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Chromatographic determination of the physico-chemical parameters of adsorption on activated carbon fibres

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ABSTRACT

Inverse gas chromatography was used to determine the adsorption isotherms of benzene and nitrogen on activated carbon fibres (ACFs) obtained from viscose and polyacrylonitrile cloths. For benzene the results were compared with those obtained by the static method. The entropies and pure heats of adsorption were calculated from adsorption isotherms of benzene and nitrogen determined statically and chromatographically by the method suggested by Bering and Serpinsky. The specific surface areas of these adsorbents were determined by the heat desorption method proposed by Nelsen and Eggertsen and were calculated from the isotherms by the BET method. The results were compared with the surface areas of the walls of micropores calculated assuming the slit-like model of micropores. The surface areas of the walls of micropores are smaller than those obtained using other methods. Inverse gas chromatography was used successfully for determination of the surface properties of carbon adsorbents.

INTRODUCTION

In recent years, there has been increasing interest in carbon adsorbents of the fibre type, the so-called activated carbon fibres (ACFs). They have begun to replace activated carbons, which were commonly used in pollution adsorption installations [1,2]. ACFs are obtained mainly from cellulose, viscose, polyacrylonitrile and poly(vinyl chloride) cloths and others.

In order to explain the processes occurring on the surface of ACFs, and on the surface of activated carbons, the determination of their surface properties through measurement of their porous structure, and a knowledge of the adsorption isotherms and thermodynamic functions is required. For this purpose, gravimetric and volumetric methods are widely used. These methods are accurate but time consuming. In this connection, research is in progress to find new methods that are as precise as static methods but less time consuming. Many investigators have been trying to use adsorption gas chromatography for this purpose [3–8]. The possibility of applying it in physico-chemical investigations origi-

nates from the fact that the chromatographic process is related to the properties and physico-chemical interactions of the column filling (*e.g.*, ACFs) with the analyte substances.

Adsorption gas chromatography has already been used to investigate carbon fibres with relatively small surface heterogeneity. Investigations of the adsorption phenomena have been carried out only in the Henry's law region. From the retention data the net retention volumes were calculated. From the net retention volumes at zero coverage of the surface of the adsorbate, physico-chemical parameters of the adsorption, *e.g.*, standard free energy of adsorption, surface energy, entropy of specific interactions, Kováts retention index and isosteric heat of adsorption have been calculated [9–12]. Gray and co-workers [13–16] determined adsorption isotherms using adsorption gas chromatography beyond the Henry's law region. They investigated the adsorption phenomena on the surface of cellulose fibres, darning thread, ramie cloths and Cellophane. They calculated the constants of the BET and Antoine equations and isosteric heats of adsorption from adsorption isotherms [13–16].

In this work, the adsorption isotherms of benzene and nitrogen on activated carbon fibres obtained from viscose and polyacrylonitrile cloths were determined chromatographically. From these isotherms, the constants of the Dubinin–Radushkevich (DR) and BET equations, pure heat of adsorption and molar-differential entropy of adsorption were calculated. The results for benzene obtained chromatographically are compared with those obtained by the static method.

EXPERIMENTAL

Adsorbents

The following fibrous carbon adsorbents were used: W_{w-a}, viscose fibre, carbonized at 1073 K and activated by the steam-gas method for 1 h at 1123 K; W_{w-a+k}, viscose fibre carbonized and activated in the same way as W_{w-a} and impregnated with a catalyst consisting of 6.5% (w/w) Cu(II), 3.1% (w/w) Cr(VI) and 0.035% (w/w) Ag(I); W_{p-a}, fibres obtained from polyacrylonitrile cloths, carbonized at 973 K and activated by the steam-gas method for 1 h at 1073 K; and W_{p-a+k}, polyacrylonitrile fibres carbonized and activated in the same way as W_{p-a} and impregnated with a catalyst consisting of 5.8% (w/w) Cu(II), 2.5% (w/w) Cr(VI) and 0.03% (w/w) Ag(I).

Impregnated carbon fibres (W_{w-a+k}, W_{p-a+k}) were obtained by soaking activated fibres in an aqueous solution of the complex salts of copper, chromium and silver.

Determination of adsorption isotherms by the static method

The adsorption isotherms of benzene vapour on the surfaces of activated and impregnated fibres were determined gravimetrically using a McBain–Bakr adsorption balance [17]. The sensitivity of the quartz spiral was $4.8 \cdot 10^{-3}$ kg m^{-1}. The samples of carbon fibres were degassed in a vacuum drier at 373 K and 20.6 kN m^{-2}. After degassing, the sample was thermostated at 293 K and benzene vapour was introduced.

Determination of adsorption isotherms by the chromatographic method

The chromatographic investigations were carried out by means of a Mera-Elwro 504 (INCO, Poland)

gas chromatograph with a thermal conductivity detector. The carbon fibres were placed in glass columns (65 cm × 0.2 cm I.D.). The length of the adsorbent bed in column was 15–18 cm, which corresponded to 0.10–0.15 g depending on the kind of carbon fibre used. The part of the column that was not occupied by the ACF bed was filled with glass beads of mesh size 0.20–0.25 mm [18]. The filled column was mounted in the chromatograph thermostat and heated for 8 h at 453 K in a stream of hydrogen flowing at 40 cm^3 min^{-1}. Benzene and nitrogen were used as adsorbates. Benzene was injected into the column by means of a Hamilton microsyringe. The size of the samples introduced was 45–50 μl. Nitrogen was injected into the column by means of the six-way sampler valve. The size of the sample introduced was 5.732 cm^3. The adsorption isotherms were determined at 293 and 373 K. The temperature of the injection device and of the detector was 473 K. During the measurement at 293 K the columns were placed in a water-bath cooler to thermostat the carbon fibre bed. The fluctuations of the thermostat temperature, as measured by means of Anschütz thermometers, did not exceed 0.2 K. The adsorption isotherms of nitrogen were determined at 77 K. The temperature of the injection device and of the detector was 293 K. In the determination of the isotherms, hydrogen purified and dried over Carbosorbit N active carbon and molecular sieves 5A was used.

The pressures and the corresponding adsorption values were calculated from the following equations:

$$p = \frac{m_a q R T_c h}{S_{peak} v_0} \tag{1}$$

$$a = \frac{m_a S_{ads}}{m S_{peak}} \tag{2}$$

where

m_a = amount of the adsorbate injected (mmol);

m = mass of the adsorbent in the column (g);

v_0 = reduced carrier gas flow-rate (cm^3 min^{-1}):

$$v_0 = \frac{v T_c (p_0 - p_{H_2O})}{T_0 p_0} \cdot \frac{3\left(\dfrac{p_i}{p_0}\right)^2 - 1}{2\left(\dfrac{p_i}{p_0}\right)^3 - 1}$$

v = carrier gas flow-rate at the column temperature (cm^3 min^{-1});

q = speed of the recording tape (cm min^{-1});
R = universal gas constant;
T_c = temperature of the column (K);
T_0 = temperature of the environment (K);
p_i = pressure at the column inlet;
p_0 = pressure at the column outlet;
h = height of the peak (cm);
p_{H_2O} = pressure of water vapour at the temperature of the environment;
S_{peak} = total surface area of the peak (cm^2).

When the isotherms were determined from the peak maximum, the S_{ads} value corresponded to the adsorption surface area (in cm^2) of the tested adsorbate sample. When the peak profile method was used, the value S_{ads} was found by dividing the adsorption surface area into n parts.

The peaks obtained were unsymmetrical for all the adsorption systems. This indicates the dominating effect of diffusion on the rate of establishment of adsorption equilibrium. Therefore, when calculating the adsorption isotherms we took into account the effect of diffusion of the adsorbate in the ACF bed on adsorption in accordance with the postulates of Dollimore *et al.* [19].

Determination of specific surface area

The specific surface areas of the investigated ACFs were determined by Nelsen and Eggertsen's method, which is known as the heat desorption method [20]. The column with the carbon fibre bed was immersed in liquid nitrogen. A stream of H_2–N_2 mixture was passed through the column. This mixture, of known composition, was obtained previously by mixing the streams of adsorbate and carrier gas. The amount of nitrogen adsorbed by the adsorbent bed at a given relative pressure was calculated from the desorption peak because it was more symmetrical. Each experiment performed for one concentration of adsorbate in the mixture resulted in one point on the adsorption isotherm.

The partial pressure of the adsorbate was calculated from the equation

$$p = \frac{v_{ads}}{v_p} \cdot p_b \qquad (3)$$

where

v_{ads} = volumetric flow-rate of the adsorbate (cm^3 min^{-1});
v_p = volumetric flow-rate of the H_2–N_2 mix-

ture through the carbon fibre bed during measurement (cm^3 min^{-1});
p_b = barometric pressure.

The appropriate values of adsorption for the above pressure were calculated from the expression

$$a = kS_{peak} \cdot \frac{v_p}{v_k} \qquad (4)$$

where

k = detector constant determined from a calibration plot [21] [from the function $S_{peak}v_k = \xi(m_a q)$];
S_{peak} = area of the desorption peak (cm^2);
v_k = volumetric flow-rate of the H_2–N_2 mixture during calibration (cm^3 min^{-1}).

Microscope investigation

The investigation of the surface morphology of activated carbon fibres was carried out by scanning electron microscopy (SEM) with a Tesla BS-300 microscope. These were only qualitative measurements.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the typical surface morphology of ACFs obtained from viscose and impregnated with catalysts, respectively. SEM of these ACFs did not reveal any substantial morphological changes of the fibre surface caused by the activation process. This suggests that activation causes changes mainly in the internal structure [22]. In Fig. 2 there are bright and dark spots which depend on the hue of the base. They probably represent the catalyst distributed on the surface of the ACF. They should disappear with a uniform concentration of the catalyst on the surface of the carbon fibre.

In Figs. 3 and 4, the adsorption isotherms for benzene vapour on the surface of the ACFs used, determined at 293 K by the static method, are compared with those found chromatographically at 293 and 373 K. It can be concluded that the chromatographic measurements at 293 K yield lower adsorption values than those obtained by the static method. The adsorption isotherms of nitrogen determined chromatographically at 77 K are shown in Fig. 5.

In order to characterize better the ACFs used, the constants of the two-term Dubinin–Radushkevich
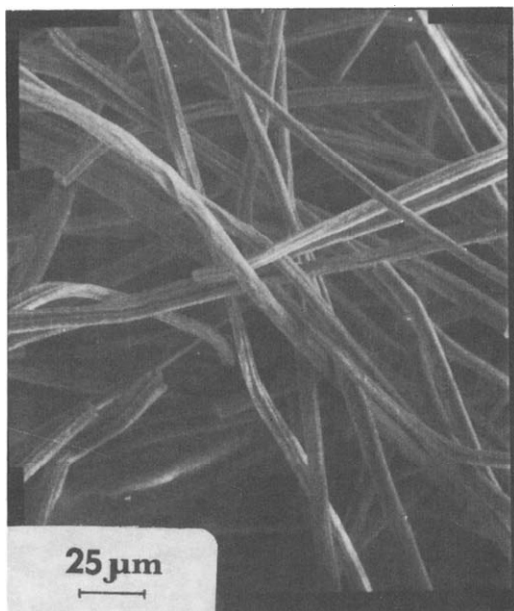
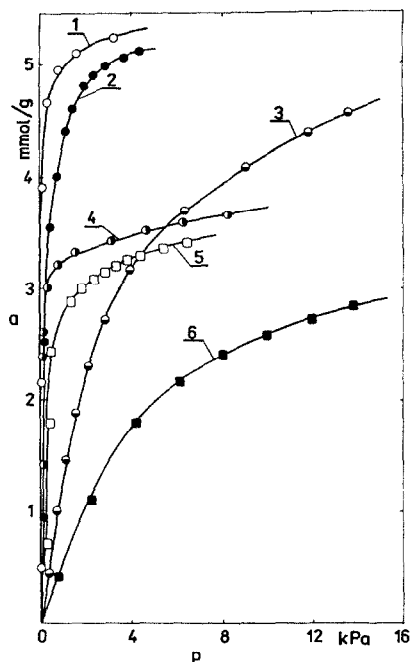Fig. 1. Microphotograph of activated carbon fibres obtained from viscose.

Fig. 3. Adsorption isotherms of benzene determined by the static method at 293 K (1, 4) and by the chromatographic method at 293 K (2, 5) and at 373 K (3, 6) on the ACFs obtained from viscose cloths.
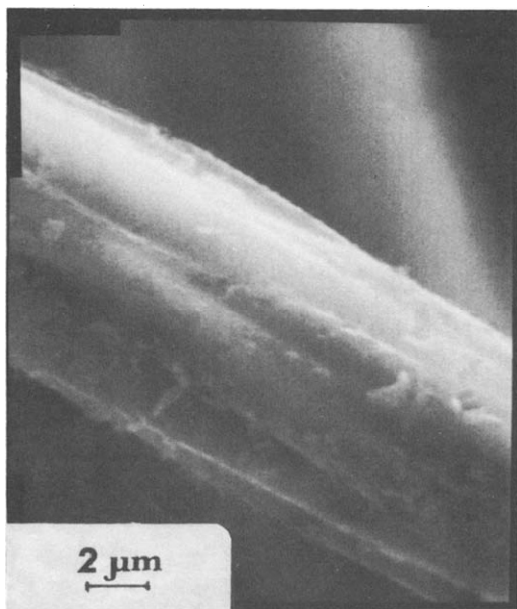

Fig. 2. Microphotograph of carbon fibres obtained from viscose, activated and impregnated with catalysts.
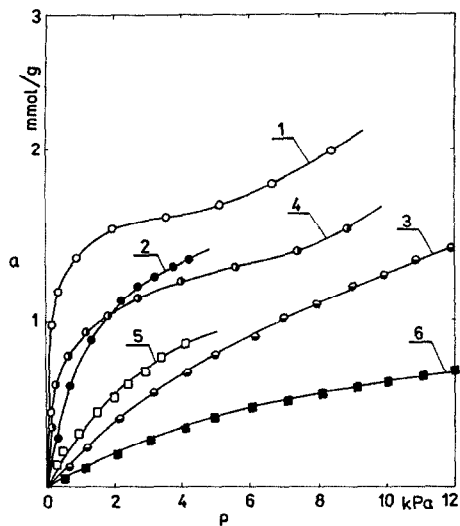

Fig. 4. Adsorption isotherms of benzene determined by the static method at 293 K (1, 4) and by the chromatographic method at 293 K (2, 5) and at 373 K (3, 6) on the ACFs obtained from polyacrylonitrile cloths.
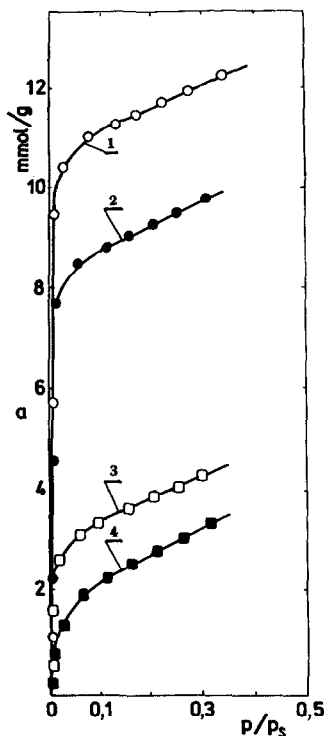
Fig. 5. Adsorption isotherms of nitrogen determined by the chromatographic method at 77 K on the ACFs: (1) W_{w-a}; (2) W_{w-a+k}; (3) W_{p-a}; (4) W_{p-a+k}.
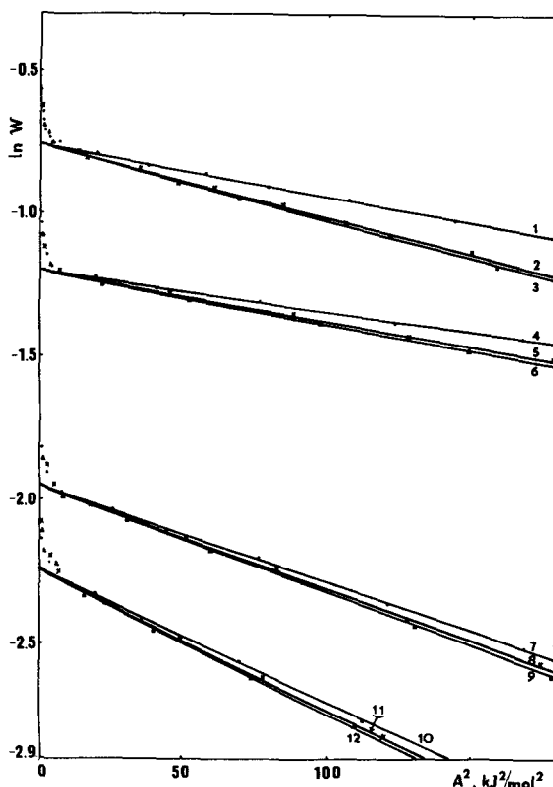

Fig. 6. Changes in the characteristic curves of the DR equation calculated from the adsorption isotherms of benzene determined statically at 293 K (1, 4, 7, 10) and chromatographically at 293 K (3, 6, 9, 12) and at 373 K (2, 5, 8, 11) on the surfaces (1, 2, 3) W_{w-a}, (4, 5, 6) W_{w-a+k}, (7, 8, 9) W_{p-a} and (10, 11, 12) W_{p-a+k} for the first (I) structure of pores.

(DR) equation were calculated from the benzene and nitrogen isotherms. The adsorption isotherms which were determined statically and chromatographically at 293 and 373 K are shown using linear coordinates of the DR equation (also called the characteristic adsorption equation [23]):

$$\ln W = \ln W_0 - \left(\frac{1}{\beta E_0}\right)^2 A^2 \qquad (5)$$

where

W = volume of the adsorption sphere of micropores (cm^3 g^{-1});

W_0 = limiting volume of the adsorption sphere of micropores (cm^3 g^{-1});

β = affinity coefficient;

A = differential molar work of adsorption (kJ mol^{-1});

E_0 = characteristic adsorption energy (kJ mol^{-1}).

A graph for the first structure of micropores is shown in Fig. 6 and that for the second structure in Fig. 7. The results are also given in Tables I and II. For every adsorption system the characteristic curves calculated from statically determined adsorption isotherms of benzene are above those calculated from the chromatographically determined adsorption isotherms. The characteristic curves calculated from adsorption isotherm of benzene at 293 K, determined chromatographically, are below those calculated from the adsorption isotherms determined chromatographically at 373 K.

It is possible to explain the temperature dependence of the characteristic curves when it is taken into account that part of the adsorption sphere is inaccessible to the adsorbate molecules. Dubinin et
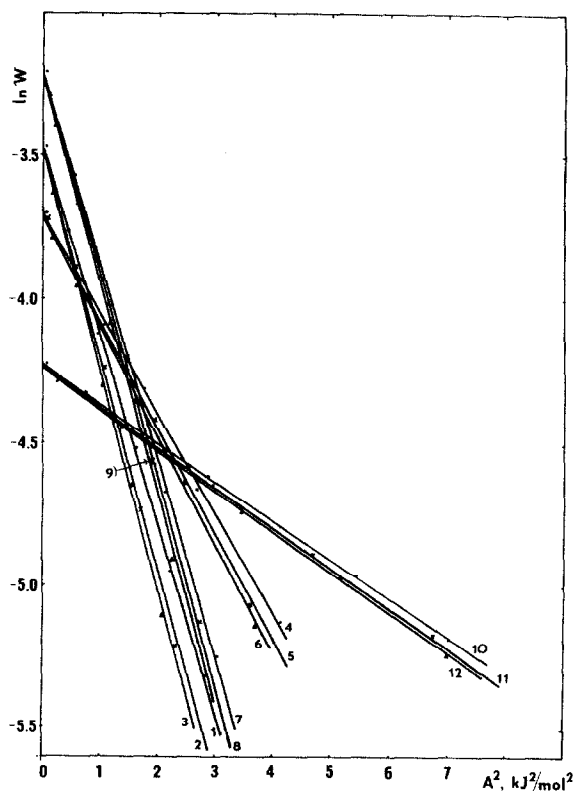
Fig. 7. Changes in the characteristic curves of the DR equation at 293 and 373 K for benzene on the ACFs for the second (II) structure of pores. Notation as in Fig. 6.

al. [24,25] suggested that this effect increases with increase in the linear dimensions of the adsorbate molecules and with decrease in the geometric dimensions of the entrances into the micropores. This effect was observed during static measurements. In adsorption from the stream of the adsorbate–carrier gas mixture flowing through the ACF bed in the column, this effect will probably increase. The diffusion coefficient increases with increase in temperature. Therefore, at higher temperatures the ACF bed in the column is better penetrated by the adsorbate molecules from the stream of the adsorbate–carrier gas mixture and therefore the values of W_0 are higher at higher temperatures.

The limiting volumes of the adsorption sphere for the first (I) and second (II) structures of pores calculated from adsorption isotherms determined statically are higher than the values calculated from chromatographic measurements.

From the results of the measurements presented in Figs. 3–5 and the numerical data in Tables I and II, we can say that the investigated ACFs are characterized by a highly developed structure of micropores, low values of W_{02} and high values of the structure–energy constants B_2. Deposition of the chromium–copper–silver catalyst on the surface of carbon fibres causes a decrease in the physical adsorption capacity of the ACFs.

The coefficients of the linear regression of the DR equation indicate that the linearity of this equation is better fulfilled for chromatographic measurements (for benzene as the adsorbate) at 373 K than 293 K.

The linearity for the second (II) pore structure for every adsorption system is worse than that for the first (I) pore structure. The values of the limiting volume of the adsorption sphere of micropores calculated from the DR equation were compared with the values of the volume of the monolayer W_m calculated from the BET equation [26]:

$$\frac{1}{(1-h)W} = \frac{1}{W_m c} + \frac{c-1}{W_m c} \cdot h \tag{6}$$

where

$W_m = a_m v$ = volume of monolayer (cm^3 g^{-1});

v = molar volume of adsorbate at the measurement temperature (cm^3 mmol^{-1});

c = constant of the BET equation;

h = relative pressure of adsorbate ($5 \cdot 10^{-3} < h < 0.1$).

Dubinin [26] suggested that the value of W_m calculated from the BET equation for the range of relative pressure of adsorbate $5 \cdot 10^{-3} < h < 0.1$ more accurately describes the structure of a monolayer compared with the value W_m calculated for the range $0.05 < h < 0.35$ usually used by other workers.

The constants of the BET equation (W_m and c) and the specific surface areas calculated for the investigated ACFs are given in Tables III and IV. In Table IV results of measurements of specific surface areas determined by the heat desorption method are also presented.

The specific surface areas were calculated from the following equation:

$$S \ (\text{m}^2 \ \text{g}^{-1}) = 602.3 \cdot \frac{\omega}{v} \cdot W_m \tag{7}$$

where

TABLE I

PARAMETERS OF THE TWO-TERM DUBININ–RADUSHKEVICH EQUATION CALCULATED FROM ADSORPTION ISOTHERMS OF BENZENE DETERMINED STATICALLY (Stat.) AT 293 K AND CHROMATOGRAPHICALLY (Chrom.) AT 293 AND 373 K

Carbon fibre	T (K)	W_{01} (cm³ g⁻¹)		E_{01} (kJ mol⁻¹)		$B_1 \cdot 10^6$ (K⁻²)		r^a	
		Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.
W_{w-a}	293	0.4225	0.3893	21.06	19.06	0.83	1.01	0.9993	0.9924
W_{w-a}	373	–	0.4001	–	19.60	–	0.94	–	0.9932
W_{w-a+k}	293	0.2869	0.2796	24.84	23.46	0.59	0.67	0.9977	0.9912
W_{w-a+k}	373	–	0.2814	–	23.82	–	0.65	–	0.9959
W_{p-a}	293	0.1160	0.0981	16.49	16.13	1.35	1.41	0.9968	0.9913
W_{p-a}	373	–	0.1022	–	16.36	–	1.37	–	0.9992
W_{p-a+k}	293	0.067	0.048	15.48	15.00	1.53	1.63	0.9991	0.9889
W_{p-a+k}	373	–	0.054	–	15.42	–	1.54	–	0.9975

		W_{02} (cm³ g⁻¹)		E_{02} (kJ mol⁻¹)		$B_2 \cdot 10^6$ (K⁻²)		r^a	
		Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.
W_{w-a}	293	0.014	0.010	1.25	1.21	235.9	250.5	0.9910	0.9898
W_{w-a}	373	–	0.012	–	1.23	–	241.4	–	0.9910
W_{w-a+k}	293	0.013	0.010	1.88	1.65	104.0	134.7	0.9903	0.9885
W_{w-a+k}	373	–	0.012	–	1.69	–	128.5	–	0.9921
W_{p-a}	293	0.020	0.019	1.23	1.20	245.2	254.7	0.9915	0.9899
W_{p-a}	373	–	0.020	–	1.22	246.4	–	0.9930	
W_{p-a+k}	293	0.008	0.007	2.83	2.66	45.9	51.8	0.9902	0.9894
W_{p-a+k}	373	–	0.008	–	2.69	–	50.6	–	0.9920

^{a} r = Linear regression coefficient.

ω = surface area occupied by one adsorbate molecule in the monolayer (nm²) (ω = 0.162 for nitrogen and 0.410 for benzene);

v = molar volume of adsorbate at the measurement temperature by the method proposed

by Nikolajev and Dubinin [27] (cm³ mmol⁻¹) (for nitrogen at 77 K v = 0.0346 and for benzene at 293 K v = 0.0889 and at 373 K v = 0.1053).

The widening of the theory for the volume filling

TABLE II

PARAMETERS OF THE TWO-TERM DUBININ–RADUSHKEVICH EQUATION CALCULATED FROM ADSORPTION ISOTHERMS OF NITROGEN DETERMINED CHROMATOGRAPHICALLY AT 77 K

Carbon fibre	W_{01} (cm³ g⁻¹)	E_{01} (kJ mol⁻¹)	$B_1 \cdot 10^6$ (K⁻²)	r	W_{02} (cm³ g⁻¹)	E_{02} (kJ mol⁻¹)	$B_2 \cdot 10^6$ (K⁻²)	r
W_{w-a}	0.3988	19.25	0.99	0.9988	0.1213	2.44	61.7	0.9895
W_{w-a+k}	0.2992	19.14	1.00	0.9953	0.098	2.38	64.6	0.9912
W_{p-a}	0.1185	11.96	2.56	0.9899	0.068	2.44	61.6	0.9907
W_{p-a+k}	0.069	9.94	3.71	0.9912	0.022	2.94	42.3	0.9908

TABLE III

PARAMETERS OF THE BET EQUATION AND THE SPECIFIC SURFACE AREAS OF THE ACFs CALCULATED FROM ADSORPTION ISOTHERMS OF BENZENE AT 293 AND 373 K

Carbon fibre	T (K)	c		W_m (cm^3 g^{-1})		r		S_{BET} (m^2 g^{-1})	
		Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.
W_{w-a}	293	169.4	172.2	0.3586	0.3618	0.9985	0.9914	995.6	1004.5
W_{w-a}	373	–	73.6	–	0.3612	–	0.9986	–	846.7
W_{w-a+k}	293	86.6	71.6	0.2786	0.2862	0.9998	0.9944	773.5	794.6
W_{w-a+k}	373	–	60.2	–	0.2876	–	0.9995	–	674.1
W_{p-a}	293	49.3	10.4	0.1125	0.1114	0.9990	0.9896	312.4	309.3
W_{p-a}	373	–	9.2	–	0.1120	–	0.9996	–	263.3
W_{p-a+k}	293	12.2	6.2	0.0673	0.0648	0.9966	0.9910	186.9	179.9
W_{p-a+k}	373	–	6.6	–	0.0619	–	0.9996	–	147.4

of micropores on adsorbents with a non-homogeneous micropore structure [28] creates new possibilities for describing the porosity of ACFs. Assuming the slit-like model of micropores, it is possible to describe the volume distribution of micropores as a function of half-width, x_0, in the slit-like model:

$$x_0 = k_0/E_0 \qquad (8)$$

where k_0 is a parameter depending on E_0, being described by the experimental equation

$$k_0 = 13.028 - 1.53 \cdot 10^{-5} E_0^{3.5}$$

For each increase in the elementary volume of the micropores, dW is responsible for the increase in the elementary geometric area of their walls, dS_g:

$$dS_g = \frac{dW}{x_0} \cdot 10^3 \qquad (9)$$

Introducing additional assumptions, Dubinin simplified eqn. 9 to a simple mathematical expression which makes it possible to calculate the geometric surface area of micropore walls. For the two-term DR equation its form is as follows:

$$S_g \ (\text{m}^2 \text{g}^{-1}) = \left(\frac{W_{01}}{x_{01}} + \frac{W_{02}}{x_{02}} \right) \cdot 10^3 \qquad (10)$$

The parameters calculated according to eqns. 8 and 10 are given in Tables V and VI. The values of the specific surface area calculated from the adsorption isotherms of benzene and nitrogen determined statically and chromatographically differ from the values of the surface area of the walls of micropores calculated from these isotherms.

Bering et al. [29] stated that the concept of the specific surface area in the case of materials with a

TABLE IV

THE PARAMETERS OF THE BET EQUATION AND SPECIFIC SURFACE AREAS OF THE ACFs CALCULATED FROM ADSORPTION ISOTHERMS OF NITROGEN AT 77 K (S_{BET}) AND DETERMINED BY THE HEAT DESORPTION METHOD (S_d)

Carbon fibre	c	W_m (cm^3 g^{-1})	r	S_{BET} (m^2 g^{-1})	S_d (m^2 g^{-1})
W_{w-a}	353.5	0.3557	0.9976	1002.6	998.6
W_{w-a+k}	244.8	0.2810	0.9985	792.0	785.7
W_{p-a}	212.9	0.1087	0.9981	306.4	305.3
W_{p-a+k}	89.1	0.0698	0.9991	196.7	191.8

TABLE V

GEOMETRIC SURFACE AREAS OF THE WALLS OF PORES AND HALF-WIDTHS OF THEIR SLITS CALCULATED FROM ADSORPTION ISOTHERMS OF BENZENE DETERMINED STATICALLY AND CHROMATOGRAPHICALLY AT 293 AND 373 K ON USED ACFs

Carbon fibre	T (K)	x_{01} (nm)		S_{g1} (m^2 g^{-1})		x_{02} (nm)		S_{g2} (m^2 g^{-1})		S_g (m^2 g^{-1})	
		Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.	Stat.	Chrom.
W_{w-a}	293	0.618	0.682	684.5	570.4	10.400	10.743	1.3	0.9	685.8	571.3
	373		0.658		607.9		10.569		1.1		609.0
W_{w-a+k}	293	0.521	0.556	550.9	504.0	6.915	7.879	1.9	1.3	552.8	505.3
	373		0.547		513.7		7.692		1.6		515.3
W_{p-a}	293	0.789	0.806	147.0	121.6	10.656	10.833	1.9	1.8	148.9	123.4
	373		0.795		129.3		10.656		1.9		130.2
W_{p-a+k}	293	0.840	0.867	79.8	55.4	4.594	4.887	1.7	1.4	81.5	56.8
	373		0.842		64.1		4.833		1.7		65.8

highly developed pore structure has no physical meaning, because no independent method for determining this area is known. However, if it is assumed that the BET surface area characterizes well the range of the micropores, mesopores and macropores in the case of carbon materials, this parameter can be used to describe the structure of the ACFs.

In Figs. 8 and 9, the values of the pure heats of adsorption of benzene and nitrogen, calculated by the method suggested by Bering and Serpinsky [30–32], from chromatographic measurements are compared with the pure heats of adsorption calculated from static measurements. For all the adsorption systems used, the pure heats of adsorption calculated from chromatographic measurements are lower than those calculated from static measurements. The greatest difference occurs in the initial range of coverages. An increase in temperature of 90 K causes a decrease in the pure heat of adsorption of *ca.* 12 kJ mol^{-1} for viscose-based ACFs and *ca.* 14 kJ mol^{-1} for polyacrylonitrile-based ACFs. Higher values for the pure heat of adsorption for benzene and nitrogen were obtained for viscose-based than for polyacrylonitrile-based ACFs.

Fig. 10 shows the variation of the molar differential entropy of adsorption of the adsorbates on viscose-based ACFs. Every adsorption system was characterized by a negative entropy.

CONCLUSIONS

The chromatographic method may be used successfully to characterize the adsorption properties of the ACFs. The fundamental advantages of the chromatographic method are speed, high reproduci-

TABLE VI

GEOMETRIC SURFACE AREAS OF THE WALLS OF PORES AND HALF-WIDTHS OF THEIR SLITS CALCULATED FROM ADSORPTION ISOTHERMS OF NITROGEN DETERMINED CHROMATOGRAPHICALLY AT 77 K ON USED ACFs

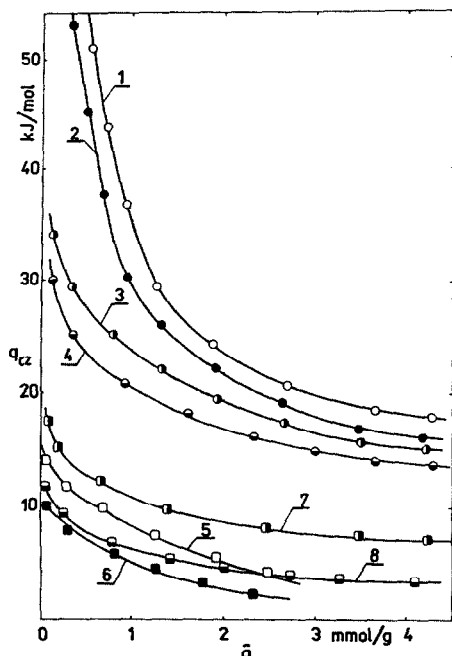| Carbon fibre	x_{01} (nm)	S_{g1} (m^2 g^{-1})	x_{02} (nm)	S_{g2} (m^2 g^{-1})	S_g (m^2 g^{-1})
W_{w-a}	0.675	591.1	5.328	22.7	613.8
W_{w-a+k}	0.679	440.4	5.462	17.9	458.3
W_{p-a}	1.087	109.5	5.328	12.8	122.3
W_{p-a+k}	1.308	52.8	4.422	5.0	57.8

Fig. 8. Changes in the pure heats of adsorption on the activated (1, 3, 5, 7) and impregnated (2, 4, 6, 8) ACFs obtained from viscose cloths calculated by the BS method from adsorption isotherms of benzene (1, 2, 3, 4, 5, 6) and nitrogen (7, 8) determined statically at 293 K (1, 2) and chromatographically at 77 K (7, 8), 293 K (3, 4) and 373 K (5, 6).
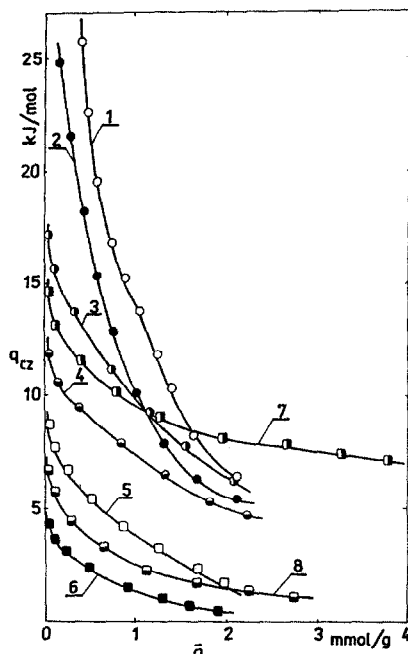

Fig. 9. Changes in the pure heats of adsorption on the activated (1, 3, 5, 7) and impregnated (2, 4, 6, 8) ACFs obtained from polyacrylonitrile cloths calculated by the BS method from adsorption isotherms of benzene (1, 2, 3, 4, 5, 6) and nitrogen (7, 8) determined statically at 293 K (1, 2) and chromatographically at 77 K (7, 8), 293 K (3, 4) and 373 K (5, 6).

bility of the adsorption systems and the possibility of investigating the adsorption phenomena in the initial range of coverges.

The isotherms obtained for all the systems studied are convex with respect to the pressure axis, indicating that the adsorbate–adsorbent interactions have a dominant effect on the initial progress of adsorption of the adsorbates.

The observed differences in the adsorption values and the pure heats of adsorption found from static and dynamic measurements may be due to (i) blocking of the active adsorption sites on the adsorbent surface by the carrier gas molecules and (ii) the so-called molecular sieve effect connected with the similarity of the dimensions of the adsorbate molecules and the entrances to the pores, which results in the whole adsorption volume of the micropores not being filled with the adsorbate in the chromatographic process; W_0 values calculated from the chromatographic measurements are higher at higher temperatures.

The viscose ACFs are characterized by a higher ability to adsorb benzene vapor and nitrogen compared with polyacrylonitrile-based ACFs.
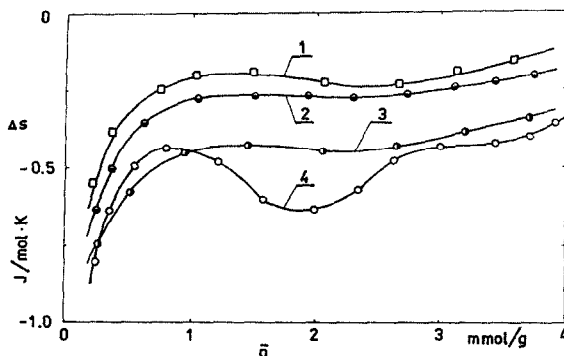

Fig. 10. Changes in the molar differential entropy of adsorption of nitrogen (1) and benzene (2, 3, 4) calculated by the BS method from adsorption isotherms, determined statically at 293 K (4) and chromatographically at 77 K (1), 293 K (3) and 373 K (4) on the surface of W_{w-a}.

The values of the specific surface areas of ACFs calculated by the BET method from the adsorption isotherm of benzene determined statically and chromatographically at 293 K are similar to the results obtained by the heat desorption method.

Taking into account the contribution of micropores to the general porosity of ACFs, it can be concluded that there is a similarity between ACFs and activated carbons of good quality.

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