

Reference isotherm for high pressure adsorption of CO₂ by carbons at 273 K

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Abstract

It is suggested that the adsorption of CO₂ on Vulcan 3G at 273 K and up to 3.2 MPa can be used as a reference isotherm for the characterization of porous and non-porous carbons. The results obtained with the proposed reference are in good agreement with those of the nitrogen (77 K) and benzene (293 K) comparison plots. The external surface areas have also been compared with those obtained from immersion calorimetry into C₆H₆ at 293 K. It also appears that at low relative pressures CO₂ adsorbed on Vulcan 3G follows the Dubinin–Radushkevich–Kaganer equation between 253 and 273 K.

Keywords: A. Activated carbon; Carbon black; D. Microporosity; Surface areas

1. Introduction

The determination of the micropore volume W_0 and the external (non-porous) surface area S_e of carbons rests either on the analysis of the adsorption isotherm within the framework of a theory, for example Dubinin's theory [1–3], or on the comparison of the experimental data with a reference isotherm [4]. The latter is determined under the same conditions on a non-porous material, usually a well characterized graphitized carbon black. This approach has the advantage that the external surface S_e corresponds to the linear section of the comparison plot, usually in the range of relative pressure $0.2-0.3 < p/p_s < 0.7-0.8$. The micropore volume is obtained by extrapolating this section, which avoids, in principle, measurements at a lowly relative pressure.

Nitrogen adsorbed at 77 K on graphitised carbon blacks has been a popular reference introduced by de Boer [5] and later developed by Sing in the form of his well-known α_s -plot [4–6]. It remains a classical approach, but presents problems related to work at low temperatures, in particular if the material is microporous (temperature gradients, activated diffusion into small micropores and difficulty to

conduct calorimetric measurements). As a consequence, other adsorbates have been used as internal references [3,7–9]. Recently, Carrott et al. [10,11] have suggested the use of benzene, dichloromethane and methanol at 298 K. This approach compares favourably with Sing's α_s -plot, as discussed in detail by these authors.

In the past, carbonaceous materials have also been characterized by CO₂ adsorption between 273 and 300 K, but in view of its relatively high saturation pressure (typically 3.5 MPa at 273 K), adsorption at pressures below atmospheric (0.1 MPa) corresponds only to a small degree of surface coverage or micropore filling. Consequently, the analysis of the adsorption data obtained at different temperatures may be misleading, in particular if the Dubinin–Radushkevich (DR) plot is not linear. This apparent contradiction can be cleared by examining the adsorption of CO₂ over a wide range of pressures and temperatures [12–18]. For example, Guillot et al. [18] have shown that for a variety of microporous carbons CO₂ adsorption leads to well-defined characteristic curves in the range of 260–350 K, in agreement with Dubinin's theory.

It appears, therefore, that the adsorption of CO₂ at high pressures may be an interesting technique for the characterization of carbonaceous adsorbents, as a complement to the techniques based on N₂ and C₆H₆, at relatively low pressures. This adsorptive also has the advantage that it is relatively simple and that it can be used in connection with

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molecular simulations [19–22]. A further advantage over nitrogen at 77 K is the fact that the differential heat of adsorption of CO₂ can be measured directly near room temperature, thus providing complementary information on the carbon under investigation [18]. The adsorption of CO₂ can also be correlated with the enthalpy of immersion of the carbon into CS₂ at 293 K, a liquid with molecular dimensions close to CO₂.

A systematic study of CO₂ adsorption between 273 and 298 K and up to the saturation pressure presents therefore a number of advantages. In the present study we provide reference data for the adsorption of this vapour by Vulcan 3G at 273 K. As shown below, the results obtained with this reference are in good agreement with the comparison plots based on Sing's α_s -plot and on benzene adsorbed by non-porous carbon blacks at 293 K. It also appears that in the low-pressure domain, the comparison plots for CO₂ reveal the same features as observed for nitrogen and discussed by Kaneko [23,24].

Finally, it should also be pointed out that in recent years the adsorption of CO₂ by active carbons under supercritical conditions has become an important tool in separation technology [25]. This justifies, in itself, a systematic study of CO₂ adsorption at high pressures.

2. Experimental

In the present study, CO₂ was adsorbed at 273 K on Vulcan 3G (Office of Reference Materials, Teddington, UK), in order to establish a reference at this temperature, but measurements were also carried out at 253 and 298 K. Similar measurements were performed on a variety of well characterized activated carbons [3] (CAF-B, CMS, U-103, AGB), on activated fiber KF-1500 [18] and on a microporous carbon black XC-72 [3,26,27]. For all these samples, N₂ (77 K) and C₆H₆ (293 K) isotherms were either available or determined specifically, in order to provide the corresponding comparison plots.

The high pressure measurements were carried out on samples of 0.5–0.9 g, in a device described earlier [18] and

upgraded to allow measurements up to 3.8 Mpa in the case of CO₂. Prior to measurements, the samples were outgassed at 473 K for 15 h under a residual vacuum of better than 10⁻³ Pa.

Nitrogen (77 K) and benzene (293 K) isotherms were also determined, in order to provide the corresponding comparison plots, using either carbon blacks Vulcan 3G or Hoechst as reference materials.

The samples were also characterized by immersion calorimetry at 293 K, as described in detail elsewhere [3,18]. This data provides information on the external surface area S_e , which can be calculated from the difference between the experimental and the calculated enthalpies [3].

The main structural characteristics of the carbons are given in Table 1.

3. Results and discussion

3.1. CO₂ adsorption on Vulcan 3G at 253, 273 K

The isotherms are shown in Fig. 1. For $T=273$ K, the BET analysis is not very reliable and leads to a statistical monolayer capacity $N_{am}(BET)=0.523$ mmol g⁻¹. Assuming a molecular surface area of 18.8×10^{-20} m², as suggested by calculations [4] based on the liquid density, one obtains a surface area of 59 m² g⁻¹, which is smaller than the value of 71 m² g⁻¹ given by nitrogen at 77 K.

The analysis of the low pressure region of the two isotherms confirms the existence of a range where the Dubinin–Radushkevich–Kaganer (DRK) equation [28–30] applies,

$$N_a = N_{am}(DRK) \exp[-(A/\beta E_o)^2] \quad \text{with } A = RT \ln(p_s/p) \quad (1)$$

For CO₂ at 273 K, the limiting amount $N_{am}=0.806$ mmol g⁻¹, which would correspond to a surface area of 95 m² g⁻¹. It is larger than the monolayer capacity suggested by the analysis of the BET range of the same isotherm. As

Table 1
Main characteristics of the microporous carbons

Carbon	Standard DR analysis					Comparison plots						Immersion C ₆ H ₆ (293 K)
	(C ₆ H ₆ and/or N ₂)		CO ₂ (273 K)			CO ₂ (273 K)		C ₆ H ₆ (293 K)		N ₂ (77 K)		
	W_o (cm ³ g ⁻¹)	E_o (kJ mol ⁻¹)	W_o (cm ³ g ⁻¹)	E (kJ mol ⁻¹)	$\beta(CO_2)$ (cm ³ g ⁻¹)	W_o (m ² g ⁻¹)	S_e (cm ³ g ⁻¹)	W_o (m ² g ⁻¹)	S_e (cm ³ g ⁻¹)	W_o (m ² g ⁻¹)	S_e (m ² g ⁻¹)	
CAF-B	0.266	28.3	0.274	10.1	0.36	0.27	44	0.30	32	0.28	97	70
CMS	0.252	28.0	0.280	9.3	0.33	0.29	2	0.26	5	0.28	3	–
U-103	0.330	20.7	0.360	7.7	0.37	0.38	19	0.35	27	0.38	70	40
AGB	0.455	14.3	0.450	5.8	0.40	0.45	135	0.45	170	0.42	252	298
KF-1500	0.580	19.1	0.620	6.4	0.33	0.60	19	0.60	28	0.63	22	14
XC-72	0.057	22.4	0.070	8.6	0.38	0.075	75	0.041	137	0.052	103	106

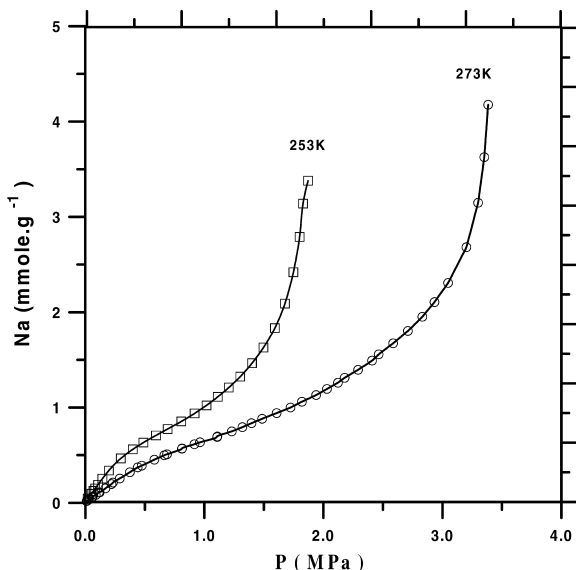


Fig. 1. CO₂ isotherms on carbon black Vulcan 3G at 253 (□) and 273 K (○).

pointed out by different authors [6,10,11,30], in the case of non-porous carbon blacks N_{am} (DRK) is frequently higher than N_{am} (BET), but no explanation can be offered.

The logarithmic plot of the DRK Eq. (1) is shown in Fig. 2. It appears that the data falls practically on a single line, with a slope corresponding to $\beta E_o = 5.4 \text{ kJ mol}^{-1}$. Taking benzene as a reference, i.e., $\beta(C_6H_6) = 1$, its characteristic energy E_o of 10.4 kJ mol^{-1} , determined from C₆H₆ adsorption at 293 K, leads to an affinity

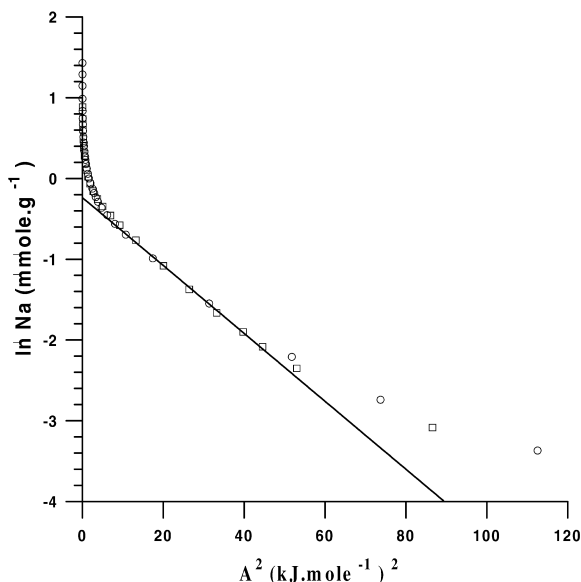


Fig. 2. DRK plot for the adsorption of CO₂ at 253 K (□) and 273 K (○) on Vulcan 3G.

coefficient $\beta(CO_2) = 0.46$. It is somewhat higher than the values of 0.35–0.41 found for microporous carbons [18,31,32] and confirmed in the present study (see below and Table 1).

The characteristic energy of 10.4 kJ mol^{-1} for Vulcan 3G is in good agreement with the values of 9.4–9.8 kJ mol^{-1} reported by Carrott et al. for benzene adsorbed at 298 K on carbon blacks Sterling FT, Elftex, N330 and N375 [10]. Recently, Hugi-Cleary and Stoekli [30] have confirmed that the adsorption of simple molecules on carbon black Hoechst reflects a true DRK behaviour, by considering the adsorption of N₂ at 77 K and of C₆H₆, CH₂Cl₂ and CCl₄ at different temperatures. The characteristic energy appears to be temperature invariant, with a value $E_o = 10.8 \text{ kJ mol}^{-1}$ for this carbon. The differences in E_o observed for various carbon blacks probably reflect differences in the heterogeneity of their respective surfaces. This is suggested by the fact that E_o appears in the analytical expression for the differential heat of adsorption associated with the DRK equation [Eq. (1)].

Modelling shows that for a fixed value of N_{am} (DRK), variations in E_o will modify the shape of the isotherm. This means, formally, that the shape of a comparison plot will depend on the values of E_o on the reference material and on the external surface S_e to be characterized. In the case of activated carbons, S_e will certainly be more heterogeneous than the surface of graphitised carbon blacks such as Vulcan 3G or Hoechst and their characteristic energy E_o may be in the range of 11–14 kJ mol^{-1} . As a consequence, the value of the external surface area given by the comparison plot may differ somewhat from its real value. However, it should be kept in mind that the accuracy of such plots is no better than 10–15% [3]. The linear section of the plot may also be reduced by capillary condensation occurring in the sample under investigation.

For pressures up to 3 MPa ($p/p_s = 0.86$), the adsorption isotherm of CO₂ on Vulcan 3G at 273 K, to be used as a reference, can be fitted to the following polynomial expression

$$N_a(\text{mmol g}^{-1}) = 0.96719 \times p - 0.43812 \times p^2 + 0.12241 \times p^3 \quad (2)$$

The pressures being given in MPa (correlation coefficient $R = 0.9997$).

Since adsorbed amounts are usually given in mol g^{-1} or mmol g^{-1} , it is more convenient to use these units, rather than to norm the reference isotherm, as it is the case in Sing's α_s -plot. Under these conditions, $S_e = \text{slope} \times 71 \text{ m}^2 \text{ g}^{-1}$ and the extrapolated micropore volume corresponds directly to a number of mmol g^{-1} .

3.2. CO₂ isotherms on microporous carbons

As shown in Fig. 3, for carbon AGB and reported earlier [18], the CO₂ isotherms lead to characteristic curves, thus

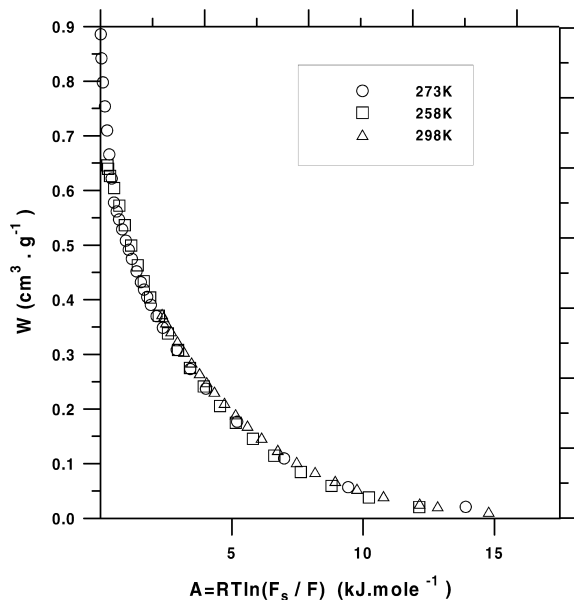


Fig. 3. Characteristic curve for the adsorption of CO_2 by carbon AGB at 258 (\square), 273 (\circ) and 298 K (\triangle).

confirming that their adsorption follows Dubinin's theory. The CO_2 isotherms can be analysed in terms of the Dubinin–Astakhov equation

$$N_a = N_{a0} \exp[-(A/\beta E_o)^n] \quad \text{with } A = RT \ln(p_s/p) \quad (3)$$

where N_{a0} represents the limiting amount adsorbed in the micropores. Their volume is $W_o = N_{a0} V_m$ and it is assumed, to a first approximation, that V_m corresponds to the volume in the condensed state (liquid or solid) at the corresponding temperature. In the case of CO_2 , the molar volume in the adsorbed state has been a matter of debate [13–15], but coherent values have been suggested [14–17]. These are in agreement with empirical relations proposed by Dubinin [1] and by Ozawa et al. [33]. In the present work, we used the latter equation, which leads to $V_m(\text{CO}_2; 273 \text{ K}) = 42.90 \text{ cm}^3 \text{ mol}^{-1}$. It is close to the other approximations, but smaller than the volume in the free liquid ($48.23 \text{ cm}^3 \text{ mol}^{-1}$).

At high pressures p_s/p is replaced by the ratio of the fugacities f and for temperatures above critical, p_s is replaced by $p_c(T/T_c)^2$, as suggested by Dubinin [1]. For the majority of carbons of low and moderate activation, exponent $n=2$, which corresponds to the Dubinin–Radushkevich (DR) equation. As discussed in detail elsewhere [3], Eq. (3) leads to an equation for the enthalpy of immersion of the carbon into the corresponding liquid,

$$\Delta_i H (\text{J g}^{-1}) = -\beta E_o W_o (1 + \alpha T) / 2V_m + h_1 S_e \quad (4)$$

where α is the thermal expansion coefficient of the liquid and $h_1 S_e$ represents the wetting of the external surface area

S_e of the solid. The last term is relatively small, but in favourable cases the difference between the experimental and the calculated enthalpies leads to a good estimate of S_e . (For C_6H_6 at 293 K, $h_1 = -0.114 \text{ J m}^{-2}$). The corresponding values are given in Table 1, to be compared with those resulting from the comparison plots.

The analysis of the CO_2 adsorption data with the DR equation leads to the micropore volumes, W_o , and the characteristic energies $E(\text{CO}_2)$ of the carbons given in Table 1. The comparison of $E(\text{CO}_2)$ with E_o obtained from C_6H_6 , adsorbed mainly at 293 K, leads to the corresponding values of $\beta(\text{CO}_2)$. Their average is 0.36, which is very close to the standard value of 0.35 reported earlier [1,14,15,18,32].

3.3. Comparison plots

Figs. 4–6 show, as typical examples; the comparison plots for the adsorption of CO_2 at 273 K, C_6H_6 at 293 K and N_2 at (77 K) on carbons CAF-B, AGB and KF-1500, taking the isotherm on Vulcan 3G as the reference, except for benzene, where Hoechst was used (the latter is very similar to Vulcan 3G [30]). The linear sections and their extrapolations lead to the external surface areas S_e and the micropore volumes W_o given in Table 1. However; it must be pointed out that the selection of the points used in the plots may have an influence on the outcome. In general, one observes a compensating effect between the slope and the intercept, meaning that a decrease in W_o leads to an increase in S_e .

The data given in Table 1 compares the micropore volumes and the external surface areas obtained either

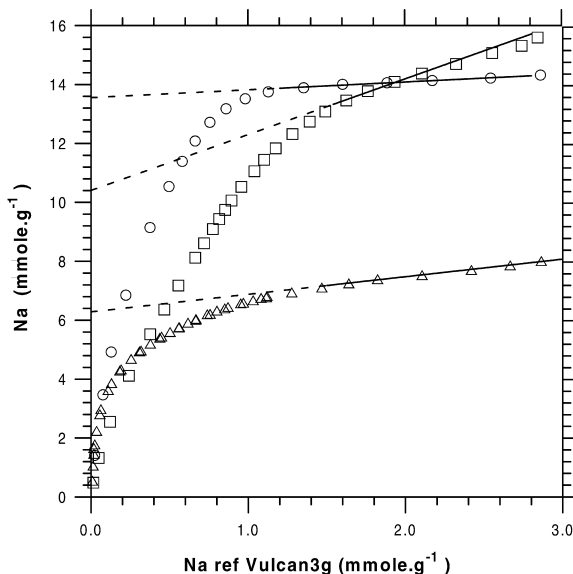


Fig. 4. Comparison plots for CO_2 at 273 K on carbons CAF-B (\triangle), AGB (\square) and KF1500 (\circ).

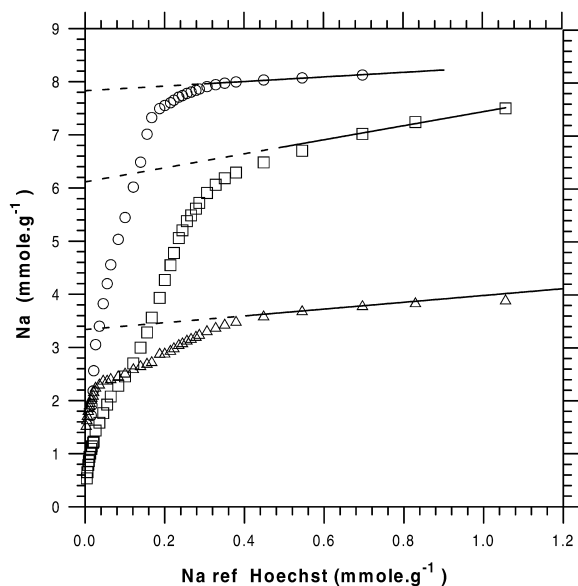


Fig. 5. Comparison plots for C_6H_6 at 293 K on carbons CAF-B (Δ), AGB (\square) and KF1500 (\circ).

from the DR equation or the comparison plots of the three vapours, namely N_2 (77 K), C_6H_6 (293 K) and CO_2 (273 K). It appears that the DRK analysis leads to compatible results as far as W_0 is concerned and from the comparison of the characteristic energies $E(CO_2)$ with $E_o = E(C_6H_6)$ one obtains a good average for $\beta(CO_2)$. In the case of the comparison plots, the micropore volumes are in good agreement, but the external surface areas show some scatter. For comparison, the values derived from immer-

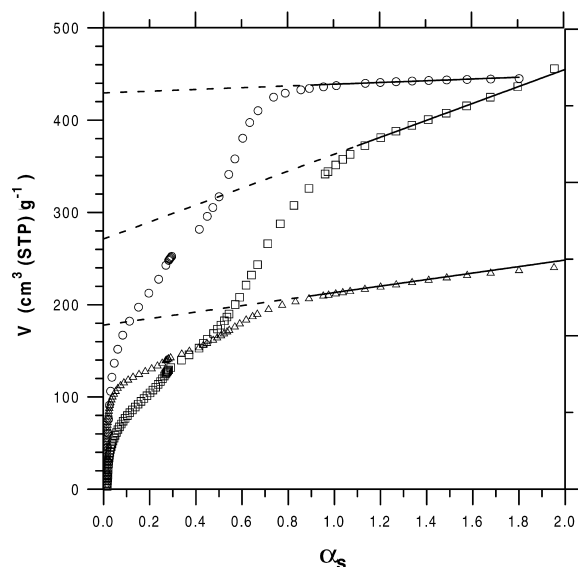


Fig. 6. Comparison plots for N_2 at 77 K (α_s -plot) on carbons CAF-B (Δ), AGB (\square) and KF1500 (\circ).

sion calorimetry, using Eq. (4), are also given. As discussed elsewhere [3], a reliable estimate of S_e requires several independent determinations and the resulting average may still have an uncertainty of 15–20%. In the case of samples U-103 and XC-72, earlier determination led to 60 and $107 \text{ m}^2 \text{ g}^{-1}$, against 40 and $105 \text{ m}^2 \text{ g}^{-1}$ in the present study.

The use of the CO_2 reference isotherm at 273 K, given by Eq. (2), seems justified with respect to Sing's α_s -plot or the adsorptives recently proposed by Carrott et al. [10,11]. CO_2 adsorption at 273 K also presents the advantage that the isotherm can be scanned accurately up to the saturation pressure, which is not the case for methane. (This adsorptive has a critical temperature of 195 K and near room temperature even high pressures cover only part of the isotherm). With modern equipment, it is also possible to determine the differential heat of adsorption of CO_2 , which provides further information on the carbon. In this context, it is worthwhile mentioning that the adsorption of CO_2 by carbons is probably not specific, as suspected in the past. As indicated recently by López-Ramón et al. [34], it appears that the CO_2 isotherm on typical active carbons is not affected by the change in oxygen content from 1 to 7 mmol g^{-1} , following the oxidation with $(NH_4)_2S_2O_8$. (This treatment introduces oxygen-containing complexes, without modifying the structure of the carbon). The same is true for the adsorption of benzene, but not for methanol, which depends on the amount of oxygen. This effect must still be explored further by considering the adsorption of CO_2 at higher pressures, but it is unlikely that new interactions will result from pressure alone.

Finally, the CO_2 isotherm at 273 K can be analysed in terms of model isotherms derived from computer simulations [19–22]. This approach provides a good estimate of the micropore distributions and results will be published later. The procedure requires the knowledge of the external surface area S_e , provided by the comparison plot for 273 K. Adsorption in the micropores alone is obtained by subtracting, from the experimental isotherm, the reference isotherm (2) multiplied by the ratio $(S_e/71 \text{ m}^2 \text{ g}^{-1})$. This shows that a maximum of information can be gained from adsorption of CO_2 at 273 K and the use of the reference isotherm (2).

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