

On the Physical Meaning of Parameters E_0 and β in *Dubinin's* Theory*

Fritz Stoeckli and Daniel Morel

Chemistry Department of the University, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Abstract

A comparative study of limiting adsorption energies in microporous carbons and on graphitized carbon blacks shows that their difference is proportional to the quantity βE_0 which appears in *Dubinin's* theory. It follows that the characteristic energy E_0 must be related to an average pore size, as found empirically. The affinity coefficient β , on the other hand, can be regarded as a shifting factor, directly related to the ratio of gas-solid adsorption potentials.

Physical adsorption of vapours and gases by microporous solids such as active carbons and zeolites is described by *Dubinin's* theory [1]. Its fundamental equation is the relation proposed by *Dubinin* and *Astakhov* [1, 2]

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

where $A = RT \ln(p_s/p)$; W_0 represents the total volume of the micropores and W is the volume filled at relative pressure p/p_s and at temperature T ; the so-called similarity or affinity coefficient β is a shifting factor which depends on the adsorbate, the reference vapour being benzene by convention. With a very good approximation, β can be calculated from the ratio of the parachores [1] of the adsorbates. The quantity E_0 , on the other hand, depends only on the adsorbent and it reflects the influence of the micropore system. For active carbons, it is found that exponent n varies from 1 to $n = 3$, depending on the degree of homogeneity of the micropores [3]. The value $n = 3$ seems to apply exclusively to homogeneous systems of fine micropores [1, 3, 4].

The case $n = 2$ corresponds to the equation of *Dubinin* and *Radushkevich* [1]

$$W = W_0 \exp\{- B(T/\beta)^2 \log^2(p_s/p)\} \quad (2)$$

which has been used extensively in the case of active carbons.

Structural constant B and the quantity E_0 are related through

$$E_0 [\text{kJ/mole}] = 0.01915/\sqrt{B}$$

It has been recognized at an early stage that B , and

therefore E_0 , are related to an average pore dimension since B increases with the degree of activation [5].

As shown by *Stoeckli* [6], and independently by *Dubinin* [7], these quantities can be related empirically to the average gyration radius R_i of the micropores. This is expressed conveniently by

$$R_i = (14.8 \pm 0.6)/E_0 [\text{nm kJ/mole}] \quad (3)$$

From eqn (3) it is possible to derive model-based relations between pore widths and the characteristic energy E_0 [8].

It has also been found experimentally that the following alternative empirical relation holds for a number of active carbons,

$$x = 13.0 [\text{nm kJ/mole}]/E_0 \quad (4)$$

x being a characteristic dimension of the micropore [3, 8].

Another useful information, as to the physical meaning of the quantity βE_0 in eqn (1), is illustrated by fig. 1.

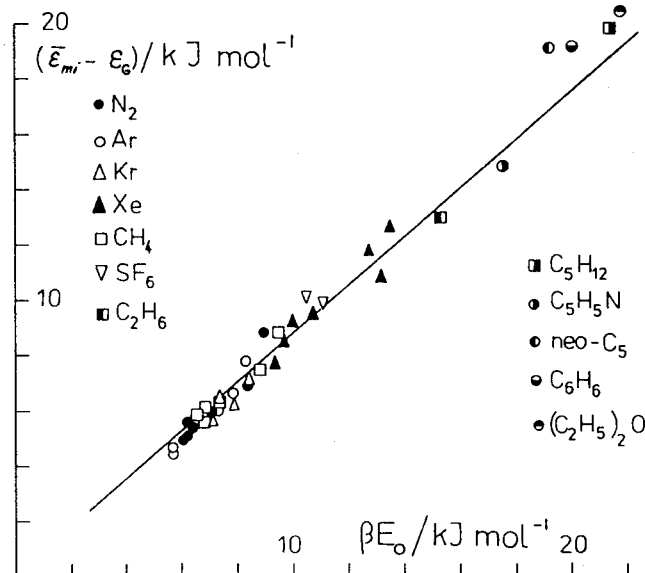


Fig. 1: Relation between the increase in adsorption energy in micropores with respect to graphitized carbon black, and the characteristic energy βE_0 of the *Dubinin-Astakhov* equation (1)

Table 1: Values of affinity coefficients β [1, 11, 21] and of the adsorption potential minima ϵ_G [13–15] used in the present study.

molecule	N ₂	Ar	Kr	Xe	CH ₄	SF ₆	C ₂ H ₆	C ₅ H ₁₂	C ₆ H ₆	pyridine	neopentane	ether
β	0.34	0.31	0.37	0.50	0.35	0.56	0.57	1.08	1.00	0.92	0.96	1.09
ϵ_G (kJ/mole)	9.02	8.98	11.65	15.93	12.36	20.3	19.3	42.9	43.0	42.6	29.2	36.0

It shows the existence of the linear relationship

$$(\bar{\epsilon}_{mi} - \epsilon_G) = (0.85 \pm 0.07) \beta E_0 \quad (5)$$

where $\bar{\epsilon}_{mi}$ and ϵ_G are the values of the adsorption potentials [9] of a given molecule in the micropore system [10, 11, 12] and on the surface of a well graphitized carbon black [13, 14, 15]. In the case of a distribution $\chi(\epsilon_{mi})$ of the adsorption potentials in the micropores, the quantity $\bar{\epsilon}_{mi}$ represents a weighted average of ϵ_{mi} [9].

The values of $\bar{\epsilon}_{mi}$ and ϵ_G are conveniently obtained from gas-solid chromatography at high relative temperatures [15, 16], where adsorption is mobile. The values of ϵ_G found in the literature [13–15] are usually very close, but a choice has to be made in order to obtain a coherent comparison. The values selected for the present study are given in table 1. Our results for $\bar{\epsilon}_{mi}$ correspond to 12 simple gases including benzene [10–12], adsorbed on a total of 8 different and well characterized active carbons [3, 11].

It appears that βE_0 represents an average excess of adsorption energy in the micropores, with respect to the open graphitic surface. The latter, as shown by theoretical models [17, 18], is the limit for large micropores (widths of 3–4 times the molecular diameter of the adsorbate). The models have also been applied to the ratio $\bar{\epsilon}_{mi}/\epsilon_G$, to establish that the average pore width or radius of typical active carbons is 0.6–0.8 nm [10, 17, 18]. Eqn (5) implies that βE_0 must be some inverse function of the average pore width or radii, in agreement with eqns (3) and (4). Further, as shown by *Kiselev*, ϵ_G [19] and ϵ_{mi} [20] are both proportional to the electronic polarizabilities α of the adsorbates. This quantity has also been used for the calculation of β [1, 21]. Eqn (5) suggests that β should be related directly to potentials ϵ_{mi} and ϵ_G , an assumption which is confirmed by the comparison of simultaneously available values of β [1, 11, 12] and of ϵ_G [13–15]. It is found that there exists a good overall proportionality between the two quantities; and β can therefore be identified, formally at least, with a ratio of adsorption potentials. A similar relationship had already been suggested by *Kadlec* [22].

It is hoped, that the information obtained in this study will provide the basis for a rational description of eqn (1), the fundamental relation of TVFM.

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