Adsorption of Carbon Dioxide, Sulfur Dioxide and Water Vapour on Microporous Active Carbons

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The values of differential heat and entropy of adsorption of carbon dioxide and sulfur dioxide obtained at 295 K and 298 K, respectively, for a series of microporous active carbons have been analyzed in order to determine the nature of adsorbate/adsorbent interaction.

The content of primary active centres in the microporous carbon samples was determined from the adsorption isotherms of water vapour.

The adsorption data of carbon dioxide were interpreted by the equations of the theory of volume filling of micropores. The degree of heterogeneity of the microporous active carbons was evaluated from the characteristic parameters of the equations applied and the thermodynamic adsorption data.

It was found that the active centres, in addition to the distribution of pores with respect to their dimensions, influence the degree of heterogeneity of the microporous carbon adsorbents.

INTRODUCTION

It is known that the adsorption properties of active carbons are determined not only by their porous structure but also by their chemical composition and crystal structure. The presence of non-carbonic admixtures changes the adsorption characteristics of the active carbons. Disturbance in the elementary microcrystalline structure, like, for example, by the presence of imperfect graphitic layers, influence also the adsorption properties of carbon adsorbents. Carbon atoms in the defect positions of the crystal lattice as well as the presence of non-carbonic substances form polar (more active) adsorption centres where molecules of polar substances are physically adsorbed in a state of reduced mobility. The pore size distribution and the presence of active contres, therefore, influence the degree of heterogeneity of microporous carbons in a complex manner.

The heterogeneity of microporous carbons is usually considered as structural heterogeneity related to pore size, disregarding the presence of active centres. The subject of the present paper is to consider the nature of adsorbate/adsorbent interaction related to both the size of micropores and the presence of more active (primary) adsorption centres. The main point is concerned with the influence of the size of micropores and the active centres

on the values of the differential heat and entropy of adsorption and on the equilibrium adsorption data of gases on microporous active carbons. For this purpose, the values of differential heat and entropy of adsorption and the isotherms of carbon dioxide, sulfur dioxide and water vapour (adsorbtives with different polar characteristics), measured for a series of microporous active carbons, have been analyzed. In this context, the carbon dioxide adsorption data are interpreted by the equations of the theory of volume filling of micropores.

<div align="center">THEORETICAL PART</div>

The most applicable theory for adsorption of gases on microporous adsorbents is the theory of volume filling of micropores developed by Dubinin and his co-workers.[1-4] The basic relations which describe the adsorption isotherms, expressed as temperature invariant characteristic curves, are the Dubinin-Radushkevich and Dubinin-Astakhov equations. The Dubinin-Astakhov equation is of the form

$$W/W_0 = \exp\left[-\left(A/\beta\, E_o\right)^n\right] \tag{1}$$

where W is the volume of the liquid-like adsorbate present in the micropores at temperature T and relative pressure P/P_o, W_o is the total volume of the micropores, E_o and n are equation parameters depending on the system under investigation, β is the affinity coefficient which depends on the adsorbate only, and A is the differential molar work of adsorption which (with opposite sign) is equal to the differential free energy of adsorption, ΔG, given by the expression

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

The Dubinin-Astakhov equation includes the Dubinin-Radushkevich equation as a special case when parameter n is equal to 2. The Dubinin-Radushkevich equation is usually given by

$$W/W_o = \exp\left\{-B\left[(T/\beta) \log\left(P_o/P\right)\right]^2\right\} \tag{3}$$

where B is the structural constant related to average pore dimensions.

Ozawa *et al.*[5] have proposed a modified form of the Dubinin-Astakhov equation where the contribution of parameter n in the distribution of W with A is replaced by the sum of contributions with different n values. The equation is expressed in the following form

$$\ln\left(W/W_o\right) = \sum_{n=1}^{\infty} k_n \left(A/\beta\right)^n = k_1 \left(A/\beta\right) + k_2 \left(A/\beta\right)^2 + \ldots \tag{4}$$

As an alternative to the Dubinin-Astakhov equation, Stoeckli[6] proposed a generalization of the Dubinin-Radushkevich equation. It is postulated that the Dubinin-Radushkevich equation is only valid when it is applied to an almost homogeneous system (*i. e.* narrow size distribution) of micropores and that adsorption on adsorbents with wide micropore size distribution is better expressed by a sum of contributions each of which can be described by equation (3). Involving a new function, $f(B)$, which represents the differential distribution of the volume of a given class of micropores, W_{oj}, with

the respective structural constant, B, and assuming the distribution to be expressed by the Gaussian function, *i. e.*

$$f(b) = \frac{dW_{oj}}{dB} = [W_o/\Delta (2\pi)^{1/2}] \exp[-(B-B_o)^2/2\Delta^2] \qquad (5)$$

Stoeckli derived the following equation

$$W(y) = W_o \exp[-B_o y] \exp[y^2 \Delta^2/2] \cdot [1 - erf(x)]/2 \qquad (6)$$

In expressions (5) and (6), B_o is a value of B at the maximum of distribution, Δ is the dispersion, $y = [(T/\beta) \log(P_o/P)]^2$, $x = (y - B_o/\Delta^2) \Delta/(2)^{1/2}$ and $erf(x)$ is the error function.

Equation (6), known as Dubinin-Radushkevich-Stoeckli equation, has been used to interpret adsorption data of different systems.[7-10]

Independence of the characteristic curve, $W = f(A)$, of temperature usually presented in the form

$$\left(\frac{\partial A}{\partial T}\right)_\Theta = 0 \qquad (7)$$

allows the calculation of the adsorption isotherm for an arbitrary temperature from a single measured isotherm; then the heat of adsorption can be evaluated by means of the Clausius-Clapeyron equation (Θ is the degree of volume filling of micropores, $\Theta = W/W_o$). Toda *et al.*[11] determined the heat of adsorption of carbon dioxide on coal samples by using the Dubinin-Radushkevich equation to calculate the adsorption isotherm for an arbitrary temperature. However, for this purpose any equation given above can be employed. So, at temperature T_i and T_{ii}, the following equations are obtained from equation (4)

$$\ln W_i = \ln W_o + k_1(A_i/\beta) + k_2(A_i/\beta)^2 + \ldots \qquad (8)$$

$$\ln W_{ii} = \ln W_o + k_1(A_{ii}/\beta) + k_2(A_{ii}/\beta)^2 + \ldots \qquad (9)$$

where i and ii refer to T_i and T_{ii}, respectively. From the relation between volume W and the density of adsorbate, ρ, at a constant amount of adsorption, the expression

$$\ln W_{ii} = \ln W_i + \ln(\varrho_i/\varrho_{ii}) \qquad (10)$$

is obtained. By means of expressions (8), (9) and (10) and the Clausis-Clapeyron equation, the isosteric and hence the differential heat of adsorption, q_d, can be calculated from a single measured isotherm.

Useful information for the interaction of gases with microporous adsorbents can be provided from the differential distribution of the degree of volume filling of micropores, Θ, with respect to the differential molar work of adsorption, A.[12,13] The distribution function is derived from the Dubinin-Astakhov equation, giving

$$\frac{d\Theta}{dA} = -\frac{nA^{n-1}}{(\beta E_o)^n} \exp[-(A/\beta E_o)^n] \qquad (11)$$

EXPERIMENTAL

Samples of microporous active carbon adsorbents, labeled 203A, 208A, 207B and 208C, were produced by Sutcliffe Speakman Co. Ltd. Leigh, England. The adsorbtives (carbon dioxide and sulfur dioxide) supplied by British Oxygen Co. Ltd. were of high purity grade. The adsorption measurements of carbon dioxide at 295 K and sulfur dioxide at 298 K were carried out by volumetric and dynamic methods, respectively. The adsorption isotherms of water vapour were determined by the gravimetric method at 298 K. The differential heat of adsorption was calculated from the integral heat of adsorption measured by means of the flow microcalorimetry.[14,15]

RESULTS AND DISCUSSION

The adsorptions isotherms of water vapour were measured in order to determine the content of primary active centers in carbon samples. The isotherms, plotted as the degree of volume filling of micropores, Θ, against the relative pressure, X, are presented in Figure 1.
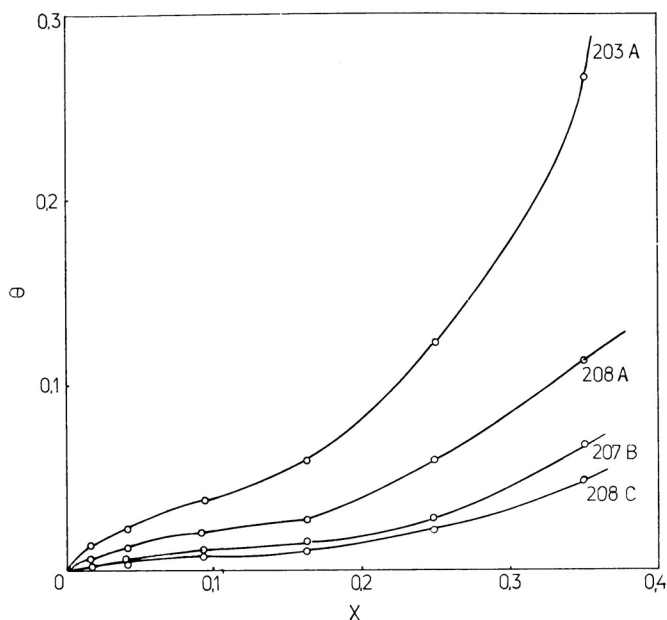

Figure 1. Adsorption isotherms of water vapour at 298 K.

The polar (more active) sites localized in the pore walls can be regarded as primary active centres for adsorption of water molecules. According to the approach of Dubinin and Serpinsky,[16,17] the content of primary adsorption centres can be determined by means of the equation

$$\frac{X}{a} = \frac{1}{a_o C} - \frac{X}{a_o} \tag{12}$$

where a_o is the amount of water vapour adsorbed on the primary adsorption centres and C is a constant equal to the ratio of the kinetic constants. The a_o values can be calculated from the plot of equation (12) for the steeply

rising branch of water adsorption isotherms. The values of a_o, expressed in moles of water vapour adsorbed in unit adsorption space of micropores were: 8.43, 3.83, 2.36 and 2.27 mol dm^{-3} for active carbons: 203A, 208A, 207B, and 208C, respectively. These values, as well as the water vapour adsorption isotherms, Figure 1, show that active carbon 203A contains the greatest number of primary active centres per unit adsorption volume and that the content of these centres decreases from active carbon 203A to active carbon 208C.

Dubinin also used water vapour adsorption for geometrical surface area determination of active carbons.[18,19]

The differential heats of adsorption of carbon dioxide and sulfur dioxide have been calculated from the integral heats of adsorption determined by means of the flow microcalorimetry. The variation of the differential heats of adsorption, q_d, with the degree of volume filling of micropores, Θ, is presented in Figures 2 and 3.
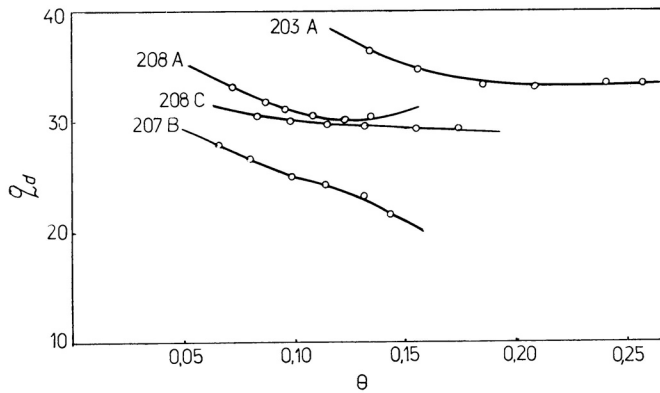

Figure 2. Variation of differential heat of adsorption of carbon dioxide at 295 K with the degree of volume filling of micropores (q_d in kJ mol^{-1}).
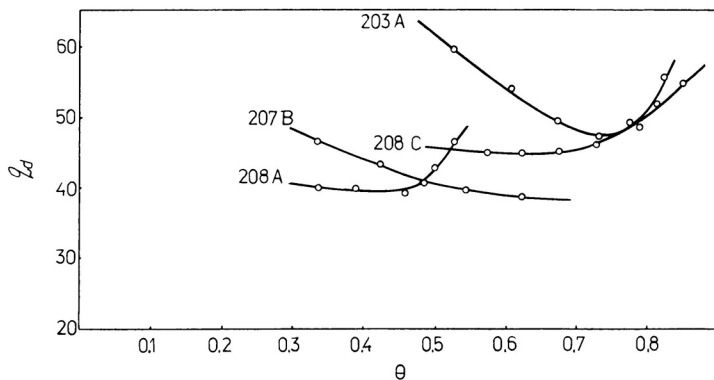

Figure 3. Variation of differential heat of adsorption of sulfur dioxide at 298 K with the degree of volume filling of micropores (q_d in kJ mol^{-1}).

The relatively high values of the differential heats of adsorption are attributed to the fact that in microporous carbons the potential field from the opposite walls overlap so that the attraction forces acting on the adsorbed molecules are stronger than on an open surface.

The higher heats of adsorption of sulfur dioxide as compared with the heats of adsorption of carbon dioxide are due to stronger adsorbate/adsorbent and adsorbate/adsorbate interactions, owing to the dipole character of the sulfur dioxide molecules. The adsorption of gases on carbonic adsorbents comprises the following three interactions: a) dispersive adsorbate/adsorbent interaction b) specific adsorbate/adsorbent interaction c) mutual adsorbate/ /adsorbate interaction. Since the above interactions are more intensive in the case of adsorption of dipole molecules, the heat evolved by adsorption of sulfur dioxide is higher than the heat evolved by adsorption of carbon dioxide.

Analysis of adsorption isotherms of other polar substances on microporous active carbons can be found in the papers of Rozwadowski and Wojsz.[20,21]

Diminution of the values of heat of adsorption at low Θ values results from the heterogeneity of the adsorbate/adsorbent interaction. As it can be seen in Figure 2, the most homogeneous interaction is in the case of adsorption on active carbon 208C. It is considered to be due to the lowest content of primary active centres and to the narrow range of pore distribution.[12] The rise of heats of adsorption of sulfur dioxide at higher Θ values results from the interaction of the adsorbed molecules.

The values of heat of adsorption are determined by the pore dimensions and by the presence of active centres. The influence of the small pore dimensions of carbon 208C is more predominant than the influence due to the content of primary active centres in carbon 207B; as a result, higher heats of adsorption are recorded by adsorption on carbon 208C than on carbon 207B. However, the higher content of primary active centres in carbon 208A as compared with carbon 208C results in a higher heat of adsorption of carbon dioxide on carbon 208A although carbon 208C contains pores with smaller dimensions than carbon 208A.[12] The heat of adsorption of sulfur dioxide on carbon 208C is higher than the heat of adsorption on carbon 208A because the adsorption of sulfur dioxide is measured at higher Θ values than the Θ values for carbon dioxide adsorption where the influence of the primary active centres on the values of heat of adsorption diminishes and the influence of the pore dimensions becomes dominant. However, the highest values of heat of adsorption of carbon dioxide and sulfur dioxide on carbon 203A are due to the remarkably high content of primary active centres.

The state of the adsorbed molecules is analyzed by the data of the differential entropy of adsorption. The values of the differential entropy of adsorption of carbon dioxide and sulfur dioxide were determined from the differential heat of adsorption and the adsorption isotherms. The entropy values are presented in Tables I and II.

TABLE I

Differential entropy of adsorption, — ΔS (J mol⁻¹ K⁻¹), of carbon dioxide at 295 K

203 A		208 A		208 C		207 B	
Θ	$-\Delta S$	Θ	$-\Delta S$	Θ	$-\Delta S$	Θ	
0.135	119.6	0.074	110.3	0.083	98.0	0.067	90.5
0.156	117.1	0.098	106.8	0.100	99.3	0.080	88.0
0.186	113.4	0.111	106.0	0.132	100.9	0.099	86.0
0.208	114.0	0.124	105.7	0.155	101.2	0.114	85.2
0.241	117.3	0.135	108.2	0.173	104.4	0.132	83.3

TABLE II

Differential entropy of adsorption, — ΔS (J mol⁻¹ K⁻¹), of sulfur dioxide at 298 K

203 A		208 A		208 C		207 B	
Θ	$-\Delta S$	Θ	$-\Delta S$	Θ	$-\Delta S$	Θ	$-\Delta S$
0.533	189.4	0.336	125.9	0.576	143.8	0.344	146.6
0.609	174.2	0.391	127.4	0.675	148.5	0.426	141.3
0.729	154.1	0.459	129.3	0.773	164.1	0.485	136.3
0.784	161.1	0.498	142.1	0.815	174.9	0.544	132.2
0.817	188.4	0.529	155.0	0.850	185.5	0.618	131.0

In order to determine the loss of the degrees of freedom of the adsorbed molecules, the values of the translational entropy of the adsorbtives in ideal gas state, $_gS_{tr}$, were calculated to be 155.8 J mol⁻¹ K⁻¹ and 160.7 J mol⁻¹ K⁻¹ for carbon dioxide and sulfur dioxide, respectively. A comparison of the data in Table I with the $_gS_{tr}$ value shows that the carbon dioxide molecules adsorbed on active carbon 203A lose most of their translational freedom of motion owing to the stronger interaction. The results in Table II show that the adsorbed molecules of sulfur dioxide almost completely lose their original translational entropy and that there is partial restriction of their vibrations and rotations, particularly marked in adsorption on active carbon 203A. The findings obtained from the entropy results for the nature of the interaction of carbon dioxide and sulfur dioxide with the microporous carbon adsorbents are in logical accordance with the findings obtained from the differential heat of adsorption.

The adsorption isotherms of carbon dioxide are interpreted in terms of the theory of volume filling of micropore by means of the Dubinin-Astakhov equation (1), Dubinin-Radushkevic-Stoeckli equation (6) and equation (4). The adsorption isotherms of carbon dioxide plotted in the linear form of the Dubinin-Astakhov equation and the characteristic adsorption curves determined experimentally and calculated from the Dubinin-Radushkevic-Stoeckli equation and equation (4) are illustrated in Figures 4 and 5.
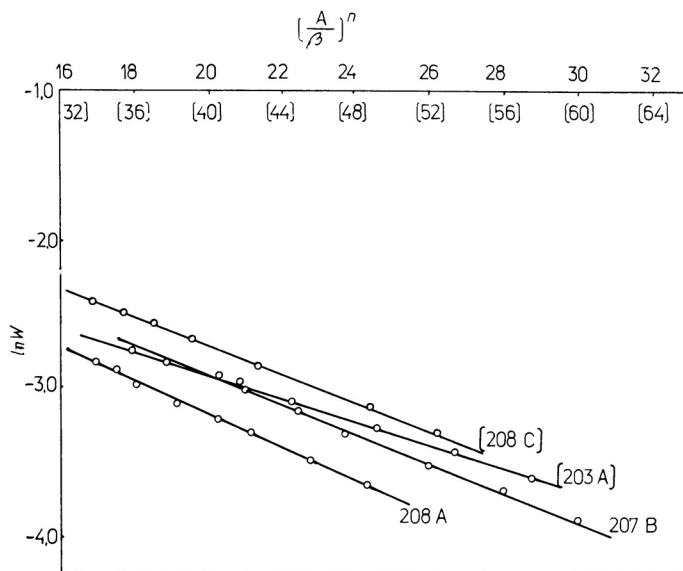
$$\left[\frac{A}{\beta}\right]^n$$

Figure 4. Dubinin-Astakhov plots for adsorption of carbon dioxide at 295 K (W in cm^3 g^{-1}, A in kJ mol^{-1}).
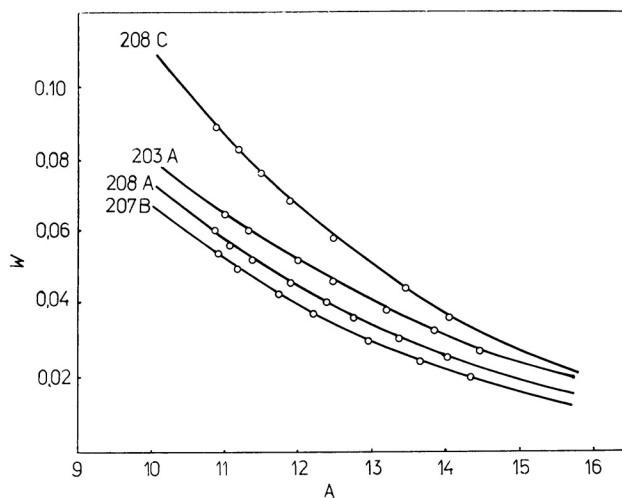

Figure 5. Characteristic curves of carbon dioxide adsorption (—○— experimental data, ——— values calculated from the equations (4) and (6)) (W in cm^3 g^{-1}, A in kJ mol^{-1}).

Figures 4 and 5 indicate that the agreement between the equations applied and the experimental adsorption data appears to be satisfactory. The differences between the experimental and theoretical values are within the limits of experimental error.

The characteristic parameters of equations (1), (4) and (6) are listed in Table III.

TABLE III

Characteristic parameters of equations (1), (4) and (6)

Active carbon	Eq. (1)		Eq. (4)	Eq. (6)	
	n	E_o (kJ mol^{-1})	k_2/k_1	Δ (K^{-2})	B_o (K^{-2})
203 A	1.72	6.72	0.272	0.93 10^{-7}	2.47 10^{-7}
208 C	1.70	6.01	0.257	1.11 10^{-7}	3.06 10^{-7}
207 B	1.45	5.01	0.088	1.60 10^{-7}	3.85 10^{-7}
208 A	1.37	4.86	0.066	1.77 10^{-7}	3.95 10^{-7}

The differential distributions of the degree of volume filling of micropores with the differential molar work of adsorption, as determined from equation (11), are shown in Figure 6.
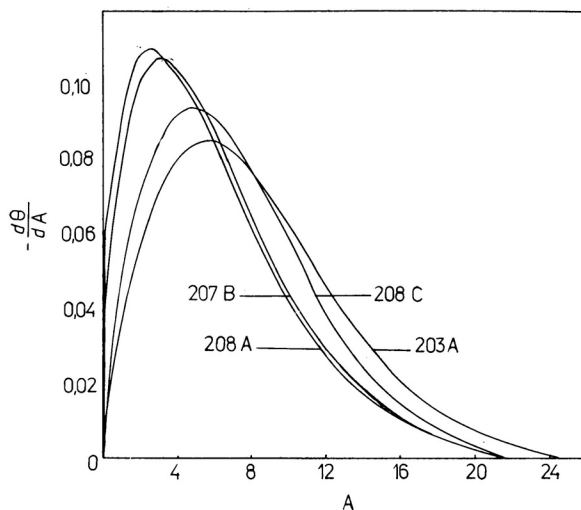

Figure 6. Differential distributions of Θ with A, determined from equation (11), (A in kJ mol^{-1}).

As it can be seen from the data presented in Table III, the values of n and k_2/k_1 decrease from carbon 203A to carbon 208A and the dispersion, Δ, increases in the same direction. This indicates that the adsorption of carbon dioxide on carbon 203A follows more close the Dubinin-Radushkevic equation than does the adsorption on the other carbons. This is usually attributed to the homogeneous micropore structure. However, the results for the distribution of the pores with respect to their dimensions[12] and the differential distribution of the degree of volume filling of the micropores with the differential molar work of adsorption, Figure 6, point out the heterogeneous character of carbon 203A. The close agreement between the Dubinin-Radushkevic equation and the adsorption data on carbon 203A is probably due

to a complex influence of the pore size distribution and the primary active centres on the equilibrium adsorption data, particularly at low Θ values.

The parameters of equation (1), n and E_o, characterize the differential distribution of Θ with A, Figure 6, whereas the parameters of equation (6), Δ and B_o, characterize the distribution presented by equation (5).

The differential heat of adsorption of carbon dioxide on active carbons 203A and 208C, determined by calorimetric measurements and calculated from a single adsorption isotherm by means of equation (4) [expressions (8), (9) and (10)], are presented in Table IV. In the case of adsorption on carbon

TABLE IV

Differential heat of adsorption of carbon dioxide at 295 K

| | Active carbon 203 A q_d (kJ mol^{-1}) | | | Active carbon 208 C q_d (kJ mol^{-1}) | |
Θ	exper.	calcul.	Θ	exper.	calcul.
0.135	36.70	29.42	0.083	30.56	29.67
0.156	35.30	29.53	0.099	30.35	29.24
0.186	33.49	28.62	0.115	30.10	28.98
0.208	33.21	27.75	0.132	29.83	28.35
0.241	33.49	27.61	0.155	29.30	27.98
0.257	33.49	27.54	0.173	29.83	27.23

203A, a considerable disagreement is noticed between the values of the differential heat of adsorption obtained from calorimetric measurements and calculated from a single adsorption isotherm. A possible explanation for this can be given as follows. The non-dipolar carbon dioxide molecule in the field of polar adsorption centres may behave like a molecule with a permanent dipole. For this reason, the bonding between the carbon dioxide molecules and the primary active centres is due to enhanced electrostatic interactions, involving the dispersion forces. As the result to the enhanced electrostatic interactions, the adsorption isotherm at arbitrary temperature calculated by means of the equations for the characteristic adsorption curves assuming the dispersion interaction only need not be exactly the same as the experimentally determined isotherm at the assumed temperature.

Owing to the two desirable properties of carbon dioxide, its small molecular dimension and high critical temperature, it is widely employed for the analysis of adsorption isotherms on active carbons.[12,15,22-25]

In conclusion, it can be underlined that the primary active adsorption centres, in addition to the distribution of the pores with respect to their dimensions, considerably influence the equilibrium and the thermodynamic adsorption data; a fact that has to be taken into account when determining degree of heterogeneity of the interaction of gases with microporous active carbons.

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SAŽETAK

Adsorpcija ugljen-dioksida, sumpor-dioksida i vodene pare na mikroporoznim aktivnim ugljenima

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Vrednosti diferencijalne topline i entropije adsorpcije ugljen-dioksida i sumpor-dioksida dobivene na 295 K odnosno 298 K, za niz mikroporoznih aktivnih ugljena, analizirane su radi određivanja prirode uzajamnog dejstva adsorbat/adsorbent.

Određena je sadržina primarnih aktivnih centara u uzorcima mikroporoznih ugljena iz adsorpcijskih izotermi vodene pare.

Adsorpcijske vrednosti za ugljen-dioksid interpretirane su jednačinama iz teorije za zapreminsko popunjavanje mikropora. Iz karakterističnih parametara primenjenih jednačina i iz termodinamičkih adsorpcijskih vrednosti određen je stepen heterogenosti mikroporoznih aktivnih ugljena.

Nađeno je da aktivni centri, pored distribucije pora prema njihovim dimenzijama, utiču na stepen heterogenosti mikroporoznih ugljenih adsorbenata.