Analysis of Monolayer Capacity of Adsorbents

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The adsorption isotherms of carbon dioxide and nitrogen on different adsorbents have been analyzed in terms of the free energy of adsorption. The monolayer capacity of the adsorbents was considered from the standpoint of the differential distribution of the molar free energy of adsorption. Distribution functions were determined by means of the BET, Huttig and Langmuir case VI equations. The analysis of the adsorption equlibrium with respect to the free energy of adsorption yields valuable data that can be used for selection of a suitable adsorption equation applicable to monolayer capacity evaluation.

INTRODUCTION

One of the main practical applications of physical adsorption of gases is the determination of the specific surface of solids. The specific surface area is calculated from the monolayer capacity, which can be estimated from the adsorption isotherms. A great number of adsorption equations have been proposed for interpretation of adsorption isotherms. Agreement between an adsorption isotherm equation and experimental data is the necessary, but not sufficient, condition for testing the applicability of the equation. The thermodynamical analysis of adsorption systems is used as an additional and essential criterion for the validity of the adsorption model.

It is known that there is a change in the properties of the adsorbed film in the region where the monolayer is complete. According to the evolution of adsorption energy and the state of adsorbed film, the differential heat and entropy of adsorption should markedly change at the point where the adsorption reaches the monolayer capacity.[1,2] In an actual system, however, complications are to be expected concerning the heterogeneity of the adsorb-

ent surface and the lateral interaction between the adsorbate molecules. Thus data of the differential heat and entropy of adsorption appear to be of limited value in relation to the determination of monolayer capacity.

In the present paper, the monolayer capacity is considered from the standpoint of the differential distribution of the molar free energy of adsorption. This distribution is derived from the BET, Huttig and Langmuir case VI equations. For the purpose of testing the method, the adsorption isotherms of carbon dioxide and nitrogen, obtained at 195 and 77 K, respectively, on different adsorbents are analyzed.

THEORETICAL PART

The fact that the adsorption equilibrium is governed by the free energy of adsorption allows consideration of the monolayer capacity of adsorbents in terms of the change in differential molar free energy of adsorption. Because of the change in the nature of adsorbate/adsorbent interaction in the monolayer completion region, the value of adsorption at which the monolayer is formed should be a characteristic point on the dependence of the differential molar free energy of adsorption, ΔG, on the amount of gas adsorbed, a. This point is to be more clearly marked on the plot of $\mathrm{d}(\Delta G)/\mathrm{d}a$ aginst a. Thus, the differential distribution of ΔG could serve as a useful function for determination of the monolayer capacity value.

The derivative of the function $\Delta G = f(a)$, $\mathrm{d}(\Delta G)/\mathrm{d}a$, can be obtained by differentiation of the inverse function $a = g(\Delta G)$ or by means of numerical differentiation of the former function. Function $a = g(\Delta G)$ can be presented by a suitable adsorption isotherm equation. In this work, the BET, Huttig and Langmuir case VI[3,4] equations will be used. The equations are given by the following expressions

$$a = \frac{a_{\mathrm{m}} C X}{(1 - X)\,[1 + (C - 1)X]} \qquad \text{(BET eq.)} \qquad (1)$$

$$a = \frac{a_{\mathrm{m}} CX (1 + X)}{1 + CX} \qquad \text{(Huttig eq.)} \qquad (2)$$

$$a = \frac{a_{\mathrm{m}} CX P_{\mathrm{o}}/P^{*}}{(1 - X P_{\mathrm{o}}/P^{*})[1 + (C - 1)X P_{\mathrm{o}}/P^{*}]} \qquad \text{(Langmuir case VI eq.)} \qquad (3)$$

In the equations, a is the amount of gas adsorbed at relative pressure $X (= P/P_{\mathrm{o}})$, a_{m} is the monolayer capacity, C and P^{*} are equation parameters and P_{o} is the pressure of the adsorbate.

The change in differential molar free energy of adsorption, ΔG, can be expressed by the relation

$$\Delta G = RT \ \ln(P/P_o) \qquad (4)$$

hence

$$X = \exp(\Delta G/RT) \qquad (5)$$

Substitution for X from expression (5) in equations (1–3) and differentiation of the functions obtained yield

$$\frac{d(\Delta G)}{da} = \frac{RT \ [1 + (C - 2) \exp(\Delta G/RT) - (C - 1) \exp(2\Delta G/RT)]^2}{a_m \ C \ \exp(\Delta G/RT) \ [1 + (C - 1) \exp(2\Delta G/RT)]} \qquad (6)$$

(from BET eq.)

$$\frac{d(\Delta G)}{da} = \frac{RT \ [1 + C \exp(\Delta G/RT)]^2}{a_m \ C \ \exp(\Delta G/RT) \ [1 + 2\exp(\Delta G/RT) + C \ \exp(2\Delta G/RT)]} \qquad (7)$$

(from Huttig eq.)

$$\frac{d(\Delta G)}{da} = \frac{RT \ [1 + (C - 2) \ P_o/P^* \exp(\Delta G/RT) - (C - 1)(P_o/P^*)^2 \exp(2\Delta G/RT)]^2}{a_m \ C \ P_o/P^* \exp(\Delta G/RT \ [1 + (C - 1)(P_o/P^*)^2 \exp(2\Delta G/RT)]} \qquad (8)$$

(from Langmuir case VI eq.)

The idea that there is a characteristic point in the variation of the free energy of adsorption with the amount of adsorption at the monolayer completion region will be illustrated by the differential distribution of the free energy of adsorption.

EXPERIMENTAL

The adsorption isotherms of carbon dioxide and nitrogen were determined on the following adsorbents: gasil silica, graphon and alumina. Samples of gasil silica and graphon were supplied by the British Petroleum Company Ltd., BP Research Centre, Sunburg-on-Thames. The alumina sample was obtained from Gamag, Muttenz, Switzerland. The gases, carbon dioxide and nitrogen, supplied by the British Oxygen Co. Ltd., were of high purity (> 99.999%). Adsorption measurements were carried out on volumetric apparatus.

RESULTS AND DISCUSSION

For the purpose of determining the monolayer capacities, the BET, Huttig and Langmuir case VI equations are used in the linear forms

$$\frac{X}{a(1-X)} = \frac{1}{a_{\mathrm{m}} C} + \frac{C-1}{a_{\mathrm{m}} C} X \qquad \text{(BET eq.)} \qquad (9)$$

$$\frac{X(1+X)}{a} = \frac{1}{a_{\mathrm{m}} C} + \frac{X}{a_{\mathrm{m}}} \qquad \text{(Huttig eq.)} \qquad (10)$$

$$\frac{XP_{\mathrm{o}}/P^*}{a(1-XP_{\mathrm{o}}/P^*)} = \frac{1}{a_{\mathrm{m}} C} + \frac{(C-1)XP_{\mathrm{o}}/P^*}{a_{\mathrm{m}} C} \qquad \text{(Langmuir case VI eq.)} \qquad (11)$$

The plots for adsorption of carbon dioxide at 195 K on gasil silica are presented in Figures 1–3.

It is evident from the linearity of the plots that the Huttig and Langmuir case VI plots, in comparison with the BET plot, give better agreement between theoretical equations and the experimental adsorption data.

Due to the fact that the free energy of adsorption is a measure of the affinity of an adsorbate for an adsorbent, the point where a marked change occurs on the $\mathrm{d}(\Delta G)/\mathrm{d}a$ *vs.* a plot is assumed to indicate completion of the
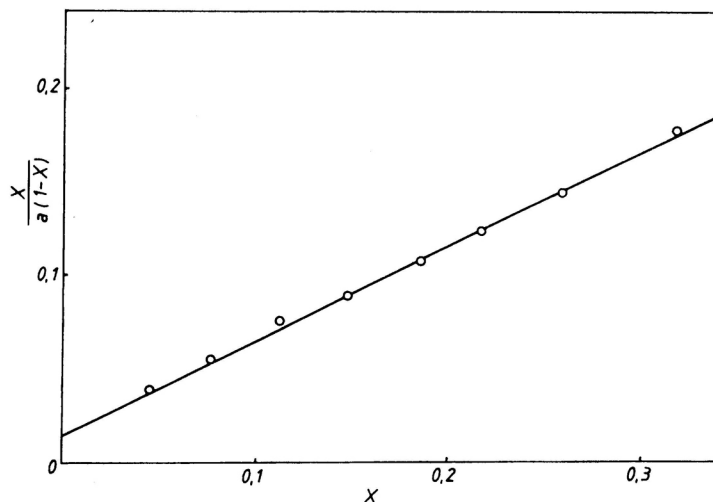

Figure 1. BET plot for adsorption of carbon dioxide on gasil silica.
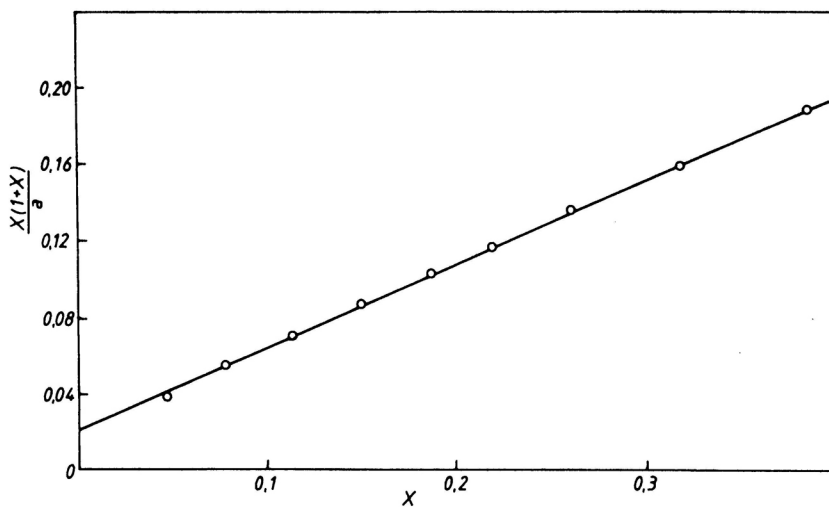
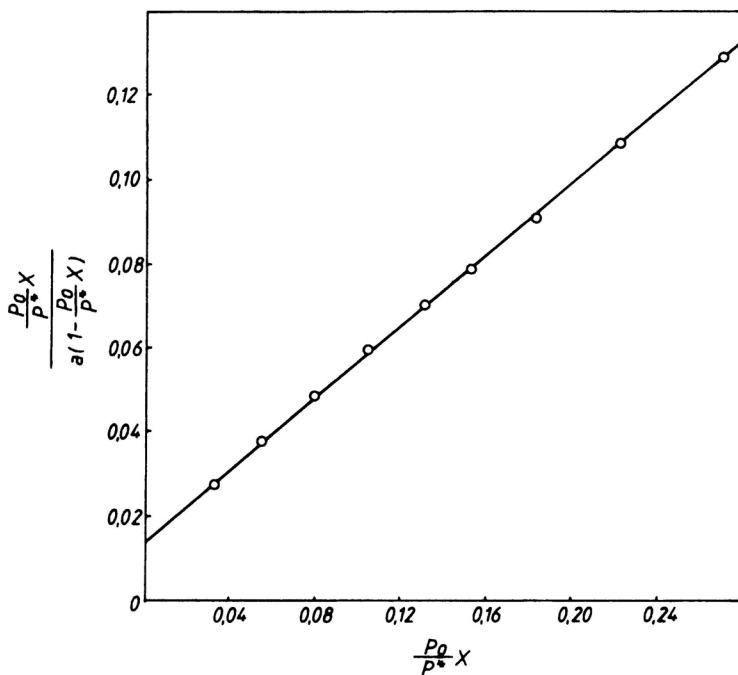Figure 2. Huttig plot for adsorption of carbon dioxide on gasil silica.

Figure 3. Langmuir case VI plot for adsorption of carbon dioxide on gasil silica.
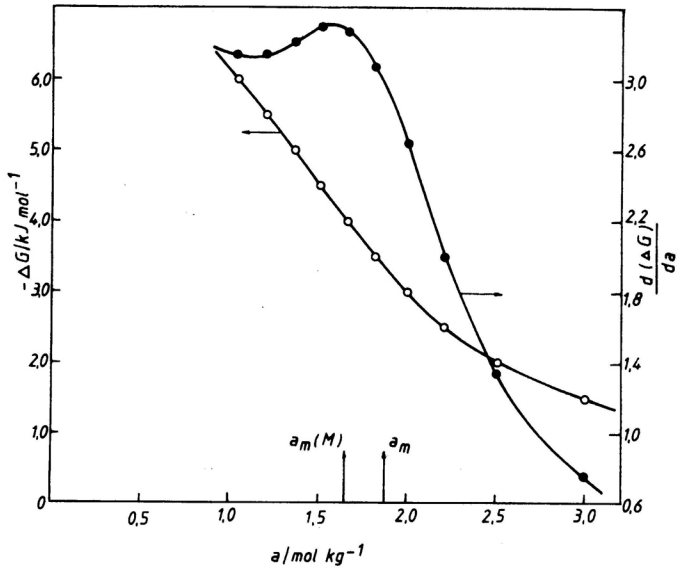
Figure 4. Integral and differential distribution of free energy of adsorption for carbon dioxide on gasil silica determined from the BET equation and expression (6).
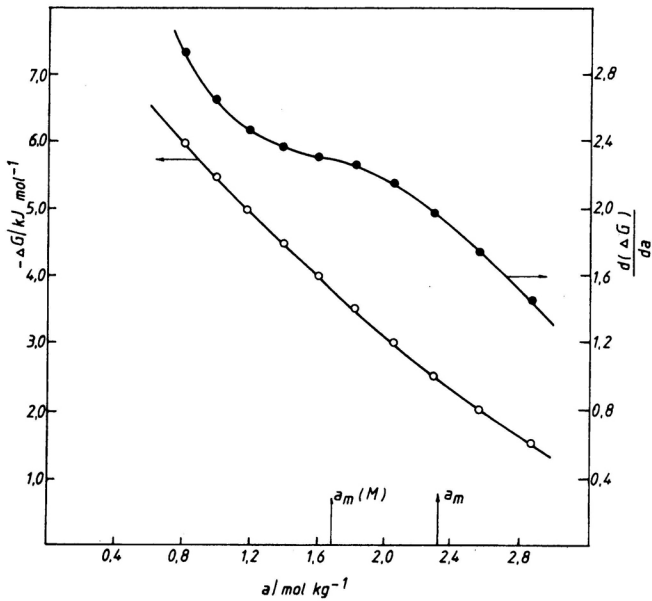
Figure 5. Integral and differential distribution of free energy of adsorption for carbon dioxide on gasil silica determined from Huttig equation and expression (7).
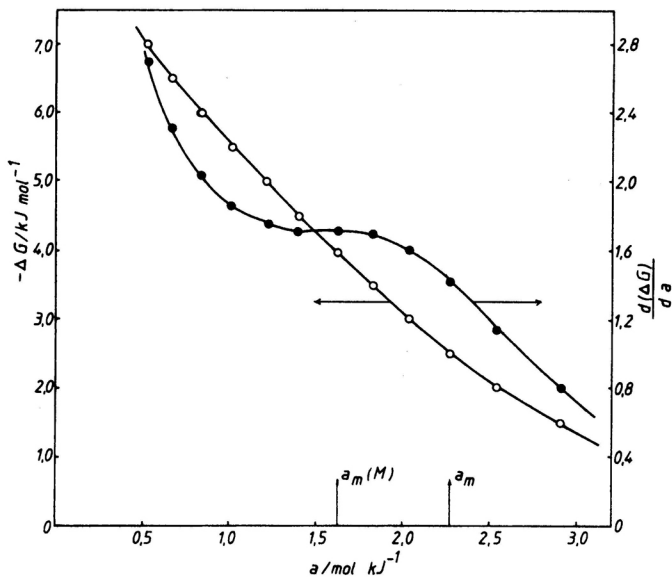
Figure 6. Integral and differential distribution of free energy of adsorption for carbon dioxide on gasil silica determined from Langmuir case VI equation and expression (8).
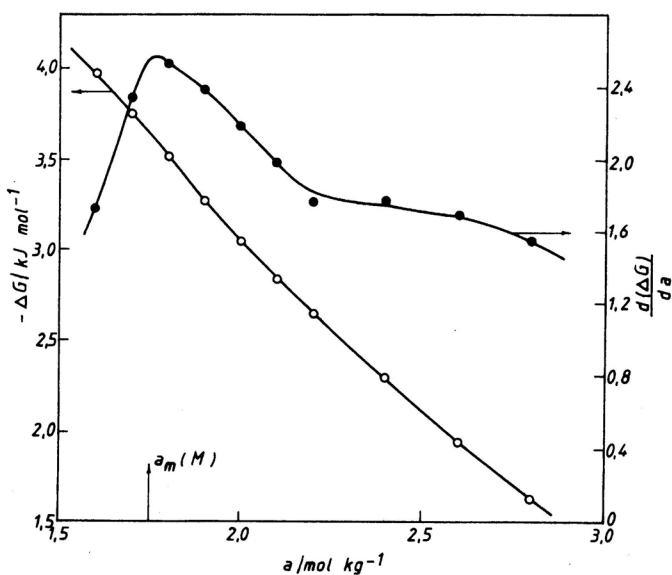

Figure 7. Distribution of free energy of adsorption for carbon dioxide on gasil silica determined by means of numerical differentiation.

monolayer. To illustrate this point the differential distribution of the free energy of adsorption is shown graphically. The integral and differental distribution of the free energy of adsorption, determined from the BET, Huttig and Langmuir case VI equations and from expressions (6), (7) and (8) are given in Figures 4–6.

The corresponding distribution determined by means of numerical differentiation is illustrated in Figure 7.

Bearing in mind the above cosiderations, the adsorption value at which the differential distribution lines reach maximum or have inflexion is accepted to correspond to the completion of the monolayer. The monolayer capacity values determined in this way, designated as $a_m(M)$, and from equation plots, determined by the method of least squares and designated as a_m, are indicated on the graphs. The values of monolayer capacity are recorded in Table I.

TABLE I

Monolayer capacity values of gasil silica determined from the BET, Huttig and Langmuir case VI equations

BET		Huttig		Langmuir case VI	
a_m	$a_m(M)$	a_m	$a_m(M)$	a_m	$a_m(M)$
mol kg^{-1}		mol kg^{-1}		mol kg^{-1}	
1.87	1.64	2.30	1.62	2.27	1.54

It can be seen that the monolayer capacity values evaluated from the BET plot, a_m, and from the distribution of free energy of adsorption, $a_m(M)$, are in close agreement. However, the values obtained from Huttig and Langmuir case VI plots differ markedly from the values determined by the present method. The above results lead to the conclusion that the BET equation is more appropriate for monolayer capacity determination of gasil silica than the Huttig and Langmuir case VI equations, although these equations fit better the experimental isotherm than does the BET equation. This finding can be supported by the $a_m(M)$ (= 1.75 mol kg^{-1}) value evaluated from the distribution of free energy of adsorption determined by means of numerical differentiation, Figure 7.

In the present work, the BET equation is used for the analysis of adsorption equilibrium data of nitrogen at 77 K and carbon dioxide at 195 K on graphon and alumina. The BET plots are presented in Figures 8 and 9.

Distribution of the free energy of adsorption determined from the BET equation and expression (6) for the former adsorption systems are illustrated in Figures 10–12.
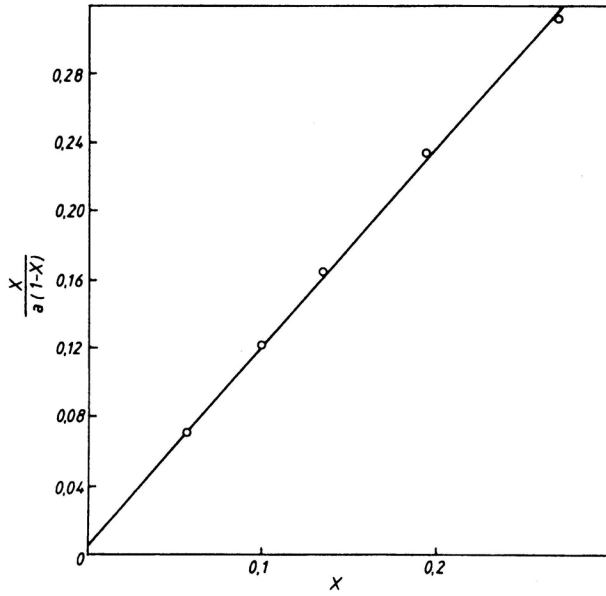
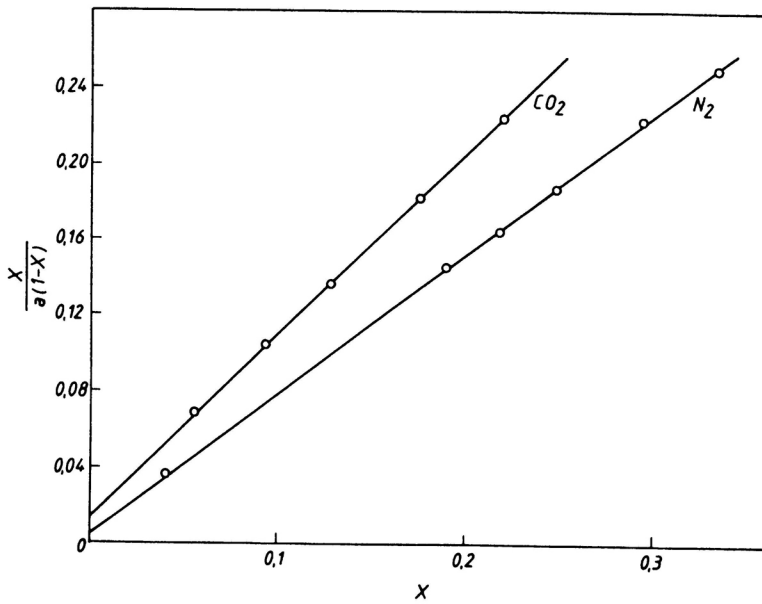Figure 8. BET plot for adsorption of nitrogen on graphon.

Figure 9. BET plots for adsorption of nitrogen and carbon dioxide on alumina.
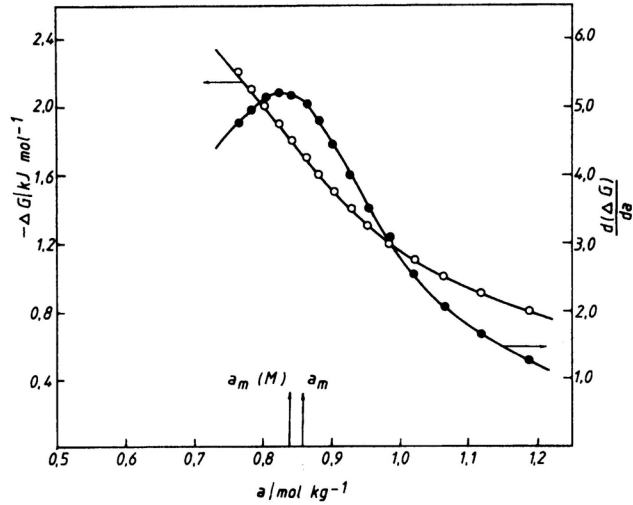
Figure 10. Integral and differential distribution of free energy of adsorption of nitrogen on graphon determined from the BET equation and expression (6).
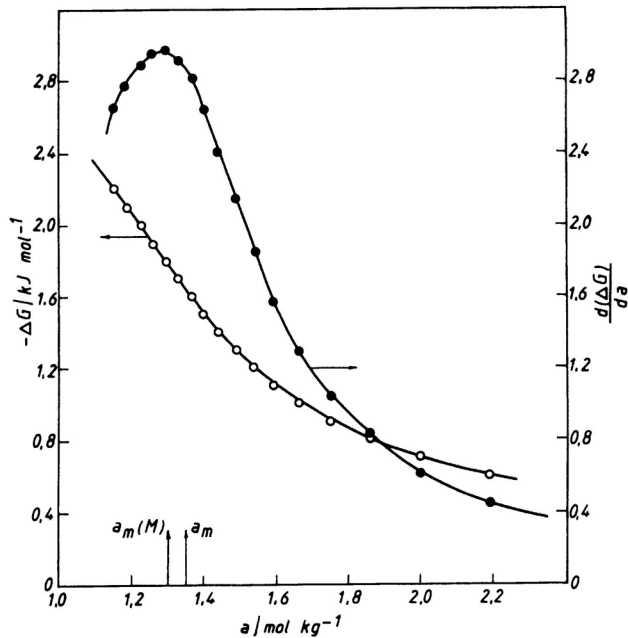

Figure 11. Integral and differential distribution of free energy of adsorption of nitrogen on alumina determined from BET equation and expression (6).
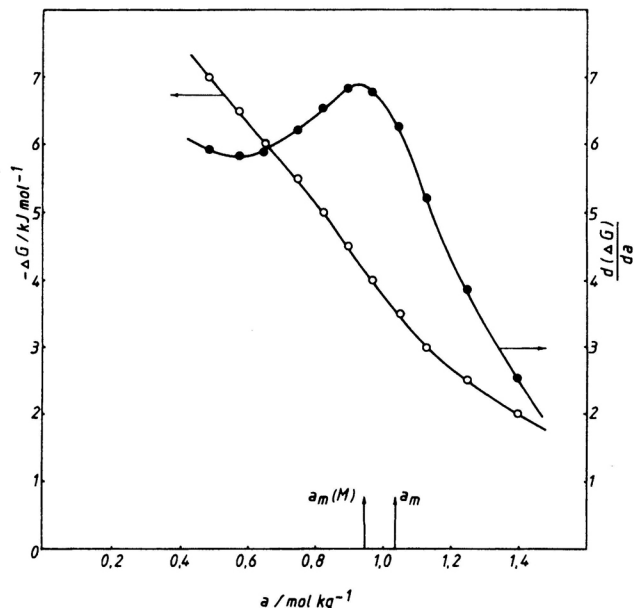
Figure 12. Integral and differential distribution of free energy of adsorption of carbon dioxide on alumina determined from the BET equation and expression (6).

The monolayer capacity determined from the BET plots, a_m, and from the differential distribution of the free energy of adsorption, $a_m(M)$, and the values of specific surface area, S, of the adsorbents investigated, calculated from the monolayer capacity data, are recorded in Table II.

The concordance between the values of monolayer capacity obtained from the BET plots and by means of the present method and the specific surface area evaluated from the respective monolayer capacity is evident. It

TABLE II

Values of monolayer capacity and specific surface area

Adsorption system	$\dfrac{a_m}{\text{mol kg}^{-1}}$	$\dfrac{S}{\text{m}^2\,\text{kg}^{-1}}$	$\dfrac{a_m(M)}{\text{mol kg}^{-1}}$	$\dfrac{S}{\text{m}^2\,\text{kg}^{-1}}$	C
N_2/Graphon	0.86	0.84×10^5	0.85	0.83×10^5	187
N_2/Alumina	1.35	1.32×10^5	1.30	1.27×10^5	147
CO_2/Alumina	1.03	1.43×10^5	0.95	1.32×10^5	67
CO_2/Gasil silica	1.87	2.60×10^5	1.64	2.28×10^5	47

should be emphasized that the differential distribution lines of the free energy of adsorption exhibit a well-defined maximum, point $a_m(M)$, even when the value of the constant C is low; unlike point B (the beginning of the midle linear range of the isotherm which corresponds to completion of the monolayer), its location is uncertain if the value of constant C is less than 80.[5] These data show that the BET equation can be applied to monolayer capacity determination for adsorption systems where the value of constant C is as low as 50.

Thermodynamical analysis of the adsorption equilibrium can be also applied to monolayer capacity evaluation of microporous adsorbents using the n-layers BET and Dubinin-Astakhov[6,7] equations. Distribution of the free energy of adsorption, as determined from the Dubinin-Astakhov equation, depends on the micropore structure of adsorbents and the nature of adsorbate/adsorbent interaction.[8-11] Due to this fact, the mode value in the differential distribution of the free energy of adsorption evaluated from the Dubinin-Astakhov equation does not necessarily correspond to the monolayer capacity.

In a next paper the monolayer capacity of microporous adsorbents will be considered using the method described in this work.

The findings of the investigation carried out in this work lead to the conclusion that the analysis of monolayer capacity of solids in terms of free energy of adsorption yields useful data which could be used for: 1) selection of an appropriate adsorption equation for monolayer capacity determination and 2) evaluation of the monolayer capacity by means of numerical differentiation of the integral distribution of the free energy of adsorption.

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SAŽETAK

Analiza kapaciteta adsorbiranig jednosloja

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Pomoću adsorpcijske slobodne energije analizirane su adsorpcijske izoterme ugljikova dioksida i dušika na različitim adsorbensima. Kapacitet adsorbiranog jednosloja razmatran je s gledišta diferencijalne raspodjele molarne slobodne energije adsorbcije. Raspodjelne funkcije određene su pomoću izotermi BET, Huttiga i Langmuira (slučaj VI). Analiza adsorpcijske ravnoteže s obzirom na slobodnu energiju adsorpcije daje vrijedne podatke koji se mogu iskoristiti za izbor prikladne adsorpcijske jednadžbe za proračun kapaciteta jednosloja.