

## **Chromatographic determination of the physico-chemical parameters of adsorption on active carbons**

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### **ABSTRACT**

The adsorption isotherms of several polar and non-polar compounds on active carbons with modified surfaces were determined chromatographically at different temperatures. The results were compared with those obtained by the static method. The entropies and heats of adsorption were calculated from the adsorption isotherms and compared with the values obtained from calorimetric measurements. The results were closest for adsorbents with a weakly developed microporous structure. The effect of the carrier gas flow-rate through the adsorbent bed in the column on the shape of the chromatographically determined adsorption isotherm was tested. The linear forms of equations corresponding to the BET, Hüttig, Kiselev and Hill physical adsorption models were used. The adsorption isotherms of aliphatic alcohols chromatographically were best described in terms of the Hill model.

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### **INTRODUCTION**

In recent years, a good knowledge of the processes taking place on the phase boundary has become very important. The most important of these processes include, for both practical and theoretical reasons, primarily adsorption and heterogeneous catalysis [1]. The explanation of processes proceeding on the surfaces of adsorbents and catalysts requires the determination of their surface area and porous structure, in addition to the adsorption isotherms and thermodynamic functions. For this purpose common and widely used static methods are applied. These methods are fairly accurate but time consuming.

A more rapid method of testing adsorbents and catalysts is afforded by adsorption gas chromatography [2,3]. The possibility of applying it in physico-chemical investigations follows from the fact that chromatographic separation is related to the properties and physico-chemical interactions of the column filling (*e.g.*, adsorbent or catalyst) with the chromatographed substances. The carrier gas also has some influence, but its effect is minor so in practice the course of the chromatographic process depends predominantly on the properties of the adsorbent and the chromatographed substance (adsorbate). The properties of the adsorbate-adsorbent system can be characterized by adsorption isotherms. The latter can be determined chromatographically and from them the basic physico-chemical quantities characterizing the adsorbent can be found. The chromatographic method supplements the static proce-

dures which are fundamental for studying the adsorption mechanism, and the adsorbate-adsorbent as well as the competitive adsorbate-adsorbate interactions. Chromatography allows adsorption to be studied at very small coverages of the surface and at elevated temperatures. Static measurements are very difficult and in some instances impossible under these conditions.

In the literature one can find many examples showing that the chromatographic method is useful in investigations of adsorption. However, there are still doubts, mainly as to the range of its application and the related reliability of the results obtained. It was therefore decided that a systematic study of the usefulness of the chromatographic method for investigating carbon adsorbents, with surfaces modified by superficial oxidation, deposition of transition metal cations and silanization, using different adsorbents was necessary.

The chromatographically determined adsorption isotherms were used to test the suitability of equations corresponding to the models of physical adsorption on homogeneous surfaces for interpreting the adsorbate-adsorbent and adsorbate-adsorbate interactions on the surfaces of several active carbons. The results obtained by adsorption gas chromatography are compared with those obtained by static methods.

## EXPERIMENTAL

### *Adsorbents*

The following carbon adsorbents were used in the study: active carbon, obtained by the steam-gas method from hard coal, and denoted A-2, and its modifications obtained by mild oxidation in aqueous nitric acid by the method of Rychlicki [4] (denoted A-2o), by deposition of copper and chromium salts by the Alves and Clark method [5] and by silanization with trimethylchlorosilane (TMCS) by the Wójcik and Karpiński method [6] (denoted S1-S6); and active carbon SKS-2, obtained from commercial porous styrene-divinylbenzene copolymers in the form of spherical particles (supplied by the Institute of General and Inorganic Chemistry, Kiev, USSR).

The active carbons and their modifications were fractionated and degassed in a vacuum drier at 453 K and  $1.5-2.5 \text{ kN m}^{-2}$  for 10 h. For adsorbents A-2, A-2o and S1-S6 the 0.250-0.300 mm fraction and for SKS-2 the 0.250-0.315 mm fraction was used.

In order to characterize the adsorbents, their apparent and real densities were measured, using toluene as the pycnometric liquid, and the volumes of the micropores and mesopores and the constants in the two-term Dubinin-Radushkevich (DR) equation [7,8] were calculated from the isotherms benzene vapour adsorption determined at 293 K after degassing at  $1.33 \cdot 10^{-3} \text{ N m}^{-2}$ . The characteristics of the tested adsorbents are given in Table I.

### *Chromatographic measurements*

The chromatographic investigations were carried out using a Mera-Elwro 504 gas chromatograph with a thermal conductivity detector. The adsorbents were placed in glass columns (65 cm  $\times$  2 mm I.D.) with an adsorbent bed length of 8-15 cm, which corresponded to 0.12-0.35 g depending on the kind of active carbon used. The part of the column that was not occupied by the adsorbent was filled with glass beads

TABLE I  
CHARACTERISTICS OF THE PORE STRUCTURE OF THE ADSORBENTS USED

Parameter	A-2	A-2o	Amount of catalyst on support A-2o (%)						SKS-2
			0.99 Cr(VI): S1	2.00 Cr(VI): S2	2.69 Cr(VI): S3	4.27 Cu(II): S4	2.00 Cr(VI), 6.44 Cu(II): S5	2.00 Cr(VI), 6.44 Cu(II), TMCS: S6	
Apparent density, $d_{app}$ (g dm <sup>-3</sup> )	1.015	1.150	1.020	1.100	1.140	1.010	0.995	1.055	0.800
Solid density, $d_{real}$ (g dm <sup>-3</sup> )	1.600	1.700	1.620	1.640	1.700	1.650	1.680	1.780	1.680
Volume of micropores, $V_{mi}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.306	0.284	0.280	0.276	0.268	0.240	0.218	0.200	0.399
Volume of mesopores, $V_{me}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.235	0.231	0.235	0.214	0.217	0.170	0.157	0.130	0.322
$\frac{100V_{mi}}{V_{mi} + V_{me}}$ (%)	55.67	55.18	54.36	56.33	55.26	58.54	58.13	60.61	64.25
Constants of the Dubinin-Radushkevich equation:									
$W_{o1}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.151	0.192	0.152	0.155	0.157	0.155	0.162	0.166	0.220
$W_{o2}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.182	0.126	0.122	0.118	0.115	0.097	0.078	0.070	0.182
$B_1 \cdot 10^6$ (K <sup>-2</sup> )	0.460	0.580	0.480	0.520	0.550	0.580	0.630	0.650	0.630
$B_2 \cdot 10^6$ (K <sup>-2</sup> )	2.310	2.510	2.420	2.480	2.450	2.490	2.520	2.580	2.600

of the same mesh size [9]. The packed column was mounted in the chromatograph thermostat and heated for 8 h at 453 K in stream of argon at a flow-rate of 50 cm<sup>3</sup> min<sup>-1</sup>.

The following adsorbates were used in the tests: benzene and cyclohexane (pure for chromatography) and methanol, ethanol and *n*-propanol (analytical-reagent grade). The purities were additionally checked chromatographically in a capillary column filled with a liquid crystal stationary phase.

The adsorbates were injected into the column by means of a Hamilton micro-syringe. The amount of sample introduced depended on the method used to determine the isotherm. Two procedures were used for this purpose: determination from the peak maximum and determination from the peak profile [2]. In the first procedure different amounts of the adsorbates ranging from 3 to 50 μl were injected. In the second procedure the size of the sample was 30–50 μl or 12 μl. When larger amounts of the adsorbates were injected it was possible to determine the isotherms up to a relative pressure of about 0.3. With smaller samples a more accurate determination of the initial section of the isotherm was possible up to a relative pressure of about 0.1.

The adsorption isotherms were determined at 298 K and in the range from 373–423 K in 10 K steps at carrier gas flow-rates (measured by means of a bubble gauge) ranging from 30 to 70 cm<sup>3</sup> min<sup>-1</sup> in 10 cm<sup>3</sup> min<sup>-1</sup> steps. The temperature of the injection device and of the detector was 473 K. The fluctuations of the thermostat temperature, as measured by means of Anschütz thermometers, did not exceed 0.1 K.

In the determination of the isotherms, the carrier gases used, purified and dried

on Carbosorbit N active carbon and on molecular sieves 5A, were argon, helium and hydrogen. When helium or hydrogen was used, after the initial heat treatment of the carbon in a stream of argon the latter was replaced with helium or hydrogen and the selected gas was passed through the column for at least 2 h before starting the measurements.

The pressures ( $p$ ) and the corresponding adsorption values ( $a$ ) were calculated from the following equations:

$$p = \frac{m_a q R T_c h}{S_{\text{peak}} v_0} \quad (1)$$

$$a = \frac{m_a S_{\text{ads}}}{m S_{\text{peak}}} \quad (2)$$

where

$m_a$  = amount of the adsorbate injected (mmol);  $m$  = mass of adsorbent in the column (g);  $v_0$  = reduced carrier gas flow-rate ( $\text{cm}^3 \text{min}^{-1}$ );

$$v_0 = \frac{v T_c (p_0 - p_{\text{H}_2\text{O}})}{T_0 p_0} \cdot \frac{3 \left( \frac{p_i}{p_0} \right)^2 - 1}{2 \left( \frac{p_i}{p_0} \right)^3 - 1};$$

$v$  = carrier gas flow-rate at the column temperature, as measured in the flow meter at ambient temperature ( $\text{cm}^3 \text{min}^{-1}$ );  $q$  = speed of the recording paper ( $\text{cm min}^{-1}$ );  $R$  = universal gas constant;  $T_c$  = temperature of the column (K);  $T_0$  = temperature of the environment (K);  $p_i$  = pressure at the column inlet ( $\text{kN m}^{-2}$ );  $p_0$  = pressure at the column outlet ( $\text{kN m}^{-2}$ );  $h$  = height of the peak (cm);  $p_{\text{H}_2\text{O}}$  = pressure of water vapour at the temperature of the environment ( $\text{kN m}^{-2}$ );  $S_{\text{peak}}$  = total surface area of the peak ( $\text{cm}^2$ ).

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

The peaks obtained were unsymmetrical for all the adsorption systems. This points to the dominating effect of diffusion on the rate of establishment of adsorption equilibrium. Therefore, in both methods of calculating the adsorption isotherms account was taken of the effect of diffusion of the adsorbate in the carbon bed on adsorption according to Dollimore *et al.* [10].

#### Calorimetric measurements

The differential molar heat of adsorption of methanol was measured by means of a conductance calorimeter of the Tiania-Calve type [11], the dosing system of which permitted the measurement of the amount of adsorbate by the volumetric method with an accuracy of  $0.1 \mu\text{mol}$ . The minimum heat effect per unit recorder paper surface area at a paper speed of  $8.33 \cdot 10^{-5} \text{ms}^{-1}$  was  $32.8 \cdot 10^{-1} \text{J}$ .

RESULTS AND DISCUSSION

In Fig. 1 the adsorption isotherms for benzene vapour determined at 373 K by the static method (involving calorimetric determination of the differential molar heat of adsorption) are compared with those found chromatographically from the peak profile with the use of argon, helium and hydrogen as the carrier gas for the adsorbents S5 and SKS-2. Fig. 1 indicates that the chromatographic measurements yield lower adsorption values than the static method. The differences in adsorption increase with increase in the micropore volume (at a relative pressure of 0.002 this difference amounts to 0.18 and 0.36 mmol g<sup>-1</sup> for sorbent S5 and carbon SKS-2, respectively).

The results of chromatographic measurements of adsorption were closest to those obtained by the static method when hydrogen was used as the carrier gas. Lower adsorption values were obtained when helium was the carrier gas and the lowest values when argon was used. This is probably due to the fact that the adsorption of hydrogen is the poorest and that this gas penetrates better the adsorbent bed in the column, which renders the transport of the adsorbate molecules to the

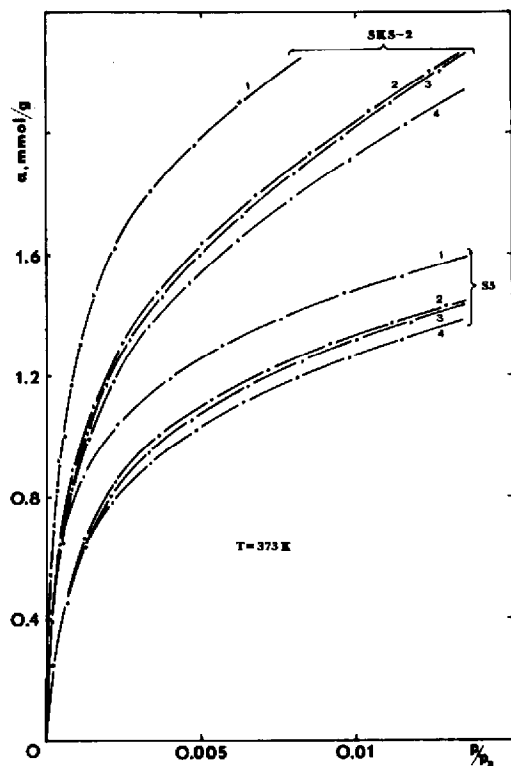


Fig. 1. Adsorption isotherms of benzene determined at 373 K (1) statically and chromatographically by the peak profile method using (2) hydrogen, (3) helium and (4) argon as the carrier gas on adsorbents S5 and SKS-2.

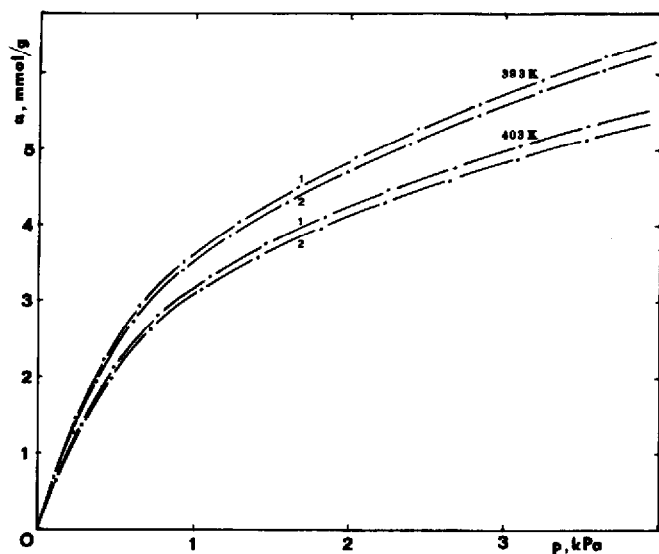


Fig. 2. Adsorption isotherms of ethanol determined chromatographically using (1) the peak profile and (2) the peak maximum method on carbon A-2 at 393 and 403 K.

adsorbent surface easier than with argon and helium. Therefore, for subsequent studies hydrogen was adopted as the carrier gas.

In Fig. 2 the ethanol adsorption isotherms obtained by the peak maximum and peak profile methods are compared [1,2]. It can be seen that the peak profile method

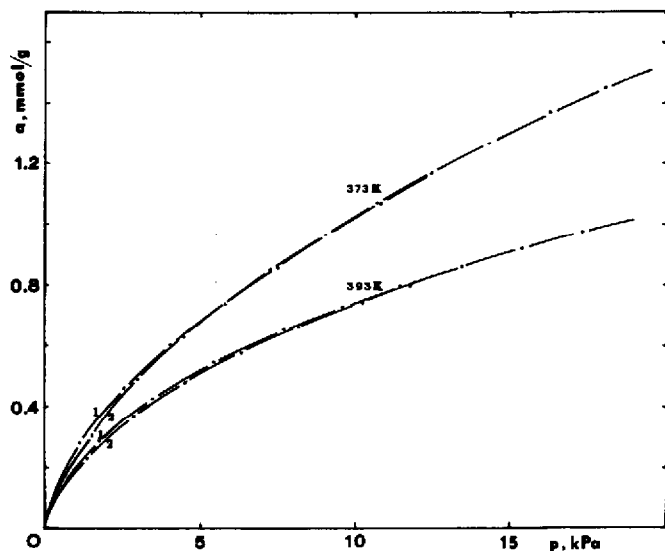


Fig. 3. Adsorption isotherms of ethanol on sorbent S5 at 373 and 393 K determined chromatographically using the profile peak method for (1) small samples of adsorbate in the range up to  $p/p_s = 0.05$  and (2) for large samples up to  $p/p_s = 0.2$ .

always yields higher adsorption values than the peak maximum method (e.g., at about  $2 \text{ kN m}^{-2}$  the difference in adsorption values is  $160 \mu\text{mol}$ , which when referred to the adsorption corresponding to that pressure, amount to about 4%). The isotherms determined by the peak profile method are therefore close to those found by the static procedure. Considering the shorter time required to determine the adsorption isotherm by the peak profile method, this method was adopted in further studies.

The ethanol adsorption isotherms on S5 at 373 and 393 K determined for small samples of the adsorbate (in the range up to  $p/p_s = 0.05$ , where  $p_s$  is the saturated vapour pressure of the adsorbate at the given temperature) are compared in Fig. 3 with those determined for large adsorbate samples (up to  $p/p_s = 0.2$ ). In the range of relative pressures of 0.005–0.05 the plots overlap. The greatest differences in adsorption occur in the range 0.005–0.02 and amount to about 0.055 mmol, which represents 5.8% when referred to the mean adsorption in this range or relative pressures.

The adsorption isotherms of benzene and ethanol determined chromatographically at 373 K on adsorbents A-2, A-2o, S5, and SKS-2 are shown in Fig. 4. Both adsorbates are very well adsorbed on SKS-2. The adsorption isotherms for benzene and ethanol on A-2 and A-2o have similar shapes. The lowest adsorptivity is observed for S5.

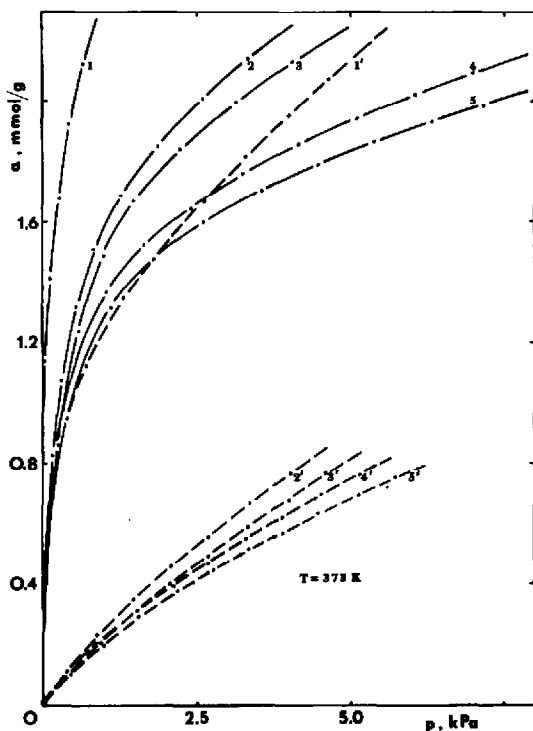


Fig. 4. Adsorption isotherms of (1–5) benzene and (1'–5') ethanol determined chromatographically at 373 K on adsorbents (1,1') SKS-2, (2,2') A-2, (3,3') A-2o, (4,4') S4 and (5,5') S5.

Fig. 5 shows the adsorption isotherms for methanol, ethanol and *n*-propanol determined at 298 and 373 K on the initial carbon A-2 and on its modifications S1, S4 and S6. It can be seen that the modification of the surface, especially its silanization, results in a decrease in the adsorptivity of the carbons with respect to alcohols. The decrease in adsorption at low relative pressures seems to suggest that in addition to physical adsorption a process of chemical adsorption also occurs or that an excessive flow-rate of the carrier gas through the adsorbent bed in the column hinders the penetration of the adsorbate molecules from the carrier gas stream to the carbon surface. The adsorption isotherms of methanol, ethanol and *n*-propanol determined chromatographically at 298 and 373 K on S5 are plotted in Fig. 6 as volume of the adsorbed substance *versus* relative pressure [ $v = f(p/p_s)$ ]. The greatest decrease in adsorption at low relative pressures is observed for methanol probably because the methanol molecule contains a polar group and an apolar group of similar size. The strong mutual interaction of the methanol molecules, competitive with the adsorbate-adsorbent interactions, reduces the adsorption potential and hence the adsorption energy.

In Fig. 7, adsorption isotherms are shown for methanol and ethanol determined at 373 K by the static and chromatographic methods at different flow-rates of the carrier gas through the S5 bed. The initial sections of the chromatographically determined isotherms are lower than those determined statically, and the extent is independent of the flow-rate of the carrier gas up to about  $50 \text{ cm}^3 \text{ min}^{-1}$ . However, above this value there is a decrease in adsorption proportional to the flow-rate. A similar

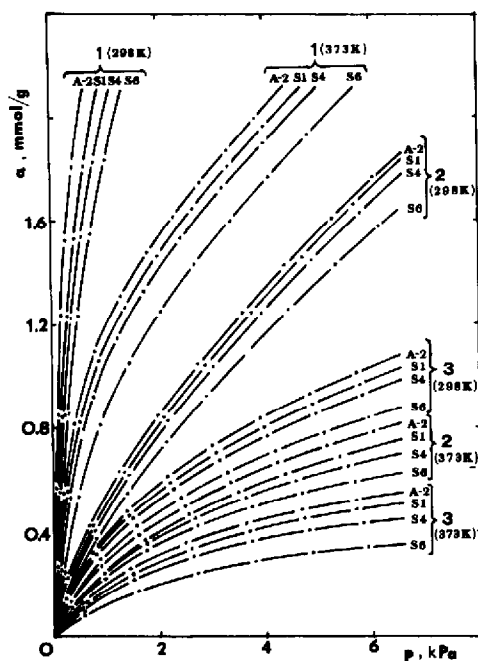


Fig. 5. Adsorption isotherms of (1) methanol, (2) ethanol and (3) *n*-propanol determined chromatographically at 298 and 373 K on the carbon A-2 and on its modifications S1, S4 and S6 (see Table I).



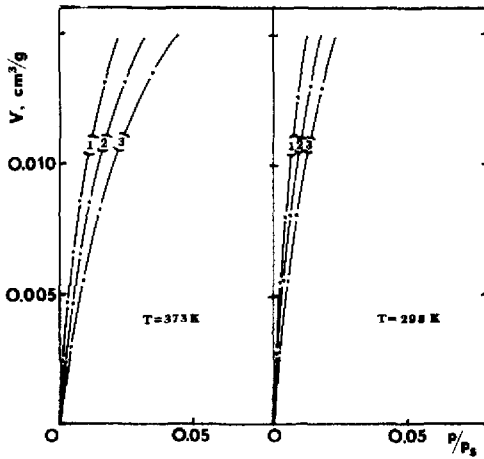


Fig. 6. Adsorption isotherms of (1) methanol, (2) ethanol and (3) *n*-propanol determined chromatographically at 298 and 373 K on sorbent S5.

effect was observed for the other aliphatic alcohol-adsorbent systems. It was therefore decided to conduct subsequent investigations on the active carbons at carrier gas flow-rates not exceeding  $50 \text{ cm}^3 \text{ min}^{-1}$ .

The decrease in the adsorption of alcohols on silanized adsorbents with respect

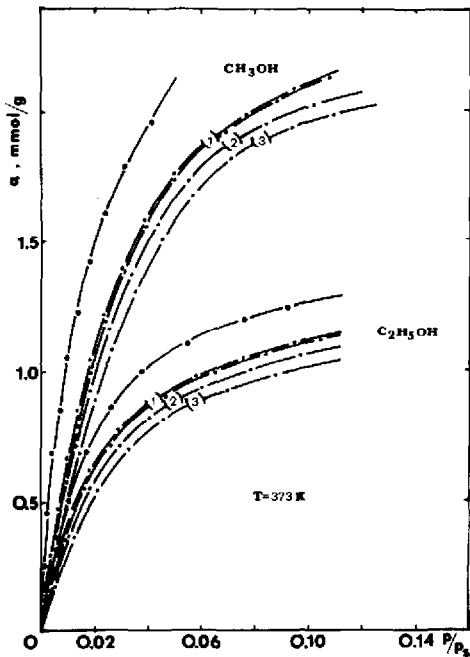


Fig. 7. Adsorption isotherms of methanol and ethanol determined at 373 K by (○) static and (●) chromatographic methods. The latter method was applied at different flow-rates of the carrier gas through the S5 bed: (1) 30 and 50, (2) 60 and (3)  $70 \text{ cm}^3 \text{ min}^{-1}$ .

to other adsorbents may be due to either the lowering of the lyophilic properties of the surface of silanized carbons and a consequent decrease in the adsorptivity of compounds with polar groups, or strong adsorbate-adsorbate interactions [12-15].

On the basis of the adsorption isotherms determined chromatographically at different temperatures, the adsorption isosteres were calculated and the relationships  $\ln p = f(1/T)$  were found. From the slope of the straight lines obtained, the isosteric heat of adsorption was calculated according to

$$q = -R \left[ \frac{\partial \ln p}{\partial \left( \frac{1}{T} \right)} \right]_{a = \text{const.}} \quad (3)$$

In Fig. 8 the differential molar heat of adsorption of benzene, calculated from chromatographic measurements ( $q_{\text{diff}} = q_{\text{st}} - RT$ ) [16,17], is compared with the heats of adsorption found calorimetrically at 373 K for adsorbents A-2, A-2o, S5 and SKS-2. The closest values of the heats of adsorption were obtained for A-2, A-2o and S5, the differences for these adsorbents not exceeding  $2.6 \text{ kJ mol}^{-1}$ . The largest difference (*ca.*  $12.0 \text{ kJ mol}^{-1}$ ) was obtained for SKS-2.

The differential molar heats of adsorption and the entropy of adsorption were calculated from the statically and chromatographically determined benzene adsorption isotherms, by the method suggested by Bering and Serpinsky (BS) [18-20] according to

$$q = L + \alpha RT^2 \left[ \frac{\Delta \ln \left( \frac{p}{p_s} \right)}{\Delta \ln a} \right] - RT \ln \left( \frac{p}{p_s} \right) \quad (4)$$

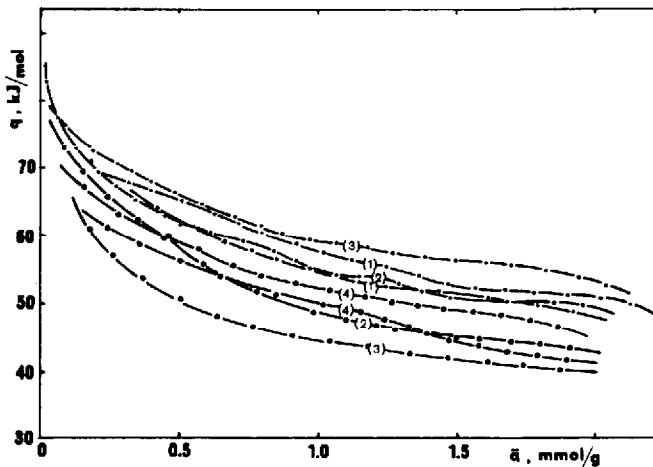


Fig. 8. Changes in the differential molar heats of adsorption of benzene (O) calculated from chromatographic measurements and (●) determined calorimetrically at 373 K on adsorbents (1) A-2, (2) A-2o, (3) SKS-2 and (4) S5.

where  $L$  = heat of adsorbate condensation,  $\alpha$  = coefficient of thermal expansion of the adsorbate and

$$\Delta S = -\alpha RT \left[ \frac{\Delta \ln a}{\Delta \ln \left( \frac{p}{p_s} \right)} \right] \quad (5)$$

The values calculated in this way were compared with those found calorimetrically and chromatographically on sorbent S5 (Fig. 9). The results obtained for carbons A-2, A-2o and S5 were closer to the heats determined calorimetrically than the differential molar heats of adsorption calculated from the isosteres. The largest differences in the values occur for the initial coverages of all the adsorbents used.

The differential molar heats of adsorption of ethanol determined calorimetrically at 373 K on A-2, A-2o, S5 and SKS-2 are compared in Fig. 10 with the heats calculated by the BS method from the chromatographically determined adsorption isotherm. Comparable values were obtained for carbons A-2 and A-2o. The ethanol-SKS-2 system is characterized by higher heats (by *ca.* 20 kJ mol<sup>-1</sup>). For the above adsorbents the heats of adsorption in the initial range of coverages differ only slightly from those calculated at higher coverages.

The behaviour of the ethanol-S5 sorbent system was different. In the initial range of coverages the heat of adsorption is larger than that on carbons A-2 and A-2o by *ca.* 115 kJ mol<sup>-1</sup>. As the degree of coverage increased, this heat decreased to values comparable to those found for carbons A-2 and A-2o.

In Fig. 11 the plots of the differential molar heats of adsorption of methanol determined calorimetrically and calculated by the BS method from the chromato-

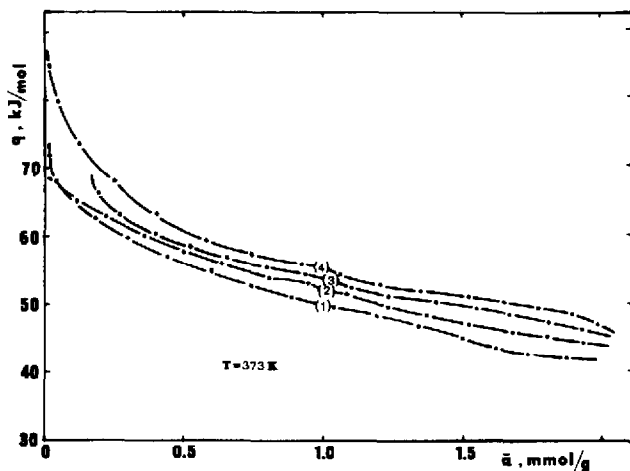


Fig. 9. Changes in the differential molar heats of adsorption of benzene on sorbent S5 at 373 K: (1) calculated from chromatographic measurements of isosteric heats of adsorption; (2) calculated from chromatographically determined adsorption isotherm using BS method; (3) calculated from statically determined isotherm using BS method; (4) determined calorimetrically.

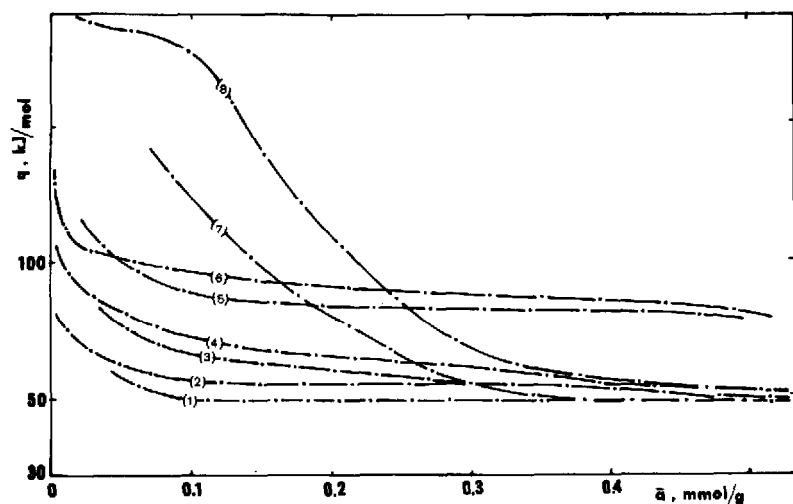


Fig. 10 Changes in the differential molar heats of adsorption of ethanol on carbons (1,2) A-2, (3,4) A-2o, (5,6) SKS-2 and (7,8) S5 at 373 K: (1,3,5,7) calculated from chromatographically determined adsorption isotherms using BS method; (2,4,6,8) determined calorimetrically.

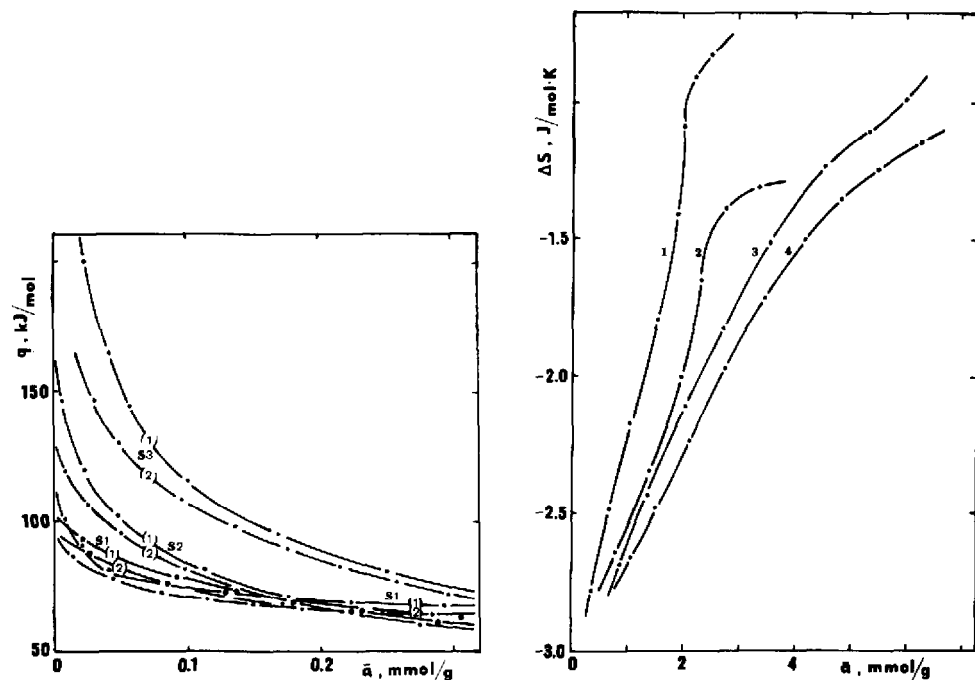


Fig. 11. Changes in the differential molar heats of adsorption of methanol (1) determined calorimetrically and (2) calculated from chromatographic isotherms using the BS method at (○) 298 and (●) 373 K on sorbents S1, S2 and S3.

Fig. 12 Changes in the differential molar entropy of adsorption of (1) cyclohexane, (2) benzene, (3) ethanol and (4) *n*-propanol on carbon A-2.  $T = 373$  K.

graphically determined isotherm at 298 and 373 K are compared. The heat of adsorption of methanol increases in the range of the initial coverages of the adsorbent surface with increasing content of Cr(VI) on the carbon surface. An increase in temperature of about 75 K produces no significant decrease in the differential molar heat of adsorption, which seems to support the earlier conclusion that in addition to physical adsorption, chemical adsorption may also occur on carbons with cations deposited on their surface.

In Fig. 12 the variation of the entropy of adsorption of the adsorbates on carbon A-2 is shown. All adsorption systems were characterized by a negative entropy which increased with temperature and with the coverage of the surface. The increase in entropy with temperature indicated the progress of delocalization of the adsorbate molecules on the carbon surface and a decrease in the interactions of these molecules with the carbon surface.

The energy of interaction of methanol and ethanol with the modified active carbon surfaces was larger than that on non-polar compounds (see Fig. 10 and 11). We therefore decided to check the adequacy of the theory of physical adsorption on homogeneous surfaces for describing adsorption on carbon adsorbents in terms of the Brunauer, Emmett and Teller (BET) model [21]:

$$\frac{h}{a(1-h)} = \frac{1}{a_m C_{\text{BET}}} + \frac{C_{\text{BET}} - 1}{a_m C_{\text{BET}}} \cdot h \tag{6}$$

the Hüttig model [22]:

$$\frac{(1-h)h}{a} = \frac{1}{a_m C_H} + \frac{1}{a_m} \cdot h \tag{7}$$

the Kiselev model [23,24]:

$$\frac{\theta}{(1-\theta)h} = K_1 + K_1 K_n \tag{8}$$

and the Hill model [25-27]:

$$\ln \left\{ \frac{\theta(1-h)^2}{h[1-\theta(1-h)]} \right\} + \frac{\theta(1-h)}{1-\theta(1-h)} = \ln K_1 + K_2 \theta(1-h) \tag{9}$$

where:

$a$  = adsorption at relative pressure  $h = p/p_s$  (mmol g<sup>-1</sup>);  $a_m$  = amount of adsorbate necessary to cover the adsorbent surface area accessible for its molecules with a compact monolayer (mmol g<sup>-1</sup>);  $p$  = pressure of the adsorbate vapour (N m<sup>-2</sup>);  $\theta$  = coverage of the adsorbent surface;  $C_{\text{BET}}, C_H, K_1$  = constants characterizing the adsorbate-adsorbent interactions;  $K_2, K_n$  = constants characterizing the adsorbate-adsorbate interactions.

In the calculations, use was made of chromatographically determined adsorption isotherms for adsorbates undergoing reversible adsorption on carbon adsorbents, *i.e.*, methanol and ethanol, so the above considerations have a full physical

TABLE II  
PARAMETERS OF BET [21], HÜTTIG [22], KISELEV [23,24] AND HILL [25,26] EQUATIONS FOR ETHANOL AT 373 K

Equation	Parameter	A-2	A-2o	S1	S4	S5	S6
BET	$a_m$ (mmol g <sup>-1</sup> )	7.93	9.78	4.63	2.29	8.60	2.16
	$C_{\text{BET}}$	7.8	5.5	8.6	21.5	10.2	22.7
	Linearity: from $h =$	0.045	0.090	0.030	0.027	0.048	0.080
	to $h =$	0.239	0.236	0.238	0.241	0.230	0.244
Hüttig	$a_m$ (mmol g <sup>-1</sup> )	6.07	5.95	6.25	3.67	4.85	2.88
	$C_{\text{H}}$	31.1	29.4	22.1	22.6	26.2	19.6
	Linearity: from $h =$	0.050	0.055	0.070	0.085	0.043	0.072
	to $h =$	0.239	0.236	0.238	0.241	0.230	0.244
Kiselev	$K_1$	3.82	3.83	3.05	3.65	1.86	3.61
	$K_n$	1.05	1.02	0.91	0.93	0.94	0.75
	Linearity: from $h =$	0.095	0.070	0.043	0.043	0.051	0.038
	to $h =$	0.239	0.236	0.238	0.241	0.218	0.244
Hill	$K_1$	0.78	0.76	0.70	0.92	0.83	0.91
	$K_2$	1.81	1.69	1.38	1.20	1.54	1.62
	Linearity: from $h =$	0.045	0.060	0.067	0.030	0.055	0.058
	to $h =$	0.139	0.236	0.238	0.241	0.228	0.244

meaning. The intervals in which the adsorption isotherms of alcohols on the tested adsorbents fulfilled the above equations and the corresponding characteristic quantities are summarized in Table II for several adsorbents. The characteristic quantities were determined by the least-squares method [28]. The results given in Table II can be regarded as satisfactory despite the fact that some workers question the validity of eqns. 6–9 in which homogeneity of the adsorbent is assumed [29–31].

At low coverages the BET [21] and Hüttig [22] adsorption models hold well, but as the coverage increases the effect of intermolecular interactions becomes greater. In addition to the vertical interactions, accounted for in the BET and Hüttig models, an even greater part is played by steric interactions. The effect of the latter interaction with delocalized adsorption is accounted for by the Kiselev model [23]. This model does not account, however, for the change in intermolecular interaction energy with the change in molecule coordination in surface complexes, and this is probably the reason why it does not hold in cases of strong adsorbate–adsorbate interactions. In the cases considered Kiselev's model is fulfilled the worst.

Hill's model [25–27] assumes, in contrast to that of Kiselev [23,24], non-localized adsorption. Here, the effect of lateral interactions is accounted for and it is assumed that the adsorbate molecules do not have to be completely immobile, and, depending on the character of interactions with the adsorbate molecules, they can, in the unadsorbed state, move freely on the surface according to the adsorption–desorption mechanism.

The equations for models of adsorption on homogeneous surfaces may be applied to dynamic adsorption on active carbons at low coverages of the surface area and relatively high temperatures (attainable in chromatographic processes) when the adsorption energy is controlled primarily by the adsorbate–adsorbent interactions. The

considered equations do not, however, provide for strong intermolecular interactions, especially hydrogen bonds, which result in the formation of surface associates. If the alcohols studied are associated in the liquid phase, then, depending on their concentration, they will also be associated to some extent in the adsorbent field of forces [32]. This is probably why the effects of intermolecular interactions that occur may be comparable to the effects of heterogeneity of the surface only at low coverages, when the effect of association can be neglected [33]. The use of equations for different models of adsorption on homogeneous surfaces for microporous adsorbent is therefore justified.

## CONCLUSIONS

The isotherms obtained for the systems studied are convex with respect to the pressure axis, which indicates that the adsorbate-adsorbent interactions have a dominant effect on the initial progress of adsorption of all the adsorbates and that the part played by association dominates in the overall interaction of adsorbates with the surface of the carbons.

The observed differences in the adsorption values and heats of adsorption found from static and dynamic measurements may be due to blocking of the active adsorption sites on the adsorbent surface by the carrier gas molecules, a molecular sieve effect connected with the similarity of the dimensions of the adsorbate molecules and the entrances to the pores, or not filling of the whole adsorption volume of the micropores with the adsorbate in the chromatographic process.

The change in the chemical character of the active carbon surface due to silanization with trimethylchlorosilane vapour produces a lowering of the lyophilic properties of this surface with respect to alcohols and a decrease in their total adsorption. The heats of adsorption of aliphatic alcohols depend on the kind of surface groups present, so on this basis it is possible to illustrate the character of the adsorbate-adsorbent interactions. From the point of view of these interactions the alcohols may be arranged in the order *n*-propanol > ethanol > methanol. This is confirmed by the isotherms shown in Fig. 6.

The negative values of the differential molar adsorption entropy are indicative of the localization of the adsorbate molecules on the surfaces of the adsorbents. However, the entropy values indicate low values of the energy of the bonds.

It is advantageous to conduct the investigations of adsorbents by adsorption gas chromatography with the use of gases that are poorly adsorbed in the bed (*e.g.*, helium or hydrogen). On the basis of certain premises in the literature [3], it should be noted, however, that the use of hydrogen as the carrier gas may lead to a decrease in the concentration of surface oxides on the adsorbents used (*e.g.*, A-2o).

The decrease in adsorption at carrier gas flow-rates exceeding  $50 \text{ cm}^3 \text{ min}^{-1}$  indicates that under these conditions polar adsorbates do not reach adsorption equilibrium, whereas the non-polar adsorbates do [34].

## REFERENCES

- 1 A. V. Kiselev and Ya. I. Yashin, *Adsorpcyjna Chromatografia Gazowa*, PWN, Warsaw 1969.
- 2 T. Paryczak, *Gas Chromatography in Adsorption and Catalysis*, Polish Scientific Publishers, Warsaw and Ellis Horwood, Chichester, 1986.

- 3 F. Dondi, M. F. Gonnord and G. Guiochon, *J. Colloid Interface Sci.*, 62 (1977) 303.
- 4 G. Rychlicki, *Rola Chemizmu Powierzchni Węgla w Procesach Adsorpcji i Katalizy*, Nicholas Copernicus University, Toruń, 1985.
- 5 B. R. Alves and A. J. Clark, *Carbon*, 24 (1986) 287.
- 6 G. Wójcik and K. Karpiński, *Chem. Stosow.*, 22 (1978) 351.
- 7 M. M. Dubinin and Ya. F. Polstyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 793.
- 8 M. Marsh and B. Rand, *J. Colloid Interface Sci.*, 33 (1979) 101.
- 9 J. Volf, J. Kaubek and J. Pasek, *J. Chromatogr.*, 81 (1973) 9.
- 10 D. Dollimore, G. R. Heal and D. R. Martin, *J. Chromatogr.*, 50 (1970) 209.
- 11 J. Garbacz and G. Rychlicki, *Podstawy Termodynamiki i Kalorymetrii Procesu Adsorpcyjnego*, Nicholas Copernicus University, Toruń, 1986.
- 12 U. B. Mohlin and D. G. Gray, *J. Colloid Interface Sci.*, 47 (1974) 747.
- 13 G. M. Dorris and D. G. Gray, *J. Colloid Interface Sci.*, 71 (1979) 93.
- 14 W. T. Cooper and J. M. Hayes, *J. Chromatogr.*, 314 (1984) 111.
- 15 M. Domingo-García, F. J. López-Garzón, R. López-Garzón and C. Moreno-Castilla, *J. Chromatogr.*, 324 (1985) 19.
- 16 S. Ross and J. P. Olivier, *On Physical Adsorption*, Wiley-Interscience, New York, 1964.
- 17 G. Deininger, J. Asshauer and I. Halasz, *Chromatographia*, 8 (1975) 143.
- 18 V. P. Bering and V. V. Serpinsky, *Dokl. Akad. Nauk SSSR*, 114 (1957) 1249.
- 19 V. P. Bering and V. V. Serpinsky, *Izv. Akad. Nauk SSSR*, (1957) 1254.
- 20 V. P. Bering and V. V. Serpinsky, *Dokl. Akad. Nauk SSSR*, 148 (1963) 1331.
- 21 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 22 G. F. Hüttig, *Monatsh. Chem.*, 78 (1948) 177.
- 23 A. V. Kiselev, *Kolloid. Zh.*, 20 (1958) 338.
- 24 N. N. Avgul, A. V. Kiselev and A. I. Lygina, *Kolloid. Zh.*, 23 (1961) 369.
- 25 T. L. Hill, *J. Chem. Phys.*, 14 (1946) 441.
- 26 T. L. Hill, in W. G. Frankenburg (Editor), *Advances in Catalysis and Related Subjects*, Vol. 4, Academic Press, New York, 1952, p. 211.
- 27 F. Dondi, M.-F. Gonnord and G. Guiochon, *J. Colloid Interface Sci.*, 62 (1977) 316.
- 28 C. J. H. Beaven and P. Eadington, *Chem. Ind. (London)*, (1966) 1484.
- 29 G. D. Halsey, in W. G. Frankenburg (Editor), *Advances in Catalysis and Related Subjects*, Vol. 4, Academic Press, New York, 1952, p. 259.
- 30 M. M. Dubinin and E. D. Zhukovskaja, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, (1958) 535.
- 31 M. M. Dubinin, *Carbon*, 21 (1983) 359.
- 32 A. Zukal and O. Kadlec, *Collect. Czech. Chem. Commun.*, 38 (1973) 321.
- 33 L. M. Dormant and A. W. Adamson, *J. Colloid Interface Sci.*, 38 (1972) 285.
- 34 W. W. Raczynski, *Zarys Teorii Dynamiki Sorpcji i Chromatografii*, WNT, Warsaw, 1966.