

Application of Kováts retention indices for investigation of adsorption properties of activated carbons

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Abstract

Inverse gas chromatography has been used to measure the enthalpy and entropy of adsorption of benzene, cyclohexane, cyclohexene, 1,3-cyclohexadiene, *n*-hexane, *n*-heptane and *n*-pentane on three active carbons. The high values of adsorption enthalpy at zero coverage indicated high-energy sites on the surface of the tested carbons. The magnitudes of the enthalpy and entropy of adsorption have been calculated in two ways: from the specific retention volumes referred to column temperature and zero coverage of adsorbate, and from Kováts retention indices. © 1997 Elsevier Science B.V.

Keywords: Adsorption; Inverse gas chromatography; Thermodynamic parameters; Retention indices; Carbon adsorbents; Specific retention volume; Hydrocarbons

1. Introduction

Adsorption processes occurring on the surface of active carbons are connected with their surface area, porous structure and surface heterogeneity, adsorption isotherms and thermodynamic function of adsorption [1]. As a rule, the measurements of these parameters are carried out under idealized conditions. Particles of the tested active carbons have usually been ground. No publications relating to chromatographic investigations of sorption properties of non-ground active carbons have been published yet. Therefore, we have made an attempt to qualify the usefulness of inverse gas chromatography (IGC) [2] for rapidly testing active carbons with particle shapes and diameters in which they are or can be used in technical installations. We also intended to

investigate the influence of bond configuration in six-carbon cyclohydrocarbons on the energetic effect of adsorption on active carbons with a well developed micropore structure. The investigations have been made using commonly used methods [2,3] and a new method for carbon adsorbents investigation based on Kováts retention indices.

IGC has already been used to investigate non-specific carbon adsorbents with relatively small surface heterogeneity usually within region of Henry's law [3–5], microporous active carbons [6,7] and polymers [8]. From the chromatographic data the physico-chemical parameters of the adsorption e.g., standard free energy of adsorption, surface energy and entropy of specific interactions have been calculated. The suitability of IGC for physico-chemical investigations follows from the fact, that a chromatographic process is related to the properties and physico-chemical interactions of column filling (e.g.

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carbon or non-carbon adsorbent) with the chromatographed substances.

2. Experimental

2.1. Adsorbents and adsorbates

The following activated carbons were used in the study: WS-4 (Chemviron Carbon, Pittsburgh, PA, USA), NP-5 and R (Hajnowka's Factory of Wood Dry Distillation, Hajnowka, Poland).

The mineral matter (ash) was not removed from these adsorbents. The active carbons were degassed in a vacuum drier at 453 K and $1.5\text{--}2.5\text{ kN m}^{-2}$ for 10 h. The grains of active carbons R and NP5 had an average diameter of 0.30–1.25 mm. The grains of active carbon WS4 were cylinders 7 mm in length and 3.8 mm in diameter.

Benzene, cyclohexane, cyclohexene, 1,3-cyclohexadiene, *n*-hexane, *n*-heptane and *n*-pentane were used as adsorbates. The sizes of the samples injected onto the column were in the range 0.005–0.05 μl . The range of the injected masses of adsorbates was 3.5–45 μg .

2.2. Static measurements

The basic characteristics of the tested active carbons were determined from the adsorption isotherms of nitrogen determined volumetrically at 77 K. The specific surface areas calculated from these isotherms, S_{BET} , for R, WS4 and NP5 are 990, 1290 and 1360 $\text{m}^2\text{ g}^{-1}$, respectively and volumes of micropores, V_{mi} , 0.409, 0.509 and 0.530 $\text{cm}^3\text{ g}^{-1}$, respectively. The adsorption isotherms of nitrogen on the used active carbons are presented in Fig. 1.

2.3. Chromatographic measurements

The chromatographic investigations were carried out by means of a Unicam type 610 gas chromatograph with an on-line Unicam 4880 Chromatography Data Handling System which was started when

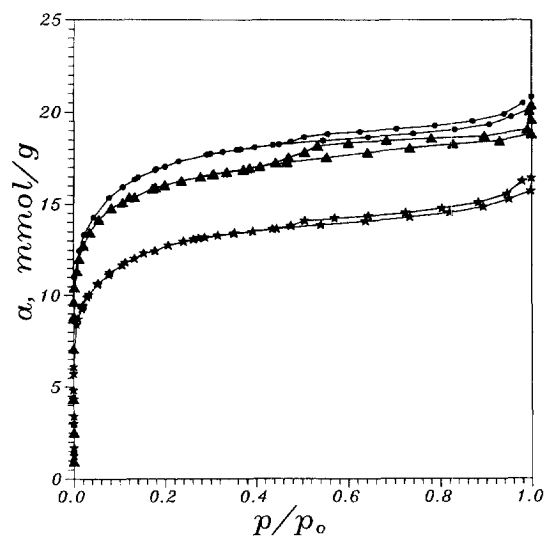


Fig. 1. The adsorption isotherms of nitrogen at 77 K on the studied active carbons; (★) R, (▲) WS4, (●) NP5.

injecting. The active carbons were placed in glass columns 65 cm \times 0.4 cm I.D.. The length of the adsorbent bed in each column was 6–7 cm. The part of the column unoccupied by the adsorbent was filled with glass beads of 80 mesh size. The filled column was mounted into the chromatograph thermostat and heated for 10 h at 603 K in a stream of helium with a flow-rate of 40 $\text{cm}^3\text{ min}^{-1}$. Measurement of retention times of the tested substances (adsorbates) was carried out over the temperature range 523–593 K (except for cyclohexane on carbon NP5; 523–553 K) in helium as the carrier gas at a flow-rate of $40 \pm 1\text{ cm}^3\text{ min}^{-1}$. The gas hold-up times, t_{M} , were determined from direct measurements using methane and checked by the homologous series method using *n*-alkanes [7,9]. The differences ranged from 0.001 to 0.002 min.

IGC allows us to determine the enthalpy of adsorption, ΔH_{ads} , and entropy of adsorption, ΔS_{ads} , at a very low (zero) coverage of the adsorbent surface by measuring the retention volume of the given adsorbate at different column temperatures. Therefore, the retention time of the given adsorbate, t_{R} , should be measured and the specific retention volume, V_{g} , referred to column temperature, T_{c} , can be calculated from the following expression [10]:

$$V_{g(T_c)} = (t_R - t_M) \cdot \frac{3}{2} \cdot \frac{\left(\frac{p_i}{p_o}\right)^2 - 1}{\left(\frac{p_i}{p_o}\right)^3 - 1} \cdot \frac{p_o - p_w}{p_o} \cdot \frac{F_c}{w} \quad (1)$$

where p_i is pressure at the column inlet; p_o is pressure at the column outlet; p_w is pressure of water vapour at the temperature of the environment; F_c is carrier gas flow-rate measured by soap flow-meter at the column temperature and w is the total mass of adsorbent in column.

The specific retention volume corrected to the standard temperature (0°C) is given by expression:

$$V_{g(273)} = V_{g(T_c)} \cdot \frac{273}{T_c} \quad (2)$$

The enthalpy and entropy of adsorption may be calculated from the following equations [11,12]:

$$\ln \frac{V_{g(T_c)}}{T_c} = \frac{-\Delta H_{ads}^V}{R} \cdot \frac{1}{T_c} + \frac{\Delta S_{ads}^V}{R} + \ln(RS_{BET}w) \quad (3a)$$

$$\ln \frac{V_{g(T_c)}}{T_c} = A \cdot \frac{1}{T_c} + B \quad (3b)$$

$$\ln V_{g(273)} = \frac{-\Delta H_{ads}^V}{R} \cdot \frac{1}{T_c} + \frac{\Delta S_{ads}^V}{R} + \ln(RS_{BET}w) + \ln(273) \quad (3c)$$

where R is the universal gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$) and A and B are coefficients of linear equation; the superscript V denotes values calculated from the specific retention volumes.

In isothermal gas chromatography the thermodynamic effects of interactions between adsorbate molecules and adsorbent surface may also be calculated from the Kováts retention indices [13–16]. The retention index of any hydrocarbon (X) can be calculated by logarithmic interpolation between two relevant n -alkanes of the series C_nH_{2n+2} [2,3]:

$$I_X = 100n + 100 \frac{\ln V_{g(273)X} - \ln V_{g(273)n}}{\ln V_{g(273)n+1} - \ln V_{g(273)n}} \quad (4)$$

where $V_{g(273)n}$, $V_{g(273)n+1}$ are the specific retention volumes corrected to 273 K of n -alkanes with the number of carbon atoms equal to n and $n+1$,

respectively and $V_{g(273)X}$ is the retention volume of the compound, the retention index of which is determined if $V_{g(273)n} < V_{g(273)X} < V_{g(273)n+1}$.

Denoting the difference of the specific retention volume logarithms for two consecutive n -alkanes as b :

$$b = \ln V_{g(273)n+1} - \ln V_{g(273)n} \quad (5)$$

Hence if $n \geq 5$ [15] the following equation was obtained:

$$\frac{b(I_X - 100n)}{100} = \frac{-\Delta H_{ads(X)}^I + \Delta H_{ads(n)}^V}{2.303RT_c} + \frac{\Delta S_{ads(X)}^I - \Delta S_{ads(n)}^V}{2.303R} \quad (6)$$

$$\frac{b(I_X - 100n)}{100} = C \cdot \frac{1}{T_c} + D \quad (7)$$

where $\Delta H_{ads(n)}$, $\Delta S_{ads(n)}$ are respectively, the molar enthalpy and entropy of adsorption of any previous n -alkane regarding the determined compounds; $\Delta H_{ads(X)}$, $\Delta S_{ads(X)}$ are respectively, the molar enthalpy and entropy of adsorption of any determined compound; C and D are coefficients of linear equation and superscript I denotes the value calculated from retention indices.

Eq. (6) allows us to estimate the molar enthalpies and entropies of adsorption through the retention indices if $\Delta H_{ads(n)}$ and $\Delta S_{ads(n)}$ for any n -alkane containing five or more carbons in its molecule are known at the studied temperature range.

3. Results and discussion

The obtained chromatographic peaks were asymmetrical and their retention times depended on the injected sample size and the self-sharpening and diffusive sides did not superimpose (see Figs. 2 and 3). Taking into account the obtained peak profiles we were in the range of non-linear and non-ideal chromatography [2]. The obtained peaks for measurements on the WS4 active carbon were the most asymmetric. For the same volume of the injected adsorbate the retention times were reproducible. Similar results were obtained by Flour and Papirer by adsorbing tetrahydrofuran on short glass fibers

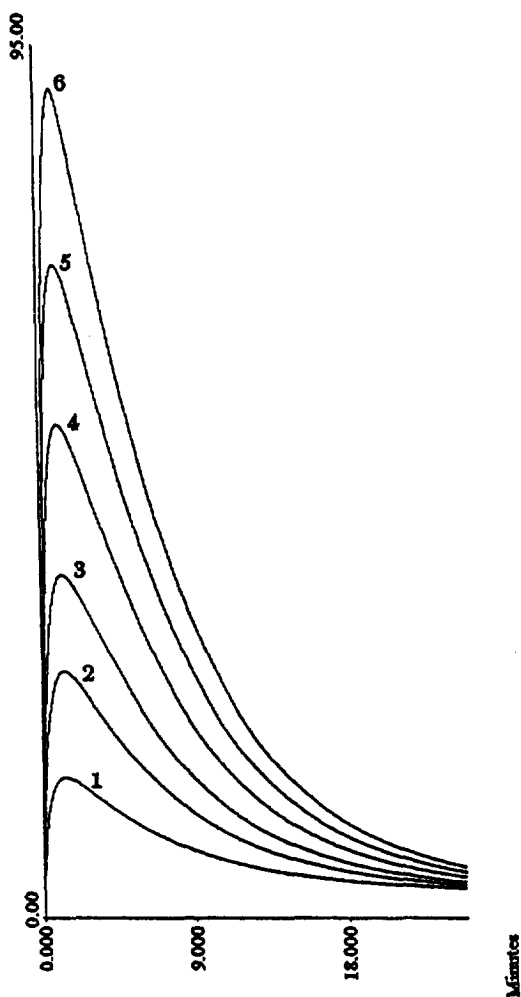


Fig. 2. Peaks of different volume sizes of 1,3-cyclohexadiene at 533.2 K on WS4 active carbon (1) 0.005, (2) 0.01, (3) 0.02, (4) 0.03, (5) 0.04, (6) 0.05 μl .

with a specific surface area $0.30 \text{ m}^2 \text{ g}^{-1}$ [17]. Jaulmes et al. [18] have studied such peak profiles in non-linear gas chromatography.

The deviations in determining the retention times and the peak areas were not higher than 0.06% and 0.12%, respectively.

We measured retention times of every adsorbate in their different amounts (0.005–0.05 μl) and calculated the specific retention volumes referred to column temperature, T_c , according to Eq. (1). The specific retention volume of the adsorbates increased to the definite value of the specific retention volume

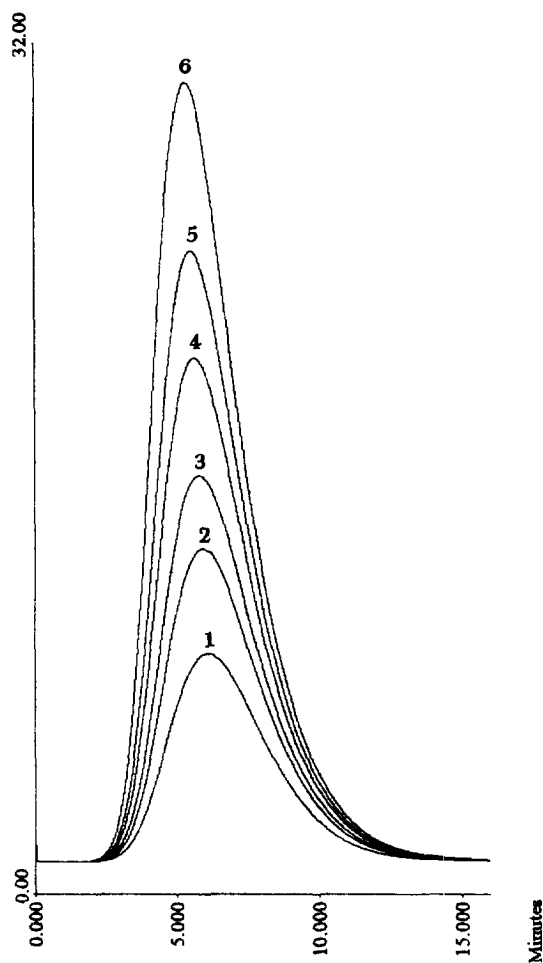


Fig. 3. Peaks of different volume sizes of *n*-hexane at 423.2 K on the R active carbon (1) 0.005, (2) 0.01, (3) 0.02, (4) 0.03, (5) 0.04, (6) 0.05 μl .

at zero concentration of adsorbate [zero coverage of surface adsorbent with adsorbate, $V_{g(T_c)}^0$] as the magnitude of the sample decreased:

$$V_{g(T_c)}^0 = \lim_{m \rightarrow 0} V_{g(T_c)}(m) \quad (8)$$

The specific retention volumes at zero coverages, $V_{g(T_c)}^0$ calculated from the peak maximum retention times in the proposed manner are connected with the same isotherm of partition and the same isotherm of adsorption of the chromatographed adsorbates at the interfaces [19].

The specific retention volumes determined for

every injected volume of adsorbate were described by semi-logarithmic equation and polynomial third power and extrapolated to zero injected sample volume i.e., to zero coverage of adsorbent surface with adsorbate. The obtained specific retention volumes at zero coverage, did not differ more than 1.6% of the values obtained from semi-logarithmic equation.

The plots of $\ln(V_{g(T_c)}^0/T_c)$ against $1/T_c$ were straight lines over the whole column temperature range. The slopes were directly proportional to the molar enthalpy change, and the intercept on the ordinate at $1/T_c=0$ gave the molar entropy change for the adsorption process.

The representatives $\ln(V_{g(T_c)}^0/T_c)$ versus $1000/T_c$ plots of *n*-alkanes C_5 and C_6 on R, WS4 and NP5 carbons and benzene, cyclohexene, cyclohexane, 1,3-cyclohexadiene, *n*-heptane on WS4 carbon are shown in Fig. 4 Fig. 5, respectively. These plots were linear over a range of column temperature applied. Despite the fact that the diffusive parts of elution peaks were not superimposed, particularly for adsorption systems with the WS4 active carbon, no differences in plots of dependencies $\ln(V_{g(T_c)}^0/T_c)=f(1000/T_c)$ have been observed in comparison with the adsorption systems with the R and NP5 adsorbents.

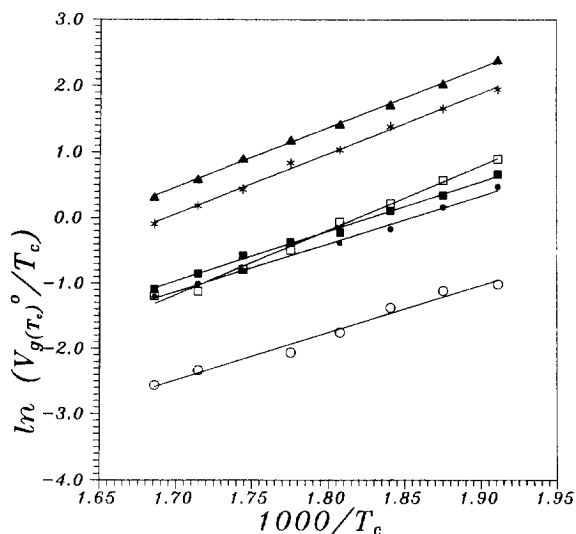


Fig. 4. The variation of $\ln V_{g(T_c)}^0/T_c$ with reciprocal column temperature for *n*-alkanes on R, WS4 and NP5 active carbons; (●) R- nC_5 , (*) R- nC_6 , (○) WS4- nC_5 , (□) WS4- nC_6 , (■) NP5- nC_5 , (▲) NP5- nC_6 .

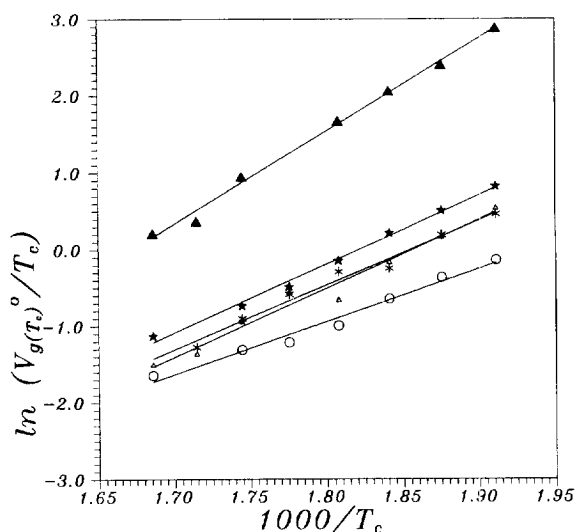


Fig. 5. Variation of $\ln V_{g(T_c)}^0/T_c$ with reciprocal column temperature for hydrocarbons on WS4 active carbon; (*) benzene, (○) cyclohexene, (★) cyclohexane, (△) 1,3-cyclohexadiene, (▲) *n*-heptane.

The regression coefficients were not lower than 0.97. The standard deviation of the magnitudes *A* and *B* from Eq. (3b) was not higher than 1.5% and 1.3% of their values, respectively.

The differences $(\Delta H_{ads(n)} - \Delta H_{ads(X)})$ and $(\Delta S_{ads(X)} - \Delta S_{ads(n)})$ in Eq. (6) were directly proportional to the slope of the straight line, and the intercept on the ordinate at $1/T_c=0$, respectively. $\Delta H_{ads(n)}$ and $\Delta S_{ads(n)}$ were calculated from the specific retention volumes.

The plot $[0.01b(I_x - 100n)]$ versus $1000/T_c$ for several tested adsorption systems is shown in Fig. 6. The molar enthalpies and entropies of adsorption of the used adsorbates for active carbons studied, calculated from the specific retention volumes referred to column temperature (denoted by "V") and from Kováts retention indices (denoted by "I"), adjusted by the least-squares method are reported in Tables 1 and 2, respectively. Taking into account the results presented in Table 1 the ΔH_{ads} values of the tested hydrocarbons on the heterogeneous surfaces of adsorbents are much higher in comparison with the results obtained for adsorption on graphitized thermal carbon blacks, [3,4] and poly(*p*-phenylene terephthalamide) fibers [5]. The values of the molar enthalpy and entropy of adsorption calculated from

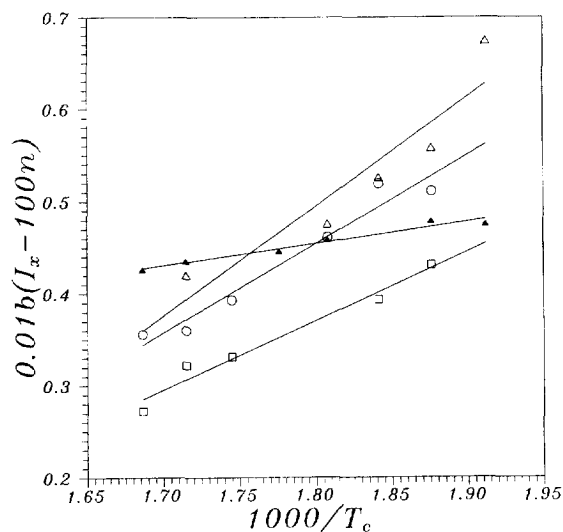


Fig. 6. Variation of $0.01b(I_x - 100n)$ with reciprocal column temperature for the several studied adsorption systems; (○) R-1,3-cyclohexadiene, (□) R-cyclohexene, (▲) WS4-benzene, (△) 1,3-cyclohexadiene.

the Kováts retention indices by the proposed method were for almost all tested systems higher than the results obtained from the specific retention volumes, but they do not differ considerably (the highest difference for enthalpy of benzene on R active carbon is equal 13.1%). The greatest differences of the values were obtained for benzene in all the tested adsorption systems. Generally, the regression coefficients were not lower than 0.88. The standard deviation of the constants C and D are not higher than 4.5% and 4.2% of their values, respectively.

Table 1

Molar enthalpies of adsorption calculated from the specific retention volumes referred to column temperature "V" and from Kováts retention indices "I"

Adsorbates	Active carbons, $-\Delta H_{\text{ads}}$ (kJ mol ⁻¹)					
	R		WS4		NP5	
	V	I	V	I	V	I
<i>n</i> -Pentane	60.6	60.1	62.7			
Benzene	72.4	81.9	69.9	72.8	67.6	
Cyclohexane	76.3	79.0	74.3	73.5	70.4 ^a	67.9 ^a
Cyclohexene	68.8	75.0	57.2	61.4	62.2	64.4
1,3-Cyclohexadiene	75.0	77.3	74.4	76.2	66.6	66.7
<i>n</i> -Hexane	75.9		81.7		74.9	
<i>n</i> -Heptane	85.5		100.2		88.3	

^a 523–553 K.

Taking into account the results presented in Fig. 6 one may say that the highest deviations from linearity of the $[0.01b(I_x - 100n)] = f(1000/T_c)$ dependency were obtained for adsorption systems adsorbate-WS4. It was probably connected with the fact that adsorbate-WS4 adsorption systems were in a stage more remote from the equilibrium state than the adsorption systems with R and NP5 adsorbents.

In order to specify the influence of the adsorbates structural effects on the adsorption enthalpy and entropy, we have plotted as an example of dependency $-\Delta H_{\text{ads}}$ versus $-\Delta S_{\text{ads}}$ for cyclohydrocarbons and *n*-alkanes in Fig. 7. Cyclohexene characterizes the lowest values of adsorption enthalpy for all tested adsorption systems. For NP5 active carbon the enthalpy and entropy of adsorption increase with increasing number of double bond in cyclohydrocarbon molecule (cyclohexene, 1,3-cyclohexadiene, benzene). This regularity is ambiguous for R and WS4 active carbons. Cyclohexane does not show any regularity of adsorption in respect to other cyclohydrocarbons for all tested adsorption systems.

4. Conclusions

The examination of the results for the systems studied reveals the following.

The enthalpy of adsorption for *n*-alkanes steadily increases with increasing carbon atom number (average increase ~ 20 kJ mol⁻¹ for WS4 and ~ 12 kJ mol⁻¹ for R and NP5 per one CH₂ group);

The ΔH_{ads} values of the adsorbates with bulky

Table 2

Molar entropies of adsorption calculated from the specific retention volumes referred to column temperature “V” and from Kováts retention indices “I”

Adsorbates	Active carbons, $-\Delta S_{ads}$ (J mol ⁻¹ K ⁻¹)					
	R		WS4		NP5	
	V	I	V	I	V	I
<i>n</i> -Pentane	168.2		181.9		173.1	
Benzene	180.6	197.4	188.8	194.5	173.3	173.5
Cyclohexane	185.4	190.1	194.4	193.0	180.7 ^a	176.2 ^a
Cyclohexene	176.2	187.0	170.0	177.8	165.3	169.5
1,3-Cyclohexadiene	185.5	186.6	197.2	200.9	171.5	171.6
<i>n</i> -Hexane	184.2		207.8		182.0	
<i>n</i> -Heptane	188.4		226.6		192.8	

^a 523–553 K.

shapes of molecules are smaller than those with rod-like molecules of adsorbates but for the same number of carbon atoms in the hydrocarbon molecule.

The adsorption enthalpies for cyclohexane and 1,3-cyclohexadiene are similar and generally have the following order: R > WS4 > NP5. The same order characterizes benzene but its values of the adsorption enthalpy are lower.

The magnitudes of the molar enthalpy and entropy of adsorption calculated from the dependency ob-

tained after conversion of the Kováts retention indices to the uniform scale based on the retention properties of *n*-alkanes have been plausible. This method can be used for evaluation of commercial active carbons. The enthalpy and entropy of adsorption can be calculated from retention index data if the corresponding values for the appropriate *n*-alkanes are known.

It has been shown that retention data were reproducible when chromatographic investigations were carried out using relatively large particles of adsorbents and high values of carrier gas flow-rates.

In IGC the diffusion effects have significant influence on the resulting quantities (particularly in the case of microporous adsorbents). Therefore, the determined quantities of enthalpy and entropy of adsorption represent some effective values.

Acknowledgments

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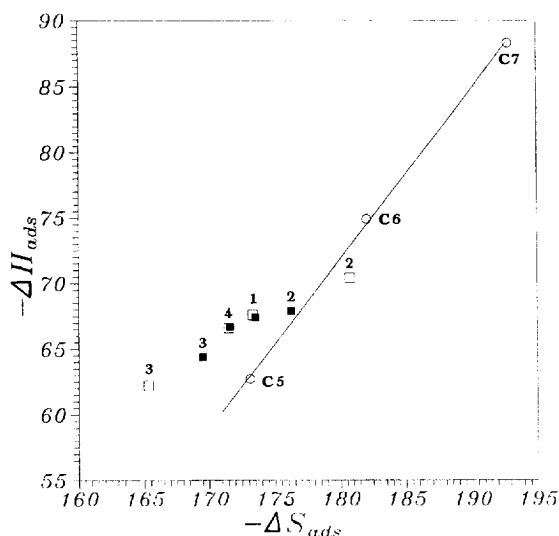


Fig. 7. The variation of $-\Delta H_{ads}$ versus $-\Delta S_{ads}$ for *ooo* *n*-alkanes, (1) benzene, (2) cyclohexane, (3) cyclohexene, (4) 1,3-cyclohexadiene on NP5; (□) calculated from specific retention volumes, (■) calculated from Kováts retention indices.

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