N_{ao} is the limiting amount filling the micropores and

* Corresponding author. Fax: +41-32-718-2511.

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

$A = RT \ln(p_s/p)$. At high pressures, the ratio p_s/p is replaced by the ratio of the fugacities and for temperatures above critical, the saturation pressure is replaced by $p_c(T/T_c)^2$ [28]. The case where $n = 2$ corresponds the Dubinin–Radushkevich equation (DR). Eq. (1) reflects the filling of a volume $W_o = N_{ao}V_m$, where V_m is the molar volume of the adsorbate. It is similar to that of the liquid at the same temperature, but not necessarily equal to it, as in the case of CO_2 discussed below. The characteristic energy, E , depends on the adsorbent and on the adsorptive. One may write that $E = \beta E_o$, where β depends on the adsorptive and by convention, $\beta(\text{C}_6\text{H}_6) = 1$. It has been shown [30,31] that E_o is related to the average width L_o of the slit-shaped micropores by

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

The approximate surface area of these pores is given by the simple geometrical relation

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

The total surface area of the carbon $S_{tot} = S_{mi} + S_e$, where S_e is the external surface. S_{tot} can be compared with the area obtained from immersion calorimetry into aqueous solutions of caffeine [30,32] or phenol [33] provided, in the latter case, that the surface does not contain too much oxygen. These molecules are adsorbed preferentially as monolayers with specific enthalpies of approximately -0.115 and -0.110 J m^{-2} .

As discussed elsewhere [30,31,34], the following micropore distribution

$$f(L) = 3 W_o L^{(3\nu-1)} a^\nu \exp[-aL^3]/\Gamma(\nu) \quad (4)$$

can be associated with a modified Dubinin equation

$$\theta(A) = N_a/N_{ao} = [a/(a + (A/\beta K_o)^3)]^\nu \quad (5)$$

where ν and a are adjustable parameters and $K_o = L_o E_o$, as confirmed by direct curve fitting.

A thermodynamic consequence of the DR equation is the following expression for the enthalpy of immersion of the carbon into the corresponding liquids [2,5,30],

$$\Delta_i H \text{ (J g}^{-1}) = -\beta E_o W_o (1 + \alpha T) \pi^{1/2} / 2 V_m + h_i S_e \quad (6)$$

where $h_i S_e$ represents the wetting of the external surface of the solid. The enthalpies of immersion into liquids of variable molecular dimensions can also be used to assess the micropore distribution of carbons between 0.4 and 1.5 nm [30,31], as illustrated below.

It has been shown [27] that adsorption of different vapours by non-porous carbon blacks follows the so-called DRK equation suggested by Kaganer [35,36]

$$N_a = N_{am} \text{ (DRK)} \exp[-(A/\beta E_o)^2] \quad (7)$$

where N_{am} (DRK) represents the limiting amount adsorbed in the monolayer. Fig. 1 illustrates the case of C_6H_6 , CCl_4 , CH_2Cl_2 and N_2 adsorbed on carbon black Hoechst [27]. As discussed elsewhere [14,26], N_{am} (DRK) is somewhat larger than N_{am} (BET), but no explanation can be offered for this difference.

For carbon black Hoechst, benzene leads to a characteristic energy E_o of 10.8 kJ mol^{-1} , against 10.4 kJ mol^{-1} for Vulcan3G and 11.4 kJ mol^{-1} for N-234G, another graphitised carbon black. Lower values, around 9.4 – 9.8 kJ mol^{-1} , have also been reported [14], which confirms that Dubinin's theory applies to porous and non-porous carbon blacks, but in different domains of p/p_s .

Values of E_o around 10 – 11 kJ mol^{-1} are close to the lower bound of 11.4 kJ mol^{-1} found in the empirical relation (2) and correspond to very wide micropores. It follows that the value of E_o provides a first indication for the presence or the absence of microporosity in unknown carbons, including carbon blacks. Typical micropores correspond to $E_o > 18$ – 20 kJ mol^{-1} , whereas values below 14 – 15 kJ mol^{-1} reflect either variable degrees of surface heterogeneity, or the presence of super-micropores (1.5 – 2.5 nm). For such carbons, no molecular sieve effects are observed by immersion calorimetry and the characterization of their porosity becomes difficult.

Computer modelling of adsorption has become increasingly popular and it has been applied to the determination of pore-size distributions in carbons. A number of studies are based on the adsorption of simple molecules such as CH_4 [9,37] and CO_2 [9,20–23]. In this approach, standard isotherms are modelled for sets of slit-shaped pores between 0.4 and 1.5 – 2 nm and the experimental isotherm

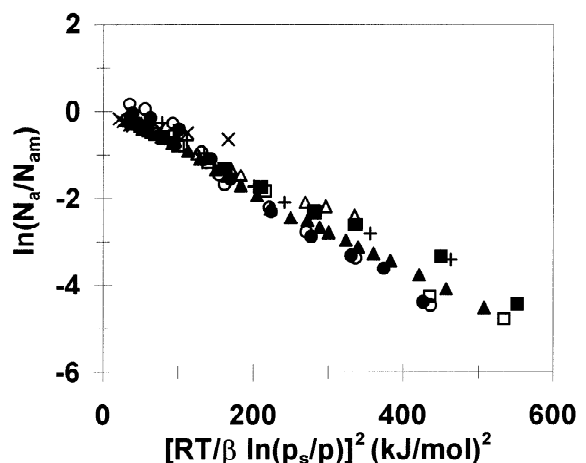


Fig. 1. Logarithmic DRK plot for the adsorption of different vapours on C black Hoechst: C_6H_6 at 282 K (Δ), 293 K (\blacktriangle), 311 K (\square) and 323 K (\blacksquare); CCl_4 at 294 K (\bullet) and 305 K (\circ); CH_2Cl_2 at 293 K ($+$) and N_2 at 77 K (\times).

is described in terms of a weighted contribution of these isotherms. From a practical point of view, a good choice seems to be CO₂ at 273 K, where full isotherms can be obtained with high-pressure equipment [16–18]. Standard CO₂ isotherms for adsorption in slit-shaped micropores at 273 K have recently been obtained by the authors, as described elsewhere [9,23].

3. Experimental

We considered two typical microporous carbon blacks, XC-72 [24,26] and XC-72-16, the product of its activation by water vapour at 950°C [23]. For comparison purposes, we also included three active carbons, CAF-B, U-103 and KF-1500 [18,26], with average micropore sizes of 0.65, 1.15 and 1.38 nm, respectively. These solids had been subjected to the same type of analysis [9,18,23] as the carbon blacks used here.

The adsorption and immersion techniques used to characterize these samples, in particular with CO₂ at 273 K, have been described in detail elsewhere [1,18,30] and

the corresponding structural parameters are given in Table 1.

4. Results and discussion

Fig. 2 shows the combined data for CO₂ (253, 273 and 298 K) and C₆H₆ (298 K) adsorbed on carbon black XC-72. With $E_o = 22.4 \text{ kJ mol}^{-1}$ and $\beta(\text{CO}_2) = 0.35$ [23,26], one obtains a single DR plot. The molar volume of CO₂ is still a matter of debate [15–17,23] and various expressions have been proposed to calculate it [28,38]. For the different carbons, the values of $42.90 \text{ cm}^3 \text{ mol}^{-1}$ at 273 K, given by Ozawa's equation [38], lead to micropore volumes $W_o(\text{CO}_2; 273 \text{ K})$, which are in good agreement with those suggested by other adsorbates (see Table 1). Comparison plots with non-porous references like Vulcan 3G or Hoechst, lead to the micropore volumes and external surfaces given in Table 1.

The structural parameters obtained by the different techniques, summarized in Table 1, show clearly the limits

Table 1
Main characteristics of microporous carbon blacks XC-72 and XC-72-16 and of activated carbons CAF-B, U-103 and KF-1500

Sample	XC-72	XC-72-16	CAF-B	U-103	KF-1500
DR analysis					
E_o (kJ mol ⁻¹) C ₆ H ₆ /N ₂	22.4	21.3	28.3	20.7	19.1
E (kJ mol ⁻¹) CO ₂	8.6	7.5	10.1	7.7	6.4
L_o (nm) (DR average)	0.96	1.08	0.65	1.15	1.38
S_{mi} (m ² g ⁻¹) (average)	145	259	856	631	918
W_o (cm ³ g ⁻¹) C ₆ H ₆	0.057	0.130	0.266	0.330	0.580
W_o (cm ³ g ⁻¹) CO ₂	0.070	0.150	0.274	0.360	0.620
Modelling (CO ₂ ; 273 K)					
L_o (nm) (DR average)	1.01	1.22	0.75	1.28	1.46
W_o (cm ³ g ⁻¹) C ₆ H ₆	0.070	0.155	0.280	0.400	0.66
Comparison plot					
W_o (cm ³ g ⁻¹) C ₆ H ₆	0.041	0.180	0.30	0.35	0.60
W_o (cm ³ g ⁻¹) CO ₂	0.075	0.147	0.27	0.38	0.60
W_o (cm ³ g ⁻¹) N ₂	0.052	–	0.28	0.35	0.63
W_o (cm ³ g ⁻¹) average	0.061	0.152	0.28	0.36	0.61
Comparison plot					
S_e (m ² g ⁻¹) C ₆ H ₆	137	117	32	27	28
S_e (m ² g ⁻¹) CO ₂	75	108	44	19	19
S_e (m ² g ⁻¹) N ₂	103	–	97	70	22
Calorimetry $\Delta H_1(\text{C}_6\text{H}_6)$					
S_e (m ² g ⁻¹)	106	139	70	40	14
S_e (m ² g ⁻¹) average	105	119	60	39	21
S_{tot} (m ² g ⁻¹) = $S_{mi} + S_e$	250	380	916	670	939
S_{tot} (phenol) (m ² g ⁻¹)	257	460	–	–	1167

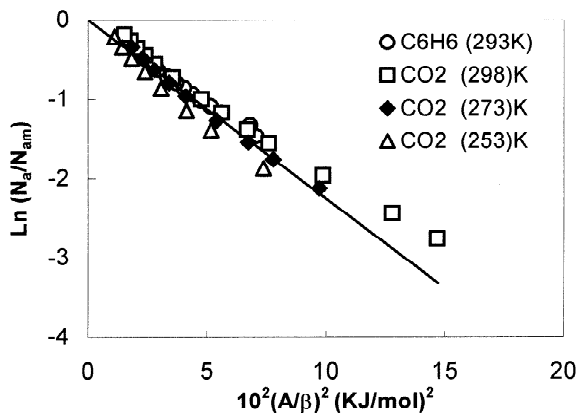


Fig. 2. DR plot for adsorption of CO_2 at 253, 273 and 298 K and C_6H_6 at 293 K on carbon black XC-72 ($E_0 = 22.4 \text{ kJ mol}^{-1}$).

for the characterization of carbons. It appears that a single determination may not be sufficient and the average values obtained for W_o , S_e and S_{tot} give an estimate of the uncertainties resulting from different adsorbates and techniques.

After correcting for adsorption on the external surfaces S_e (75 and $108 \text{ m}^2 \text{ g}^{-1}$) by using the reference isotherm on Vulcan 3G [26], the CO_2 isotherms at 273 K were fitted to a weighted contribution of the model isotherms obtained by Monte Carlo simulations, as described previously [9,23]. The corresponding micropore volumes are close to those obtained by other techniques (DR and comparison plots).

As seen in Fig. 3(a) and (b), the normalized pore size distributions for CO_2 (273 K) are in good agreement with those obtained from immersion calorimetry [21,22,26] and from Eq. (4). The CO_2 histograms lead to average micropore widths L_o of 1.01 and 1.22 nm, in good agreement with the values obtained from the DR analysis (0.96 and 1.08 nm), using Eq. (2). In the case of carbon blacks XC-72 and XC-72-16, the histograms and the analysis of the different isotherms with the help of Eqs. (2) and (3) suggest total surface areas of approximately 250 and $380 \text{ m}^2 \text{ g}^{-1}$. On the other hand, immersion calorimetry into aqueous solutions of phenol, leads to areas of 257 and $460 \text{ m}^2 \text{ g}^{-1}$. The uncertainties being around 5–10% in both techniques, the agreement is satisfactory.

In conclusion, this study shows that it is possible to characterize microporous carbon blacks with the same standard adsorption and calorimetric techniques as activated carbons. In the last analysis, this is due to the fact that both types of solids can be treated as collections of locally slit-shaped micropores, carbon blacks being closer to the ideal model. However, in both cases, reliable characterization still requires the determination of an adsorption isotherm and the use of a suitable reference. The choice of adsorptive may also be of great help and it appears that the use of CO_2 at 273 K and at pressures up to

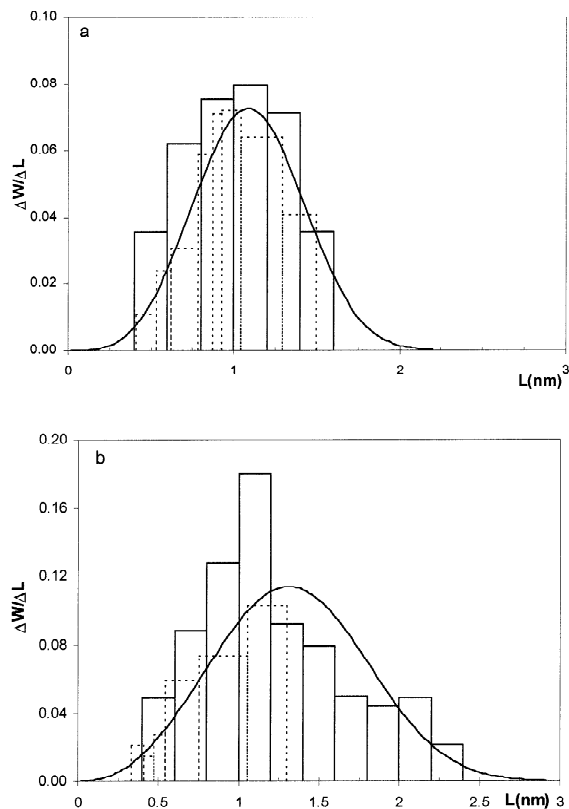


Fig. 3. Micropore distributions in carbon blacks XC-72 (a) and XC-72-16 (b) obtained from the analysis of the CO_2 isotherm at 273 K based on model isotherms (\rightarrow) from immersion calorimetry with liquids of different molecular dimensions ($---$) and from Eq. (4) (curve).

3–3.5 MPa offers a number of advantages. Firstly, a reliable standard CO_2 isotherm is now available for comparison plots, in order to establish the presence or the absence of microporosity in carbonaceous materials. Secondly, for a finer characterization of the porosity, the adsorption isotherm can also be used in connection with adsorption calorimetry into liquids of different molecular dimensions. Finally, micropore distributions can also be derived from this isotherm with the help of model isotherms based on computer simulations.

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