

On the use of standard DRK isotherms in Dubinin's t/F method

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Abstract

It is shown that the adsorption of benzene, carbon tetrachloride, dichloromethane and nitrogen by a typical non-porous carbon black follows the Dubinin–Radushkevich–Kaganer equation. The requirement for temperature invariance is fulfilled, with an average characteristic energy $E_o = 10.8 \text{ kJ mol}^{-1}$. This expression is compared with the standard isotherms for benzene and carbon tetrachloride at 293 K proposed by Dubinin and used as a reference in the so-called t/F method, which leads to the non-porous surface area of active carbons. It appears that Dubinin's isotherm contains inconsistencies, which are compensated for internally. Alternative DRK expressions, applicable to different vapours, are therefore proposed. The present study also shows the limits of Dubinin's method with respect to comparison plots at higher relative pressures.

Keywords: A. Activated carbon; C. Adsorption; D. Microporosity, Surface area

1. Introduction

Active carbons are characterised by their micropore volume and by an external surface area S_e , which can be as high as 200–300 m^2/g , depending on the precursor and the type of activation. This area can be assessed by a variety of techniques such as comparison plots [1–8], the pre-adsorption of n -nonane followed by nitrogen adsorption at 77 K [1,3,8,9], the decomposition of the experimental isotherm [3,9–11], and immersion calorimetry [8].

The comparison of these techniques leads to a relatively good assessment of S_e , often within 10 to 15% [3,8]. An interesting approach is the comparison of the adsorption isotherm with a reference isotherm, for example Sing's α_s -plot [1,5,6], or Dubinin's t/F method [4–7]. For $p/p_s > 0.05$, the micropores are practically filled and adsorption occurs essentially on the external (non-microporous) surface. Under these circumstances, the adsorption mechanism is the same on the active carbon as on the non-porous reference and the external surface S_e is obtained from the linear section of the plot.

In the method proposed by Dubinin, one considers a reference isotherm for benzene at 293 K, given by

$$\gamma \text{ (mmol m}^{-2}\text{)} = 9.16 \times 10^{-3} \exp[-(A/6.35 \text{ kJ mol}^{-1})] \quad (1)$$

and where $A = RT \ln(p_s/p)$. This relation is purely empirical.

In the case of adsorption by active carbons, the experimental isotherm is the sum of two contributions, the classical Dubinin–Radushkevich (DR) or Dubinin–Astakhov (DA) equations [4,8] and a contribution from the external surface area S_e . For benzene at 293 K, one may write

$$N_a \text{ (mmol g}^{-1}\text{)} = N_{ao} \exp[-(A/E_o)^2] + S_e \gamma. \quad (2)$$

As described by Dubinin and Kadlec [2,4], S_e is obtained from the linear section of the plot of N_a/F vs. γ/F , where $F = \exp[-(A/E_o)^2]$. The characteristic energy E_o itself is obtained from the low-pressure region of the logarithmic plot of Eq. (2), where γ is negligible. Dubinin's isotherm (1) applies to low relative pressures (typically $0.001 < p/p_s < 0.1$). It follows that for a number of active carbons the process of micropore filling may still contribute significantly to the overall isotherm and lead to an inaccurate comparison plot.

In spite of this shortcoming, relatively good results have been obtained with the method of Dubinin and Kadlec, in

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parallel with other techniques [3,8], but it appears that Eq. (1) still contains inconsistencies. As shown below, it can be replaced by a Dubinin–Radushkevich–Kaganer (DRK) equation [1,12] since, as pointed out recently [13,14], the adsorption of a variety of vapours by carbon blacks seem to follow this equation. Moreover, it appears that the requirement for temperature invariance of E_o , implied by Dubinin’s theory, is fulfilled.

The modified version of Eq. (1), proposed here, has the advantage that it lifts inconsistencies and that it correlates adsorption in micropores and on the external surfaces within the framework of Dubinin’s theory.

Gravimetric adsorption measurements were carried out following standard techniques described in detail elsewhere [8].

2. Results and discussion

Inspection of Eq. (1) shows that the proposed monolayer density of benzene on carbon blacks, 9.16×10^{-3} mmol m^{-2} , corresponds to a molecular surface area of 18×10^{-20} m^2 , instead of the classical value of 42×10^{-20} m^2 obtained from adsorption by graphitized carbon blacks in the BET range and based on the standard A_m (N_2 ; 77 K) = 16.2×10^{-20} m^2 [1,14]. At first, this difference may be ascribed to the packing of benzene at low pressures, since the molecule may assume different positions. However, at a later stage Deryagev et al. [7] proposed an equation similar to Eq. (1), to describe the adsorption of CCl_4 on carbon blacks at 293 K,

$$\gamma \text{ (mmol/m}^2\text{)} = 8.40 \times 10^{-3} \exp[-(A/\beta \times 6.35 \text{ kJ mol}^{-1})]. \quad (3)$$

β is the affinity coefficient of carbon tetrachloride, as used in Dubinin’s theory for the volume filling of micropores. In the case of Eq. (3), $\beta(CCl_4) = 1.15$. The surface density of 8.40×10^{-3} mmol m^{-2} corresponds to a molecular surface area of 20×10^{-20} m^2 , which is much smaller than the value of 37×10^{-20} m^2 obtained for adsorption by carbon blacks in the BET range [15]. The latter is also in agreement with the value calculated [1] from the liquid density.

This difference is considerable and, since CCl_4 is a spherical molecule, the discrepancy cannot be explained in

terms of packing or molecular orientation at low pressures. This suggests that the success of Eqs. (1) and (3) probably rests on an internal compensation effect. It was therefore decided to examine closely the adsorption of benzene, dichloromethane and carbon tetrachloride on a typical non-porous carbon black (Hoechst, $S_{BET} = 54$ m^2/g based on the adsorption of C_6H_6 at 293 K). The low-pressure adsorption of nitrogen itself was also re-examined.

Following recent studies on adsorption by α - MnO_2 and preliminary work on carbon blacks [13,14], the adsorption data were examined within the framework of the DRK Eq. (4) for relative pressures $p/p_s < 0.05$ – 0.1 . On the other hand, the BET method was applied to the adsorption data for $0.05 < p/p_s < 0.30$ – 0.35 .

In the modern formulation of Dubinin’s theory [4,8], the DRK equation takes the form

$$N_a = N_{am}(\text{DRK}) \exp[-(A/\beta E_o)^2] \quad (4)$$

where $N_{am}(\text{DRK})$ represents the limiting amount adsorbed in the monolayer. Obviously Eq. (4) does not include multilayer adsorption, as opposed to the BET model. $N_{am}(\text{DRK})$ is therefore an extrapolated value.

All systems revealed a linear section in the plot of $\ln(N_a)$ vs. A^2 , before multilayer adsorption set in. These sections lead to the monolayer capacities $N_{am}(\text{DRK})$ given in Table 1. The table also gives the values of the equivalent BET monolayers $N_{am}(\text{BET})$ obtained from the same isotherms, but at higher pressures.

As illustrated by Fig. 1, in the case of benzene adsorbed at 282, 293, 311 and 323 K the plot of $\ln(N_a/N_{am}(\text{DRK}))$ vs. A^2 can be fitted to a single line in the range $5 < A < 25$ kJ mol^{-1} (for $T = 293$ K, this corresponds to the domain $10^{-4} < p/p_s < 0.05$). The principle of temperature-invariance is therefore fulfilled by benzene over a temperature range of at least 40 K, which indicates a true DRK behaviour for this adsorptive. Curve fitting leads to an average characteristic energy E_o of 10.8 kJ mol^{-1} . It is close to the value of 11.2 kJ mol^{-1} obtained for benzene adsorbed by another carbon black, N-230, examined in our laboratory. This suggests that for this type of surface the limiting value of E_o be around 11 kJ mol^{-1} .

For benzene at 293 K, the limiting amount $N_{am}(\text{DRK})$ is 0.25 mmol g^{-1} , against 0.21 mmol g^{-1} from the BET range of the same isotherm. These values are relatively close, as they lead to specific surface areas of 65 and 54 $m^2 g^{-1}$, assuming a molecular surface area A_m of $43 \times$

Table 1
Monolayer capacities obtained from the DRK and BET ranges for adsorption on carbon black Hoechst. See also Fig. 1

Vapour	C_6H_6				CCl_4		CH_2Cl_2	N_2
	282 K	293 K	311 K	323 K	294 K	305 K	293 K	77 K
N_{am} (DRK) mmol g^{-1}	0.26	0.25	0.27	0.27	0.24	0.19	0.30	0.73
N_{am} (BET) mmol g^{-1}	0.22	0.21	0.22	0.23	0.19	0.18	0.30	0.80

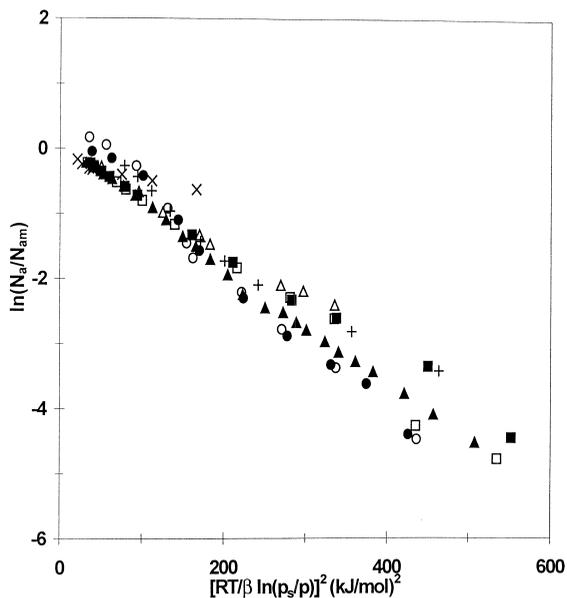


Fig. 1. Logarithmic DRK plot for the adsorption of different vapours on carbon black Hoechst: C_6H_6 at 282 K (Δ), 293 K (\blacktriangle), 311 K (\square) and 323 K (\blacksquare); CCl_4 at 294 K (\bullet) and 305 K (\circ); CH_2Cl_2 at 293 K ($+$) and N_2 at 77 K (\times).

10^{-20} m^2 for benzene. With respect to the surface area of $54 \text{ m}^2 \text{ g}^{-1}$ based on C_6H_6 , the surface density of C_6H_6 in the DRK range is $0.25/54 = 4.60 \times 10^{-3} \text{ mmol m}^{-2}$ which is closer to the theoretical value of $3.86 \times 10^{-3} \text{ mmol m}^{-2}$,

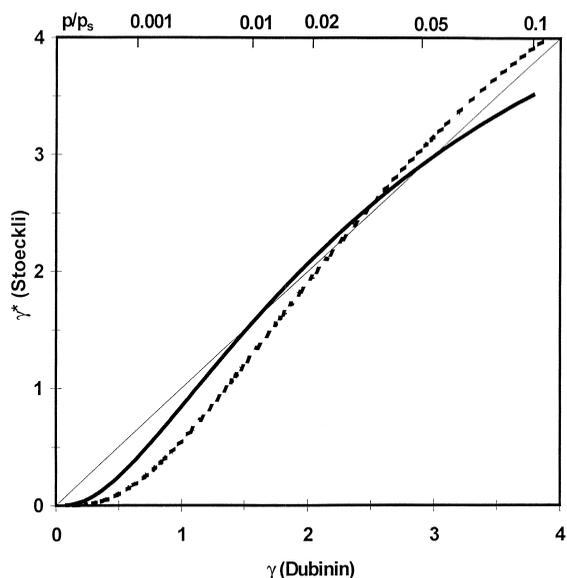


Fig. 2. Comparison of the standard isotherms γ^* and γ (Dubinin) for C_6H_6 (—) and CCl_4 (- -) at 293 K, given by Eqs. (5), (1) and (6), (3). The p/p_s scale shown corresponds to benzene.

than to the value of $9.16 \times 10^{-3} \text{ mmol m}^{-2}$ used in Dubinin's standard isotherm (1).

As shown in Fig. 1 and in Table 1, a similar pattern is observed for the adsorption of dichloromethane at 293 K and of carbon tetrachloride at 293 and 305 K. Both vapours follow the DRK equation and a good overlap with the benzene data is obtained with the affinity coefficients $\beta(CH_2Cl_2) = 0.66$ and $\beta(CCl_4) = 0.95$. The latter is somewhat smaller than the usual value of 1.05 reported in Wood's survey [16].

In the case of dichloromethane at 293 K, the limiting adsorption capacity $N_{am}(\text{DRK})$ is 0.30 mmol g^{-1} , the same as that for the BET range of the same isotherm, which suggests surface areas of 61 and $49 \text{ m}^2 \text{ g}^{-1}$ assuming $A_m(CH_2Cl_2) = 29 \times 10^{-20} \text{ m}^2$, as calculated [1] from the liquid state. For carbon tetrachloride at 293 K, $N_{am}(\text{DRK})$ and $N_{am}(\text{BET})$ are, respectively, 0.29 and 0.20 mmol g^{-1} , which corresponds to 65 and $45 \text{ m}^2 \text{ g}^{-1}$, assuming $A_m(CCl_4) = 37 \times 10^{-20} \text{ m}^2$ [1,15]. With respect to the surface area of $54 \text{ m}^2 \text{ g}^{-1}$ based on benzene, the surface density of CCl_4 in the DRK range is $0.29/54 = 4.4 \times 10^{-3} \text{ mmol m}^{-2}$ as opposed to $8.40 \times 10^{-3} \text{ mmol m}^{-2}$ used by Dubinin in Eq. (3). The latter value is much too high and unrealistic, owing to the fact that the liquid state already suggests a density of $4.5 \times 10^{-3} \text{ mmol m}^{-2}$ for this spherical molecule.

For nitrogen at 77 K, one observes a linear DRK range, but it is limited by the relatively small value of T . The classical value $\beta(N_2) = 0.33$ yields a characteristic energy E_o of 14.1 kJ mol^{-1} (a similar analysis of the standard nitrogen isotherm proposed by Carrott et al. [6], leads to $E_o = 11.8 \text{ kJ mol}^{-1}$ in the range $0.005 < p/p_s < 0.1$).

As shown in Table 1, the monolayer capacities $N_{am}(\text{DRK})$ are systematically higher than $N_{am}(\text{BET})$ by $\sim 20\%$, N_2 excepted. It is interesting to note that in the case of N_2 at 77 K and CH_2Cl_2 at 278 K, 293 K and 314 K adsorbed on non-porous $\alpha\text{-MnO}_2$ [13], the values of $N_{am}(\text{DRK})$ are also higher than $N_{am}(\text{BET})$. No explanation can be offered at this stage. However, it appears that the surface densities (mmol m^{-2}) used by Dubinin in Eqs. (1) and (3) are definitely too high and even unrealistic. This is true in particular for spherical or nearly spherical molecules such as carbon tetrachloride and dichloromethane, where no increase of the surface density can be postulated on the basis of a change in molecular orientation, as opposed to benzene.

In view of the good fits claimed for Eqs. (1) and (3), and the satisfactory values of S_e obtained with Eq. (3), it is likely that the unrealistic surface densities are compensated by the second part of the equation. It contains A and the characteristic energy of 6.35 kJ mol^{-1} raised to the power $n = 1$, as opposed to the DRK Eq. (4), where $E_o = 10.8 \text{ kJ mol}^{-1}$ and $n = 2$. This compensating effect is confirmed by the comparison of the DRK Eqs. (5) and (6) for C_6H_6 and CCl_4 at 293 K, respectively

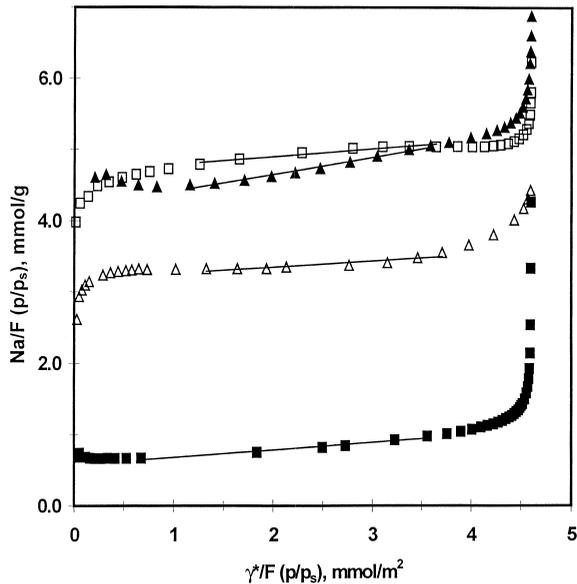


Fig. 3. Plots of $N_a/F(p/p_s)$ vs. $\gamma^*/F(p/p_s)$, where $F = \exp[-(A/E_o)^2]$, of the benzene isotherms at 293 K for carbons U-02 (\square), CECA (\blacktriangle), CAF-41B (\triangle) and XC-72 (\blacksquare). The slopes of the linear sections lead to S_e , given in Table 2.

$$\gamma^*(C_6H_6) = 4.6 \times 10^{-3} (\text{mmol m}^{-2}) \exp[-(A/10.8)^2] \quad (5)$$

and

$$\begin{aligned} \gamma^*(CCl_4) &= 5.4 \\ &\times 10^{-3} (\text{mmol m}^{-2}) \exp[-(A/\beta \times 10.8)^2] \\ (\beta &= 0.95) \end{aligned} \quad (6)$$

with Eqs. (1) and (3), proposed by Dubinin.

As shown in Fig. 2, there exists a relatively good correlation between the two sets of equations over the DRK range of $0.005 < p/p_s < 0.05-0.1$, at 293 K. This suggests that the two sets of equations can be used with a similar degree of confidence for the determination of external surface areas. This is illustrated in Fig. 3, for a series of well characterised microporous carbons (XC-72, U-02, CECA, and CAF 41-B) [8,17–19]. The external surface areas were determined from the benzene isotherms at 293 K, from the plot of $N_a/F(p/p_s)$ vs. $\gamma^*/F(p/p_s)$, where $F = \exp[-(A/E_o)^2]$.

As shown in Table 2, and reported earlier [2,8], the

external surface areas S_e are often in good agreement with the average values obtained for these carbons from a variety of techniques. However, as illustrated by carbon CAF 41-B, differences may occur. This is due to the fact that in the range of validity of the DRK equations γ^* or γ (Dubinin), the process of micropore filling may not be complete for carbons with wide pores. This is an intrinsic shortcoming of Dubinin's method, as opposed to traditional comparison plots, where S_e is derived from adsorption at higher relative pressures.

The results shown in Table 2 are close to those obtained with Dubinin's technique, but from a formal point of view, it would be better to replace Eqs. (1) and (3) by the DRK standard isotherms (5) and (6). This approach also has several advantages: firstly, as illustrated by Fig. 1, the requirement for temperature invariance is fulfilled. This means that reference isotherms (5) and (6) can be combined with Eq. (2) to assess the external surface areas S_e of a carbon at temperatures other than 293 K. By using the appropriate surface densities (mmol m^{-2}) and affinity coefficients β , the procedure can be adapted to other vapours. From a theoretical point of view, the present approach is also an interesting extension of Dubinin's theory to open surfaces.

Secondly, it appears that the characteristic energies $E_o = 10.8$ and 11.2 kJ mol^{-1} obtained for the adsorption of benzene on carbons Hoechst and N-235 are close to the limiting value of 11.4 kJ mol^{-1} found in the empirical correlation between the average width L of slit-shaped micropores and the characteristic energy of the corresponding Dubinin–Astakhov equation [3,17],

$$L(\text{nm}) = 10.8/(E_o - 11.4). \quad (7)$$

A characteristic energy E_o of $\sim 10-11 \text{ kJ mol}^{-1}$ represents therefore the limiting value when micropores become very large. This observation suggests again that the DRK description for adsorption by open carbonaceous surfaces is a logical extension of Dubinin's theory.

Acknowledgements

The authors wish to thank the Swiss National Science Foundation for the award of a Marie Heim-Vögtlin grant (1995–1997) to D.H-C., which supported part of the present study.

Table 2

External surface areas S_e obtained from the benzene isotherms at 293 K (see Fig. 3) and earlier determinations by different techniques, where the uncertainties are 10–15%

Carbon	U-02	CECA	CAF-41B	XC-72
S_e (m^2/g) this work	110	240	88	106
S_e (m^2/g) earlier determinations	105	220	107	107

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