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# On the Adsorption of CO<sub>2</sub> by Active Carbons

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**Abstract.** The combination of adsorption and calorimetric techniques shows that the adsorption of CO<sub>2</sub> is a two-step process in the case of active carbons with large micropores ( $L > 1.2$ – $1.5$  nm). For smaller pores, on the other hand, one observes a uniform filling of the volume. These mechanisms are in agreement with earlier experiments carried out with CH<sub>2</sub>Cl<sub>2</sub> at 293 K.

## 1. Introduction

Adsorption of typical organic and inorganic vapors by active carbons is described by the theory of *Dubinin*, and it is basically a process of volume filling of the micropores. The basic relation is the *Dubinin-Astakhov* equation [1],

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

where  $W$  represents the volume filled at temperature  $T$  and relative pressure  $p/p_0$ ;  $W_0$  is the total volume of the micropores,  $A = RT \ln(p_0/p)$  and  $n$ ,  $E_0$ , and  $\beta$  are specific parameters of the system under investigation. In the case of high pressures,  $p_0/p$  is replaced by the ratio of the fugacities  $f_0/f$ . 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  $E_0$ . For the main adsorptives used here, CO<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>, parameter  $\beta$  is equal to 0.44 and 0.66.

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

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

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

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

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 subtracting the contribution of the micropores, or from the enthalpy of immersion into an organic liquid (e.g. CH<sub>2</sub>Cl<sub>2</sub>, whose vapor can be used for the adsorption isotherm). From *Eqn. 1*, one can derive an expression for the enthalpy of immersion [1],

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

where  $\alpha$  and  $V_m$  are the thermal expansion coefficient and the molar volume of the liquid, and  $h_i$  is the enthalpy of wetting of

the surface by the liquid. The two techniques are usually in good agreement [1].

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 [3] or ammonia [4].

As shown elsewhere [5], in the case of strongly activated carbons (micropore width  $L$  larger than 1.2–1.5 nm and virtually no narrow pores) the adsorption of small molecules begins with the coating of the walls, before the actual filling of the volume can take place. This can be detected by a different slope in the initial part (very low relative pressures) of the logarithmic plot of *Eqn. 1*.

Further evidence is provided by the combination of adsorption and calorimetric techniques, as well as independent determination of the surface area of micropore walls. This type of investigation has already been applied to different active carbons [5] with CH<sub>2</sub>Cl<sub>2</sub> at 293 K as the main probe.

In the case of CO<sub>2</sub>, another popular adsorptive, the distinction between the coating of the walls and the subsequent filling of the micropores is clearly observed for active carbons with a high degree of burn-off. These solids contain essentially large micropores created at the expenses of the smaller pores present initially (smaller pores having been destroyed).

In the present paper, we further illustrate the various mechanisms, already observed with CH<sub>2</sub>Cl<sub>2</sub>, by combining adsorption and calorimetric data obtained for CO<sub>2</sub>. We used two well-characterized active carbons CMS and U-03 with average pore-widths of 0.7 and 1.5 nm. The main characteristics are given in the *Table* and the micropore distribution of CMS is shown in *Fig. 1*.

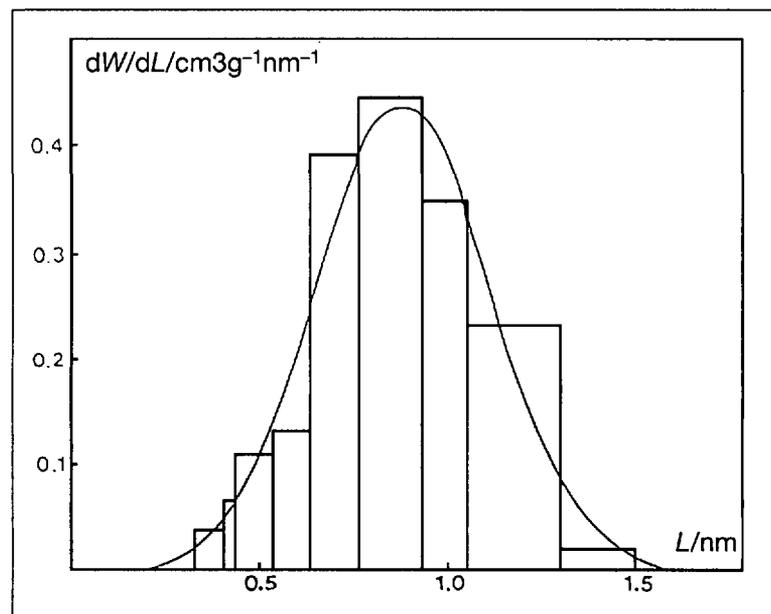


Fig. 1. The distribution of microporosity in carbon CMS.  $L$  denotes the width, as seen by various molecular probes [2].

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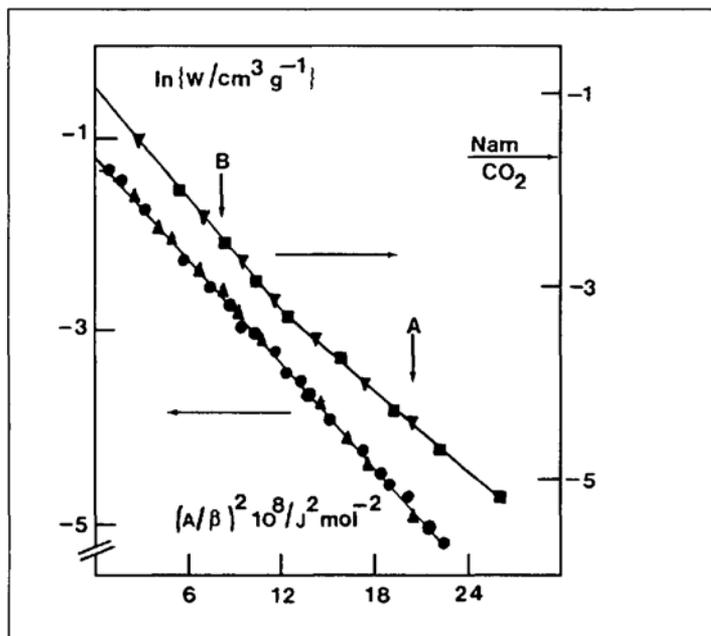


Fig. 2. The Dubinin-Radushkevich plots for the adsorption of  $\text{CH}_2\text{Cl}_2$  ( $\blacktriangle$ ) at 293 K,  $\text{CO}_2$  ( $\bullet$ ) at 248 K, 296 K, 310 K on carbon CMS (left-hand side of the plot), and for  $\text{CO}_2$  at 246 K ( $\blacktriangledown$ ) and 293 K ( $\blacksquare$ ) on carbon U-03 (right-hand side of the plot), versus the quantity  $(A/\beta)^2$ . Nam corresponds to the coating of the micropore walls of carbon U-03 by  $\text{CO}_2$ , extrapolated from section A. Not all experimental points are shown.

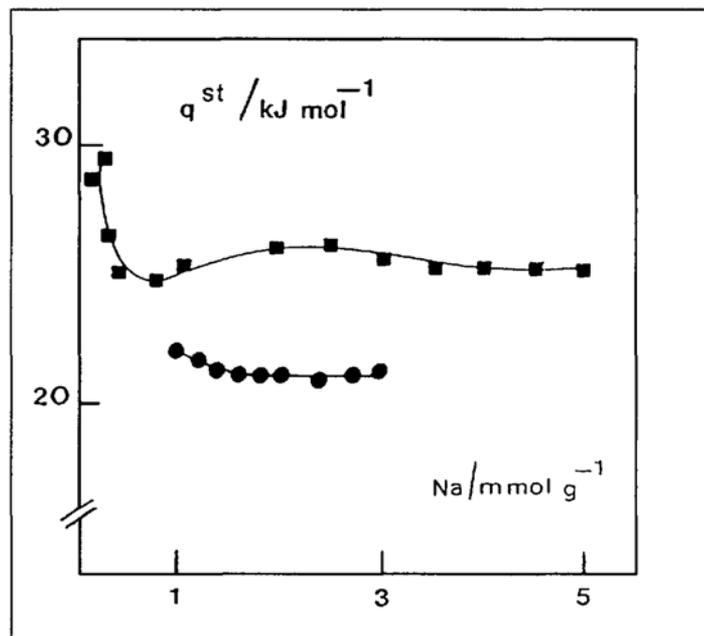


Fig. 3. The isosteric heat of adsorption of  $\text{CO}_2$  on samples CMS ( $\blacksquare$ ) and U-03 ( $\bullet$ ), as a function of the amount adsorbed

## 2. Results and Discussion

Prior to adsorption and calorimetric experiments, the solids were prepared following standard procedures [6]. The equipment and the techniques used at Neuchâtel (adsorption at low pressures and gas-solid adsorption calorimetry), and in Moscow (adsorption at pressures up to 100 atm) is described elsewhere [1][5][7].

Fig. 2. shows the logarithmic-plots of Eqn. 1 with  $n = 2$  (Dubinin-Radushkevich plot) for the adsorption on the two solids. In the case of carbon CMS, the data for  $\text{CO}_2$  at 273 K, 296 K, and 310 K and for  $4 \cdot 10^{-3} < p < 60$  atm an unusually wide range of pressures, falls on the same and unique line as  $\text{CH}_2\text{Cl}_2$  at 293 K and leads to a micropore volume  $W_0 = 0.25 \text{ cm}^3/\text{g}$ . For carbon U-03, on the other hand, the graph for  $\text{CO}_2$  at 248 K ( $9 \cdot 10^{-1} < p < 760$  mmHg) shows a clear break near  $(A/\beta)^2 = 10 \cdot 10^8 \text{ J}^2 \cdot \text{mol}^{-2}$  ( $p = 15$  Torr). Moreover, the data for 293 K covers only section A of the plot, the usual pressure range  $p < 760$  torr corresponding to smaller values of  $p/p_0$  and consequently to larger values of  $(A/\beta)^2$ . The latter extrapolates to  $3.53 \text{ mmol/g}$  or  $595 \text{ m}^2/\text{g}$  which is close to the surface area of the micropores obtained from other techniques ( $560 \pm 50 \text{ m}^2/\text{g}$ ) [4]. Section B, on the other hand, corresponds to the actual filling of the pores and it extrapolates to  $W_0 = 0.52 \text{ cm}^3/\text{g}$ , in agreement with other adsorptives. A similar pattern has been reported for other carbons [5].

The isosteric heat of adsorption of  $\text{CO}_2$

Table. The Main Characteristics of the Carbons [2][6]

Carbon	$W_0$ [ $\text{cm}^3/\text{g}$ ]	$E_0$ [kJ/mol]	$S_{mi}$ [ $\text{m}^2/\text{g}$ ]	$S_c$ [ $\text{m}^2/\text{g}$ ]	$L$ [nm]
CMS	0.25	26.2	608	28	0.75
U-03	0.52	17.2	570	60	1.8

on solid CMS, derived from the isotherms at 273, 296, and 310 K (Moscow), leads to  $27 \pm 2 \text{ kJ/mol}$  (Fig. 3). This corresponds to the filling of the relatively small micropores (0.6–0.9 nm). For carbon U-03, on the other hand, the isotherms at 248 and 293 K (Neuchâtel) lead to  $22 \pm 2 \text{ kJ/mol}$ , against  $20 \pm 2 \text{ kJ/mol}$  for the differential heat of adsorption measured calorimetrically at 293 K (gas-solid interface). The two are in good agreement and correspond to the coating of the micropore walls (section A in Fig. 2).

In the case of U-03, it is also possible to estimate the isosteric heat of adsorption for the subsequent filling of the micropores (section B in Fig. 2), on the basis of Dubinin's theory [8]. One obtains ca. 21 kJ/mol for  $W/W_0 = 0.5$ . This value is smaller than the filling of the micropores of solid CMS, but still higher than the coating of an open (nonporous) carbonaceous surface by  $\text{CO}_2$ , 18 kJ/mol [9].

The present investigation, based on  $\text{CO}_2$ , confirms the differences in the mechanisms for the adsorption of small molecules in small micropores (a one step filling) and in large micropores (two steps), as observed earlier with  $\text{CH}_2\text{Cl}_2$  [5][6].

The study also shows that care has to be taken, when  $\text{CO}_2$  adsorption is used near 273–293 K and at relatively low pressures, for strongly activated carbons. In this case, the limiting adsorption obtained from the logarithmic plot of Eqn. 1 may lead to the surface area of the micropore walls and not to their volume  $W_0$ .

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- [1] D.C. Bansal, J.B. Donnet, H.F. Stoeckli, 'Active Carbon', Marcel Dekker, New York, 1988.
- [2] H.F. Stoeckli, P. Rebstein, L. Ballerini, *Carbon* **1990**, 28, 907.
- [3] L. Ballerini, D. Huguenin, P. Rebstein, F. Stoeckli, *J. Chim. Phys.* **1990**, 87, 1709.
- [4] D. Huguenin, H.F. Stoeckli, *J. Chem. Soc., Faraday Trans.* **1993**, 89, in press.
- [5] F. Stoeckli, D. Huguenin, A. Greppi, *J. Chem. Soc., Faraday Trans.* **1993**, in press.
- [6] F. Stoeckli, D. Huguenin, P. Rebstein, *J. Chem. Soc., Faraday Trans.* **1991**, 87, 1233.
- [7] T.S. Jakubov, V.V. Serpinski, *Int. Rev. Phys. Chem.* **1993**, in press.
- [8] M.M. Dubinin, 'Progress in Surface and Membrane Science', Eds. D.A. Cadenehead, J.F. Danielli, and N.D. Rosenberg, Academic Press, London, 1975, Vol. 9.
- [9] R.J. Tyler, H.J. Wouterlood, *Carbon* **1971**, 9, 467.