

Adsorption characterization of structural and surface properties of active carbons

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Adsorption of benzene on the BPL active carbon measured in the relative pressure range from $5 \cdot 10^{-5}$ to 0.99 was used to examine methods for characterization of the structural and surface properties of active carbons. It was shown that the adsorption potential distribution can be used to determine the total surface area, micropore volume and average micropore size. Adsorption isotherm of benzene on this carbon can be also well described by Jaroniec-Choma equation.

1. INTRODUCTION

Characterization of active carbons is difficult because of their structural and surface heterogeneity caused by the presence of pores of different sizes and shapes as well as various functional groups. Adsorption measurements are most often used to characterize these adsorbents [1]. The equilibrium adsorption isotherm of a single component from the gas phase, which expresses the amount adsorbed, a , as a function of the equilibrium pressure, p , at a given temperature, T , is a fundamental measurable quantity. Adsorption can be measured by gravimetric or volumetric methods [2]. For vapors adsorbed on solids at temperatures below critical temperature, the relative pressure, p/p_0 (where p_0 is the saturation vapor pressure), is used as independent variable instead of p . The mechanism of physical adsorption depends on the nature of adsorbent and adsorbate. Adsorption can occur via (i) volume filling of micropores (in the case of pores below 2 nm), and (ii) formation of subsequent layers on the surface of

mesopores (pores of widths between 2 and 50 nm) and macropores (pores above 50 nm). At higher relative pressures the layer-by-layer adsorption is followed by capillary condensation of adsorbate inside mesopores.

Usually, gas and vapor adsorption isotherms on active carbons are used to evaluate their specific surface area, micropore volume, average micropore width and micropore size distribution [3]. Two latter quantities have been often estimated by assuming the applicability of the Dubinin semi-empirical equation [4] for the volume filling of micropores. Experimental studies [5] as well as computer simulations and density functional theory predictions indicate that the volume filling of larger micropores is a two-step process. Micropores of widths around two or three adsorbate diameters are filled in the one-step process, whereas adsorption in larger micropores occurs initially on the micropore walls (first step) and later the micropore interior is filled (second step). It should be noted that the two-step mechanism of the micropore filling could not be represented by the Dubinin equation.

The objective of the current work is to present and discuss reliable methods of characterization of the surface and structural properties of active carbons, which are based on adsorption isotherms of single gases and vapors.

2. EXPERIMENTAL

Benzene adsorption on the BPL active carbon from the Calgon Carbon Corporation measured at 293 K by the McBain-Bakr gravimetric method with quartz spirals [6] was used to examine the selected characterization methods. The BPL carbon is a commercial material prepared from selected bituminous coals for gas phase applications. Prior adsorption measurements the BPL sample was degassed for 2 hrs at 473 K. Experimental adsorption isotherm is shown in Figure 1.

3. RESULTS AND DISCUSSION

The total amount adsorbed, a , is a simple sum of the amounts adsorbed in micropores (a_{mi}) and mesopores (a_{me}):

$$a = a_{mi} + a_{me} \quad (1)$$

The amount adsorbed in macropores is negligible because their specific surface area is small, i.e., below 2 m²/g. In the case of active carbons the volume filling of micropores is a dominating process. Adsorption in micropores, a_{mi} , can be obtained from the total amount adsorbed, a , by subtraction of the amount adsorbed on the mesopore surface, i.e.,

$$a_{mi} = a - \gamma_s S_{me} \quad (2)$$

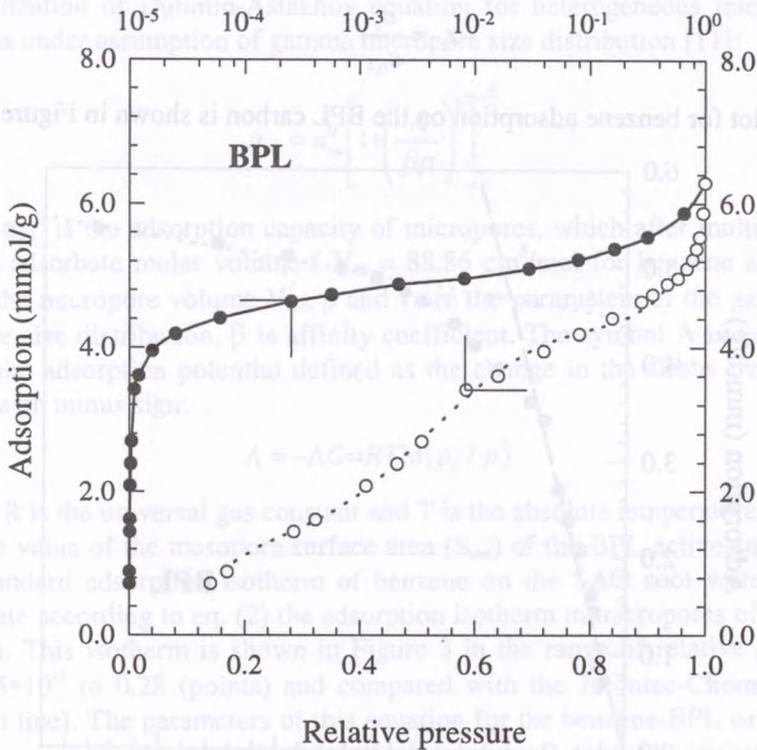


Figure 1. Experimental adsorption isotherm of benzene on the BPL active carbon measured at 293 K

The second term in eq. (2) represents the amount adsorbed on the mesopore surface, where S_{mc} is the mesopore surface area and γ_s is the amount adsorbed per the unit area of the reference macroporous carbon of the surface properties similar to the active carbon studied. The mesopore surface area of active carbons can be evaluated by the comparative method using the so-called α_s -plot or t-plot [7]. These plots can be used not only to evaluate the mesopore surface area but also to determine the total surface area and the micropore volume of the active carbon studied. In the current work we used the α_s -plot proposed by Sing [7]. According to the α_s -method the experimental adsorption isotherm measured on the active carbon studied is compared with that measured on the reference macroporous carbon. Adsorption data for the reference carbon are expressed as the standard reduced adsorption α_s , which is the ratio of the amount, a_s , adsorbed at a give relative pressure to the amount, $a_{0.4}$, adsorbed at $p/p_0 = 0.4$:

$$\alpha_s = \frac{a_s}{a_{0.4}} \quad (3)$$

The α_s -plot for benzene adsorption on the BPL carbon is shown in Figure 2.

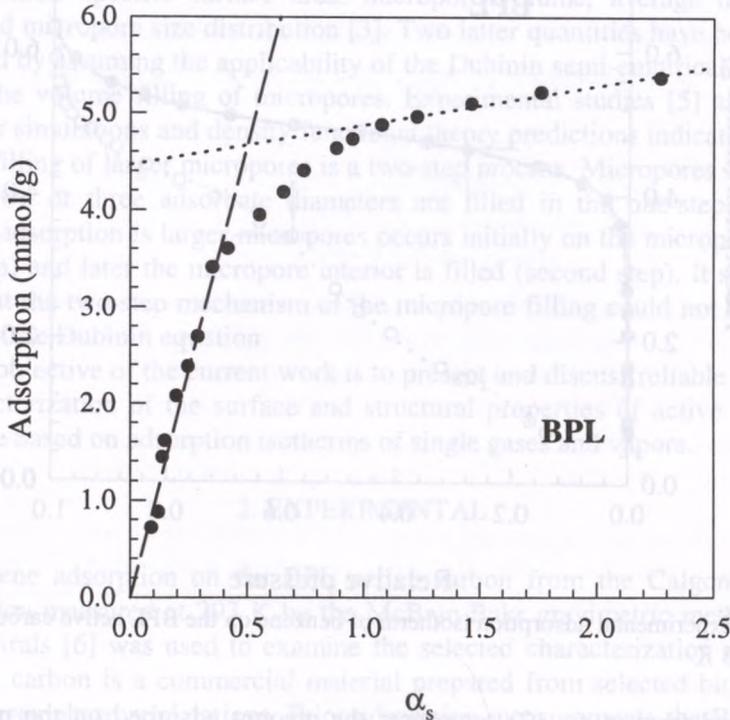


Figure 2. The α_s -plot for benzene on the BPL active carbon

This plot was constructed using the standard reduced adsorption of benzene measured at 293 K on the reference SAO soot prepared from anthracene oil and heated in argon atmosphere at 1223 K for 6 hrs [8]. The initial slope of the α_s -plot in the range of α_s below 0.4, after multiplication by the proportionality factor, gives the total specific surface area, which is equal to 1490 m²/g. The second linear segment of the α_s -plot, which is visible for α_s between 1.0 and 2.3, was used to evaluate the micropore volume V_{mi} (from the intercept) and the mesopore surface area S_{me} (from the slope) [9]. These quantities for the BPL carbon are equal to 0.40 cm³/g and 65 m²/g, respectively.

Equilibrium adsorption isotherms on active carbons have been described using different analytical expressions such as Dubinin-Radushkevich, Dubinin-Astakhov, Dubinin-Stoeckli, Jaroniec-Choma and John equations [10]. Among those the Jaroniec-Choma isotherm equation is simple and gives a good representation of vapor adsorption on active carbons. This equation was obtained by

generalization of Dubinin-Astakhov equation for heterogeneous microporous carbons under assumption of gamma micropore size distribution [11]:

$$a_{mi} = a_{mi}^0 \left[1 + \left(\frac{A}{\beta \rho} \right)^3 \right]^{-\frac{v}{3}} \quad (4)$$

where a_{mi}^0 is the adsorption capacity of micropores, which after multiplication by the adsorbate molar volume ($V_m = 88.86 \text{ cm}^3/\text{mol}$ for benzene at 293 K) gives the micropore volume V_{mi} , ρ and v are the parameters of the gamma micropore size distribution, β is affinity coefficient. The symbol A in eq. (4) denotes the adsorption potential defined as the change in the Gibbs free energy taken with minus sign:

$$A = -\Delta G = RT \ln(p_0 / p) \quad (5)$$

where R is the universal gas constant and T is the absolute temperature.

The value of the mesopore surface area (S_{me}) of the BPL active carbon and the standard adsorption isotherm of benzene on the SAO soot were used to calculate according to eq. (2) the adsorption isotherm in micropores of the BPL carbon. This isotherm is shown in Figure 3 in the range of relative pressures from $5 \cdot 10^{-5}$ to 0.28 (points) and compared with the Jaroniec-Choma eq. (4) (dotted line). The parameters of this equation for the benzene-BPL carbon system, evaluated by minimization of the sum of squared deviations, are $a_{mi}^0 = 4.19 \text{ mmol/g}$, $V_{mi, JC} = 0.37 \text{ cm}^3/\text{g}$, $\rho = 21.1 \text{ kJ/mol}$ and $v = 5.68$. As can be seen from Figure 3 the Jaroniec-Choma eq. (4) gives a good representation of benzene adsorption isotherms on active carbons.

Previous experimental and computer simulation studies of nitrogen adsorption at 77 K on active carbons [12] indicated a possibility of using the adsorption potential distribution for characterization of active carbons. It was shown that the minimum on the adsorption potential distribution curve, located between the peak reflecting the monolayer formation and that related to the formation of higher adsorbed layers, represents the adsorption potential corresponding to the monolayer capacity [13,14]. It would be interesting to check if the adsorption potential distributions for benzene on active carbons can be useful for characterization of these adsorbents. In order to check this possibility the experimental adsorption isotherm of benzene on the BPL active carbon was used to calculate the adsorption potential distribution $X(A)$. This distribution was obtained by simple differentiation of the characteristic adsorption curve $v(A)$ shown in Figure 4, which represents the amount adsorbed plotted as a function of the adsorption potential A . Thus, $X(A)$ is given by:

$$X(A) = \frac{dv(A)}{dA} \quad (6)$$

The adsorption potential distribution for the benzene-BPL carbon is shown in Figure 5. This function differs slightly from that for nitrogen on active carbons. In the case of nitrogen the adsorption potential distribution shows two peaks indicating a two-step adsorption process [5]. The peak located at high values of the adsorption potential (i.e., low values of the equilibrium pressure), reflects the formation of monolayer on the micropore walls. The second peak, located at lower values of the adsorption potential (higher equilibrium pressures), reflects the volume filling of micropores. The adsorption potential distribution for nitrogen on many active carbons exhibits a distinct minimum between these two peaks, which can be used to calculate the corresponding value of the monolayer capacity, and consequently, the specific surface area of a given active carbon. Another interesting parameter, which can be obtained from the adsorption potential distribution, is the micropore volume. Its value can be estimated on the basis of the second minimum on the adsorption potential distribution, which lies after the peak related to the micropore filling.

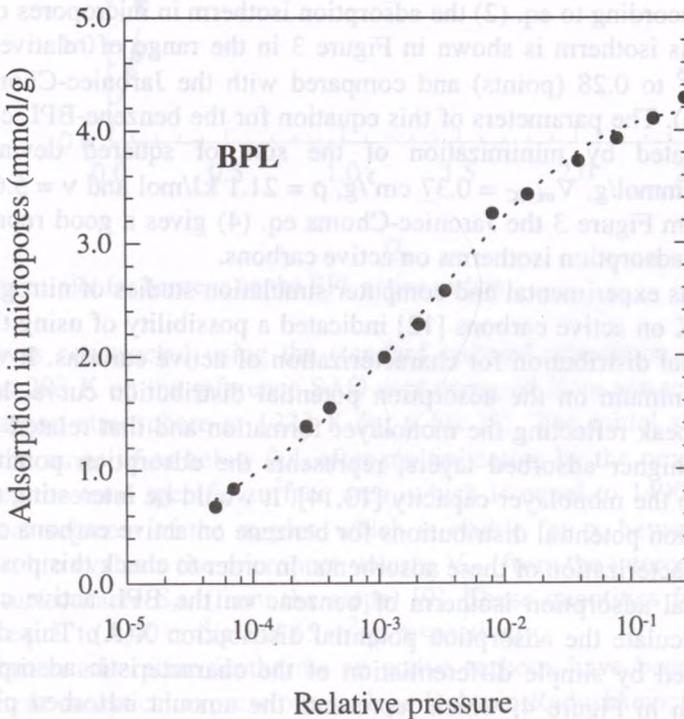


Figure 3. Adsorption of benzene in micropores of the BPL carbon: circles denote experimental points and dotted line was obtained by using the Jaroniec-Choma eq. (4)

The adsorption potential distribution for benzene on the BPL carbon shown in Figure 5 exhibits only one broad peak in the range between 6 and 20 kJ/mol. It seems that the monolayer formed by benzene molecules, which are larger than nitrogen, is essentially sufficient to fill small micropores of the BPL carbon, and therefore the micropore filling process and monolayer formation are not distinguishable. Thus, the minimum on the adsorption potential distribution at 6 kJ/mol (see Figure 5) can be used to calculate the micropore volume. The value of 6 kJ/mol relates to the relative pressure $p/p_0 = 0.085$, which corresponds to $a_{mi, X(A)} = 4.20$ mmol/g on the adsorption isotherm (Figure 1). The latter value multiplied by the molar volume for benzene gives the micropore volume $V_{mi, X(A)} = 0.37$ cm³/g. Comparing the micropore volumes of the BPL carbon obtained from the α_s -plot analysis (0.40 cm³/g), the Jaroniec-Choma equation (0.37 cm³/g) and the adsorption potential distribution (0.37 cm³/g), one can see that all procedures provide analogous value of this structural parameter.

The minimum on the adsorption potential distribution (APD) for benzene on the BPL carbon can be also used to calculate the total specific surface area, $S_{t, X(A)}$:

$$S_{t, X(A)} = a_{\min} \omega N_A \quad (7)$$

where $a_{\min} = 4.20$ mmol/g corresponds to the value of the adsorption potential 6 kJ/mol, ω denotes the area occupied by single benzene molecule on the carbon surface, which is equal to 0.41 nm²/molecule, and N_A is the Avogadro number. The total surface area of the BPL carbon estimated on the basis of APD is equal to 1040 m²/g. Its BET surface area obtained from benzene adsorption isotherm at 293 K in the range of relative pressures from $8 \cdot 10^{-3}$ to 0.16 is equal to 940 m²/g. This value corresponds to the BET monolayer capacity $a_m = 3.82$ mmol/g.

Comparing the values of the surface area for the BPL carbon obtained from the α_s -plot (1490 m²/g), the BET method (940 m²/g) and the adsorption potential distribution minimum (1040 m²/g), one can see a good agreement between last two methods. It should be noted that in the case of nitrogen adsorption the BET method gives much higher (about 50%) values of the surface area than those obtained on the basis of the adsorption potential distribution. It seems that the BET monolayer capacity is overestimated for nitrogen because it also includes molecules adsorbed inside micropores. In the case of benzene adsorbed on micropore walls of the BPL carbon, there is no much interior space available for additional benzene molecules. Therefore, the BET range from $8 \cdot 10^{-3}$ to 0.16 gives the monolayer capacity for benzene, which is analogous to that ($p/p_0 = 0.085$) corresponding to the minimum of the adsorption potential distribution. In contrast, the α_s -plot method, which uses the slope of the initial linear seg-

ment of the α_s -plot, gave an overestimated value of the specific surface area. Since estimation of the specific surface area on the basis of the α_s -plot is essentially equivalent to the BET method, the observed difference in the resulting surface areas was not expected. This difference is probably due to the difficulty in selecting proper reference adsorbent of identical surface properties with the carbon studied as well as the initial linear segment of the α_s -plot.

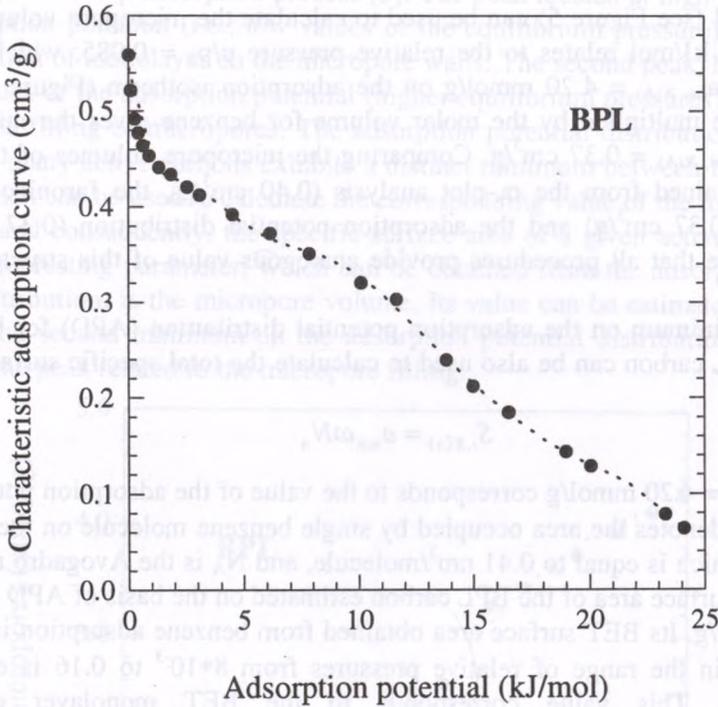


Figure 4. Characteristic adsorption curve for benzene on the BPL active carbon at 293 K

The correct total surface area can be used to evaluate the average micropore size according to the following equation:

$$w_{X(A)} = \frac{2V_{mi,X(A)}}{S_{mi}} = \frac{2V_{mi,X(A)}}{S_{t,X(A)} - S_{me,\alpha_s}} \tag{8}$$

where V_{mi} is the micropore volume and S_{mi} is the surface area of micropores, which is defined as the difference between the total surface area and the mesopore surface area. The latter can be evaluated by the α_s -plot method. Analysis of the benzene-BPL carbon data shows that the micropore volume and the total surface area evaluated on the basis of the adsorption potential distribution give a reasonable estimation of the average micropore size, $w_{X(A)} = 0.77$ nm, for the carbon studied.

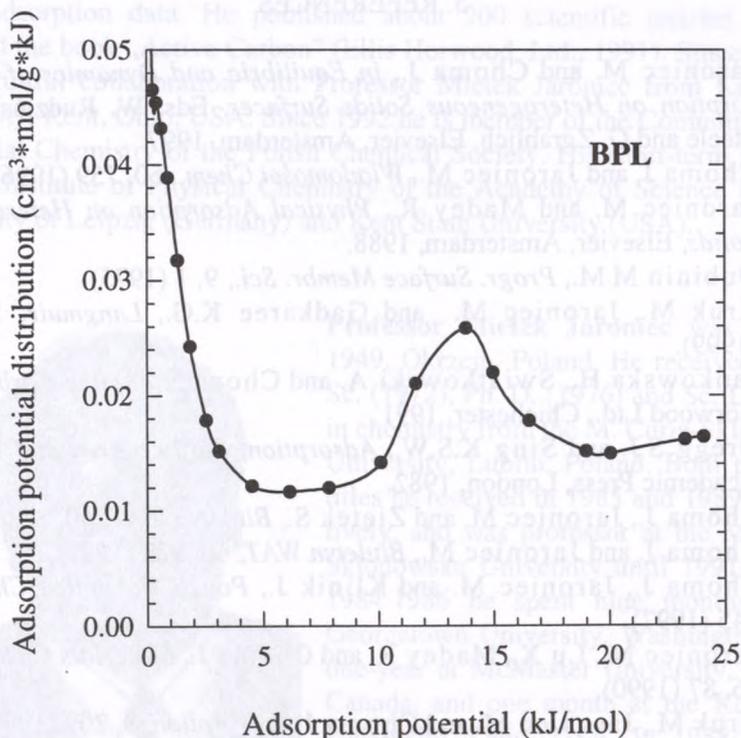


Figure 5. Adsorption potential distribution for benzene at 293 K on the BPL active carbon

4. CONCLUSIONS

Similarly as in the case of nitrogen adsorption, the adsorption potential distribution for benzene can be used to estimate fundamental parameters for active carbons such as: the total specific surface area, the micropore volume and the average micropore size. This method gives the aforementioned parameters, which are similar or better than those obtained by the α_s -plot analysis and Jaroniec-Choma equation. The current work showed that for small micropores as those in the BPL carbon the adsorption process of benzene occurs via one-step mechanism.

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Professor Jerzy Choma was born in 1952, Lublin, Poland. He studied chemistry at the Military Technical Academy in Warsaw and graduated from this school in 1978. The Ph.D. and Sc.D. degrees he obtained in 1981 and 1985, respectively. The professor title he received in 1994. Since 1995 he is vice-chairman of the Chemistry Department of the Military Technical Academy in Warsaw. Also, he has the colonel rank in the Polish Army. His major scientific interests include experimental and theoretical studies of nanoporous carbonaceous adsorbents on the basis of gas- and liquid-

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Professor Mietek Jaroniec was born in 1949, Okrzeja, Poland. He received his M. Sc. (1972), Ph. D. (1976) and Sc. D. (1979) in chemistry from the M. Curie-Skłodowska University, Lublin, Poland. Both professor titles he received in 1985 and 1989, respectively, and was professor at the M. Curie-Skłodowska University until 1991. During 1984-1986 he spent nine months at the Georgetown University, Washington, D.C., one-year at McMaster University, Ontario, Canada, and one month at the Kent State University, Ohio, USA. In 1988-1989 he visited again the Kent State University. Since 1991 he has been working at the

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