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Application of the Dubinin-Astakhov and n-Layers BET Equations to Adsorption of Nitrogen in Microporous Active Carbons

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Adsorption of nitrogen in a series of microporous active carbons was studied. The Dubinin-Astakhov and *n*-layers BET equations were used in a complementary manner for determining some adsorption characteristics of the carbons. Adsorption properties and the microporosity of the carbons were considered in relation to the equation constants and the characteristic parameters of the differential distribution of adsorption with the free energy of adsorption. In this distribution, the characteristic quantities of the free energy of adsorption, the mean and the mode, were determined from the differential distribution function derived from the Dubinin-Astakhov equation.

INTRODUCTION

The purpose of the present investigation was to obtain information on the microporosity and adsorption properties of active carbons by complementary use of the Dubinin-Astakhov and *n*-layers BET equations. An attempt was made to provide this information from the equation constants and the characteristic parameters of the differential distribution of adsorption with the free energy of adsorption. These parameters were determined from the differential distribution function derived from the Dubininin-Astakhov equation.

THEORETICAL PART

The Dubinin-Astakhov equation[1–3] has been found to represent gas adsorption data on microporous adsorbents.[4–8] The equation is usually expressed in the form

$$a = a_o \exp\left[-(A/E)^m\right] \tag{1}$$

In the equation, a is the amount of gas adsorbed at equilibrium pressure P, a_o is the micropore capacity, A is the differential molar work of adsorption, E and m are the equation constants. The differential molar work of adsorption equals, with a minus sign, variation in the differential free energy of adsorption, ΔG

$$A = -\Delta G = RT \ln (P_o/P) \tag{2}$$

where P_o is the saturation vapour of adsorbate at temperature T/K.

The Dubinin-Astakhov equation represents integral distribution of the amount of adsorption with differential molar work of adsorption. Thus, the differential distribution function can be obtained from the first derivative of the Dubinin-Astakhov equation

$$\frac{da}{dA} = - \frac{a_o\, m\, A^{m-1}}{E^m} \exp\left[- \left(\frac{A}{E} \right)^m \right] \tag{3}$$

The characteristic parameters of this distribution, the mean value of A and the mode, can be determined in the following manner. The mean value of differential molar work of adsorption, A_{mean}, can be obtained from the expression

$$A_{mean} = \frac{\int_0^{a_o} A\, da}{a_o} \tag{4}$$

The substitution of da from expression (3) in expression (4) gives

$$A_{mean} = \int_0^{\infty} \frac{m\, A^m}{E^m} \exp\left[- \left(\frac{A}{E} \right)^m \right] dA \tag{5}$$

hence

$$A_{mean} = E\, \Gamma \left(\frac{1}{m} + 1 \right) \tag{6}$$

where Γ is gamma function. The mode, A_{mode}, is determined from the second derivative of equation (1) (*i. e.* $d^2a/dA^2 = 0$) giving

$$A_{mode} = E \left(\frac{m-1}{m} \right)^{1/m} \tag{7}$$

Bearing in mind that $A = -\Delta G$, the characteristic quantities of the free energy of adsorption, the mean, $(\Delta G)_{mean}$ and the mode, $(\Delta G)_{mode}$, can be calculated from expressions (6) and (7), respectively.

The n-layer BET equation is given in the following form

$$a = \frac{a_m\, C\, X}{1 - X} \cdot \frac{1 - (n+1)\, X^n + n\, X^{n+1}}{1 + (C-1)\, X - C X^{n+1}} \tag{8}$$

where a_m is the monolayer capacity, n is the number of molecular layers, C is a constant and X is the relative pressure.

EXPERIMENTAL

The microporous active carbons in the present study, designated 203 A, 208 A, 207 B, and 208 C, were manufactured by Sutcliffe Speakman Co. Ltd., Leigh, England. The adsorbate (nitrogen) supplied by the British Oxygen Co. Ltd., was high purity grade. The adsorption isotherms were determined at 77 K using the volumetric adsorption technique.[9]

RESULTS AND DISCUSSION

For the purpose of determining the equation constants, the Dubinin--Astakhov and the n-layer BET equations are used in the linear form

$$\log a = \log a_o - \frac{0.434}{E^m} A^m \tag{9}$$

$$\frac{\Phi(n, X)}{a} = \frac{1}{C a_m} + \frac{\Theta(n, X)}{a_m} \tag{10}$$

where

$$\Phi(n, X) = \frac{X[(1 - X^n) - nX^n(1 - X)]}{(1 - X)^2} \tag{11}$$

and

$$\Theta(n, X) = \frac{X(1 - X^n)}{1 - X} \tag{12}$$

The plots of log a against A^m and $\Phi(n, X)/a$ against $\Theta(n, X)$ yield straight lines. The equation constants: a_o, E, a_m and C can be estimated from the intercept and the slope. The procedure is to select the value of m and n which gives the best accordance of the equations with experimental data. For this purpose, the use of the method of least squares is proposed. Using this procedure, the values of m and n have been determined and the resulting Dubinin-Astakhov and the n-layers BET plots are presented in Figures 1 and 2, respectively.

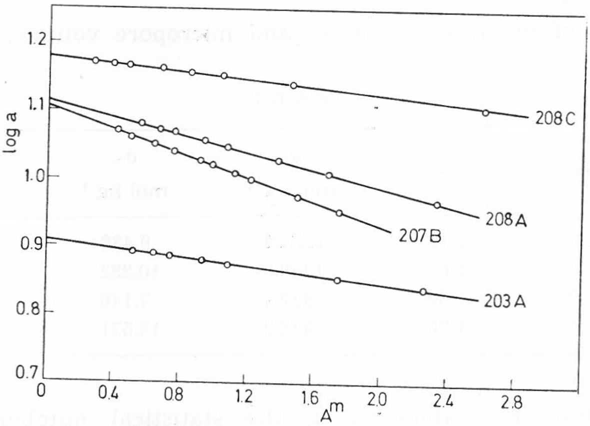

Figure 1. Dubinin-Astakhov plots for adsorption of nitrogen in microporous active carbons (a in mol kg^{-1}, A in kJ mol^{-1})

The remarkably good agreement of experimental adsorption data with the equations is evidenced by the linearity of the plots. The mean deviation of the experimental and theoretical data is within experimental error.

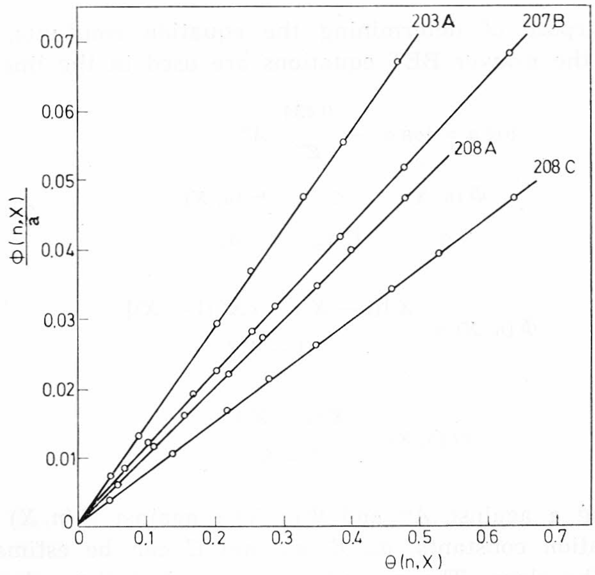

Figure 2. n-layers BET plots for adsorption of nitrogen in microporous active carbons (a *in mol kg*$^{-1}$)

Since m is an adjustable parameter, the Dubinin-Astakhov equation can be used to describe adsorption processes with different distribution of the differential molar work of adsorption and, consequently, to linearize a large number of adsorption isotherms.

The values of m, n, a_o, a_m, a_o/a_m and micropore volume, W_o, are given in Table I.

TABLE I

Carbon	m	n	a_o / mol kg^{-1}	a_m / mol kg^{-1}	a_o/a_m	W_o / cm^3 kg^{-1}
207 B	1.0	1.72	12.735	9.438	1.35	441
208 A	1.3	1.64	12.988	10.282	1.26	450
203 A	1.2	1.30	8.084	7.140	1.13	280
208 C	1.4	1.26	15.082	13.571	1.11	523

It is found that the values of n, the statistical number of adsorbed molecular layers, are in correlation with the average pore size of the carbons as determined elsewhere.[8] However, the disagreement between the a_o/a_m and n values is due to the fact that the BET equation applied to adsorption in microporous solids gives high values of monolayer capacitiy, a_m, and, consequently, gives non-realistic high values of the surface areas. The more significant adsorption quantity of microporous adsorbents is, therefore, the micropore volume, W_o, which can be calculated from the micropore capacity, a_o. In calculating the micropore volume the density of the adsorbed phase was assumed to be invariant with the amount adsorbed and taken as 808 kg m^{-3}, the bulk density of liquid nitrogen at 77 K.[10]

Considering the fact that the free energy of adsorption is a measure of the affinity of the surface for the adsorbate molecules, the differential distribution of a with ΔG can be used to give information on the gas/solid interaction. Besides, this distribution can be applied to characterization of the solid surfaces. So, the differential distribution curves give evidence on the surface heterogeneity, or in case of microporous solids with homogeneous surface these distribution curves represent the micropore size distribution. In the present study, the characteristic parameters of the differential distribution of the adsorption with the free energy of adsorption, the mean, $(\Delta G)_{mean}$, and the mode, $(\Delta G)_{mode}$, as determined from the expressions (6) and (7), respectively, are applied to give information on the carbon surfaces. The values of E, $(\Delta G)_{mean}$, $(\Delta G)_{mode}$ and C are presented in Table II.

TABLE II

Carbon	E / kJ mol^{-1}	$(\Delta G)_{mean}$ / kJ mol^{-1}	$(\Delta G)_{mode}$ / kJ mol^{-1}	C
208 A	4.55	—4.20	—1.47	133
207 B	5.17	—5.17	—	145
208 C	7.30	—6.64	—2.98	263
203 A	9.49	—8.92	—2.13	380

According to the above statement the $-(\Delta G)_{mean}$ values should be in inverse proportion to the pore size, *i. e.* to the n values; the higher the value of $-(\Delta G)_{mean}$ the lower is the value of n. From Tables I and II it can be seen that these quantities are not in such a relationship for carbons 208 A (207 B and 203 A) 208 C. This is considered to be due to a different degree of surface heterogeneity, which could arise from surface irregularities and presence of impurities. For this reason, the relation between the differential distribution of the adsorption with the free energy of adsorption and the micropore size distribution must be considered in the light of the nature of pore walls.

The data in Table II show that the $(\Delta G)_{mean}$ and the C values are in correlation. This is in accordance with the fact that constant C is dependent on the free energy of transfer of the adsorbate vapour from the liquid state adsorbate to the surface of the adsorbent. The difference between the values of $(\Delta G)_{mean}$ and $(\Delta G)_{mode}$, specially in case of carbon 203A, points the existence of an asymmetrical distribution of adsorption with the free energy of adsorption, and suggests spreading of this distribution in a wide range of free energy of adsorption. The latter can be confirmed by the fact that the low values of m and high values of E correspond to such a distribution.

The values of the Dubinin-Astakhov equation constants and the characteristic parameters of differential distribution of adsorption with the molar work of adsorption are in correlation with those given by D. Burevski[8] for adsorption of carbon dioxide. Moderate differences in the micropore values are due to the assumed values of density of the adsorbed nitrogen and carbon dioxide.

The results presented here lead to the conclusion that the Dubinin-Astakhov and *n*-layers BET equations could be used in a complementary manner for determining the adsorption and surface properties of microporous adsorbents.

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IZVOD

Primjena jednadžbe Dubinina i Astahova i n-slojne BET jednadžbe na adsorpciju dušika u mikroporoznim aktivnim ugljenima

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Proučavana je adsorpcija dušika u seriji mikroporoznih aktivnih ugljena. Za određivanje adsorpcijskih karakteristika ugljena komplementarno su primijenjene jednadžbe Dubinina i Astahova i n-slojna BET jednadžba.

Adsorpcijske osobine i mikroporoznost ugljena promatrani su s obzirom na konstante jednadžbi i karakteristične parametre diferencijalne distribucije adsorpcije s slobodnom energijom adsorpcije. Karakteristične veličine slobodne energije adsorpcije, srednja vrijednost i mod te distribucije, određivane su preko diferencijalne distribucijske funkcije izvedene iz jednadžbe Dubinina i Astahova.