



Comparison of the differential isosteric adsorption enthalpies and entropies calculated from chromatographic data

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Abstract

The differential isosteric enthalpies, $-\Delta H_{\text{ads}}$, and entropies, $-\Delta S_{\text{ads}}$, of adsorption were calculated taking the retention times of the peak maxima and the centres of gravity of peaks into account and compared with the results obtained from the adsorption second virial coefficients. A mathematical link between the $-\Delta H_{\text{ads}}$ and $-\Delta S_{\text{ads}}$ magnitudes and experimental data was derived through the Antoine-type equation which enables the $-\Delta H_{\text{ads}}$ and $-\Delta S_{\text{ads}}$ magnitudes to be found from adsorption second virial coefficients, B_{2S} , calculated on the basis of chromatographically determined adsorption isotherm data. The virial coefficients were calculated employing the values of the Tóth and Unilan equation parameters. There are no significant differences to be found between the isosteric enthalpies obtained, whereas the values of the adsorption entropies were the highest for the centre of peak gravity data.

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1. Introduction

Although static adsorption measurements are still the most precise, dynamic measurements by means of inverse gas chromatography (IGC) have become a very popular and powerful method of investigating adsorption phenomena from the phenomenological and energetic point of view. The IGC measurements are rapid and simple and commercially available equipment makes increasingly precise measurements possible. They can be undertaken in or beyond the Henry's law region. When they are undertaken in the Henry's law region, the retention times of the peak maxima and the centres of gravity of peaks do not

depend on the size of the sample injected onto the column. The peaks obtained are symmetrical (i.e. Gaussian) in shape with no superposition of their approach and diffusive sides. In this context, IGC is regarded as ideal and linear.

On the basis of the IGC data obtained in the Henry's law region, the retention volumes (the net and specific) at zero adsorbate concentration (zero coverage of the adsorbent surface with adsorbate) can be calculated [1], the net retention volume at zero coverage being a physicochemical constant in this case. It is often used for calculation of isosteric enthalpy of adsorption, Kováts retention index, standard free energy of adsorption and entropy of specific interactions, etc.

When IGC is undertaken beyond the Henry's law region, the loci (actually retention times) of the peak

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maxima and the centres of gravity of peaks depend on the size of the sample injected onto the column. The peaks obtained are asymmetrical in shape with no superposition of the approach sides but with superposition of diffusive sides. In such a case, the conditions characteristic for ideal, non-linear chromatography are attained [2,3]. Non-linear isotherms are obtained in this case [4,5].

Taking physical adsorption at an adsorbate–adsorbent interface as an example for ideal, non-linear chromatography into account, it may be stated that one of the most important quantities from the experimental point of view is the differential isosteric enthalpy of adsorption, $-\Delta H_{\text{ads}}$, which corresponds to the differential enthalpy change when an infinitesimal number of adsorbate molecules are transferred at constant pressure from the bulk gas phase to the adsorbed phase. This enthalpy can be calculated if the isotherm data at different temperatures are first replotted as isosters, i.e. the plots of $\ln p$ versus $1/T$ (reciprocal temperature) at different coverages of adsorbent surface with adsorbate molecules.

In order to obtain an adsorption characteristic of the system tested, the isotherms are described by different equations. The Tóth and Unilan equations may be successfully applied for the phenomenological description of the adsorption systems. The aforementioned equations are expressed in the following forms:

- the semiempirical Tóth equation [6–10]:

$$a = \frac{a_m p}{(b + p)^{1/t}} \text{ for } 0 \leq \frac{a}{a_m} < 1 \quad (1)$$

- the Unilan equation, which is the integration of the local Langmuir isotherm over the uniform distribution of adsorption energy [7,11]:

$$a = \frac{a_m}{2s} \ln \left[\frac{c + p \exp(+s)}{c + p \exp(-s)} \right] \text{ for } 0 \leq \frac{a}{a_m} < 1 \quad (2)$$

where a_m is the monolayer capacity, also called the saturation capacity of the stationary phase (adsorbent bed) and can be related either to the unit volume of this phase (specific saturation capacity) or to the amount contained in the column (column saturation capacity); b and c are the temperature-dependent

constants; s and t are measures of the surface heterogeneity. The t variable is varying in the interval of $0 < t \leq 1$.

Both equations reduce to the Langmuir isotherm: the Tóth for $t=1$ and the Unilan for $s=0$ (after the application of the L'Hôpital's rule for limits of the form $\frac{0}{0}$). It is necessary to emphasize that for both equations $\lim_{p \rightarrow \infty} a = a_m$. The second derivative, $\frac{d^2 a}{dp^2}$, is negative, and its absolute value decreases monotonically with equilibrium pressure [7].

The adsorption virial coefficients are employed for the general description of the attractive and repulsive interactions of the adsorbate molecules to the outermost layer of adsorbent atoms.

The value of the second adsorption virial coefficient can be calculated:

- (i) on the basis of the Tóth equation parameters [7]:

$$B_{S(T)} = RTmb \frac{-1}{t} \quad (3)$$

- (ii) and on the basis of the Unilan equation parameters [7]:

$$B_{S(U)} = \frac{RTm}{c} \cdot \frac{\sinh(s)}{s} \quad (4)$$

Taking into account the static adsorption data Valenzuela and Myers have successfully applied the adsorption second virial coefficient, B_{2S} , for energetic description of the adsorption system tested [7].

In this paper, account was taken to compare the values of the differential isosteric enthalpy and entropy of adsorption calculated from different chromatographic data for ideal, non-linear chromatography.

2. Experimental

2.1. Adsorbents

Commercial active carbon type NP5 (Gryf-Skand, Poland) was used in the study. The grains of the adsorbent have irregular flat shapes and the 0.30–1.25 mm fraction was separated for the investigation. The mineral matter was removed from the NP5 adsorbent by Korver's method using concentrated HF and HCl acids [12]. The sample was denoted as

P50. The total amount of the mineral impurities in the P50 sample was less than 0.1%.

The amounts of some metal cations in the sample were determined. The metal cations were separated from the test adsorbent as follows. A 2-g sample of dried active carbon was mineralised in a muffle oven for 4 h. The residuum obtained was treated with 3 cm³ of perchloric acid and heated until the evolution of white vapour had ceased. It was then dissolved in 1 cm³ of chloric acid (1:1) and 5 cm³ of redistilled water added to the resulting solution [13]. The amounts of cations in mineral impurities in the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) method using a Jobin-Yvon 38+ atomic emission spectrometer employing inductively coupled plasma. The potassium and sodium cation contents were determined by flame atomic emission spectrometry (FAES) using a Perkin-Elmer 3030B instrument. The lead cation content was determined by flame atomic absorption spectrometry (FAAS). The sulphur and carbon contents were determined as follows. A sample of dried active carbon was burnt in oxygen at 1623 K, and the concentrations of the elements were determined in the resulting SO₂ and CO₂ by means of the ACS-40/1500 analyser with NDIR detector (prod. PIE, Poland). The concentrations of the cations, sulphur and carbon were: Ca 33.2, Mg 22.1, Pb 0.7, Ni 2.4, Mn 0.5, Fe 19.9, Cr 0.5, Al 10.4, Cu 51.7, Na 2.3, K 62.6, and S 2350 (ppm, w/w), C 99.4 (% w/w).

The content of particular oxygen groups with an acidic character was determined by neutralization with bases of various strengths, while the number of basic groups was estimated by neutralization with hydrochloric acid [14]. These results are as follows (expressed in mequiv./g): carboxylic 0.08, lactonic 0.06, phenolic 0.20, carbonyl 0.19, and basic 0.37.

It is necessary to emphasize that the concentration of the carbon atoms in the outermost layer of the P50 adsorbent is high, so the admolecules will mainly interact with them. The interactions of the admolecules with the heteroatoms are rather negligible.

2.2. Static measurements

The sample of the active carbon was subjected to

adsorption/desorption experiments employing nitrogen gas at 77 K as the adsorbate. Measurements of the extent of adsorption/desorption observed were made using a Carlo Erba Sorptomatic 1900 automatic adsorption apparatus. The adsorption characteristics were calculated on the basis of such isotherm at 77 K. The micropore volume, W_o , and characteristic adsorption energy, E_o , (e.g. the Dubinin–Radushkevich parameters) calculated for this sample were 0.55 cm³/g and 15.9 kJ/mol, respectively. The specific surface area was 1330 m²/g, while the half-width of the micropore entrance was 800 pm.

2.3. Supercritical fluid extraction

The P50 adsorbent, thus characterized in terms of its mineral impurity content and its Dubinin–Radushkevich (DR) parameters, was separated in two parts. Each part was loaded with *tert.*-butyl acetate (*Otert.B*), and *n*-butyl acetate (*OnB*) in the proportion 0.87 g of *Otert.B* or *OnB* on 5 g of active carbon. The *Otert.B* and *OnB* were then subjected to supercritical fluid extraction (SFE) in an apparatus employing a 10 cm³ extraction cell at 325 K and 15 MPa pressure by a dynamic method using supercritical CO₂ (SCCO₂) [15,16]. Hereafter, the samples are denoted as P50+*Otert.Br* and P50+*OnBr*, respectively. Taking into account the isotherms in P (pressure) versus X (mol fraction) space (in the equilibrium diagram of the binary mixtures: *OnB*–SCCO₂ and *Otert.B*–SCCO₂), it is possible to state that a monophasic *OnB*–SCCO₂ and *Otert.B*–SCCO₂ system, i.e. complete miscibility of *OnB* and *Otert.B* in SCCO₂, existed under the extraction conditions applied.

2.4. Chromatographic measurements

The chromatographic measurements were undertaken using a Unicam type 610 gas chromatograph fitted with an on-line Unicam 4880 chromatography data handling system which was switched on when a sample was injected. The instrument was equipped with a flame ionization detector and a thermal conductivity detector. The active carbon was placed in 65 cm×0.2 cm I.D. glass columns, the length of the adsorbent bed in each column being 6–7 cm. The

part of the column which was unoccupied by the adsorbent was filled with glass beads of 80 mesh size. The filled column was mounted in the chromatograph thermostat and heated at 603 K for 10 h in a helium stream at a flow-rate of 40 cm³/min. A mixture of the known amounts of methane, and propane was used in the chromatographic tests (analytical reagent-grade, BOC Gases, UK). Measurements of retention times of propane were carried out at 303–318 K using helium at a flow-rate $F_c = 17.5 \pm 0.05$ of cm³/min.

Propane was chosen as adsorbate, because its molecule has the virtue of chemical inertness towards the majority of adsorbents (including active carbons), and its saturation pressures are such that it can be worked conveniently at temperatures around ambient. Regarding the critical dimensions of propane molecule [17]: breadth 490 pm; thickness 400 pm and length 610 pm (the dimensions given are in three directions at right angles), it may be stated that the adsorbate molecule can only have little room for movement or flexibility in micropores of 800 pm free diameter.

The gas hold-up time, t_M , was calculated from the linear dependence [13,18]:

$$\ln[(t_{Ri} - t_M)\sqrt{M_i}] = a + bU(r) \quad (5)$$

where t_{Ri} and M_i are the retention time and molar masses of the inert gases i (Ar, Kr, Ne and Xe); a and b are constants; $U(r)$ is the value of the Kirkwood–Müller potential function [19].

The basic idea of calculating the t_M values is to assume that molecules (Ar, Kr, Ne and Xe) and the active carbon surfaces are made up of collections of spherical sites which interact with the sites in adsorbates via simple functions such as the Kirkwood–Müller or Lennard–Jones 12-6 or 9-3 power that are widely used in the modeling of bulk phases. The Kirkwood–Müller and Lennard–Jones potentials appear to be a satisfactory representation of the interaction between simple molecular species. The interaction energy of simple non-polar admolecules on the active carbon can be attributed to dispersion forces (i.e. London's dispersion forces). Dispersion forces ensue from charge fluctuations that occur throughout a molecule that arises from electron/nuclei vibrations. They are random in nature and are

basically a statistical effect. Their state is determined by quantum mechanics.

The temperature of the flame ionization detector was 388 K and that of the thermal conductivity detector was 513 K.

The chromatographic peaks obtained were asymmetrical in shape, the retention times connected with their peak maxima and the centres of gravity depended on the size of the sample injected and with superposition of their diffusive sides. Therefore for calculating propane adsorption isotherms, the peak profile method was used [2,4,5]. The active carbons tested characterise a significant partition of micropore volume occurring in the total pore volume, therefore the column efficiency is poor and the adsorbate peaks exhibit tailing under linear conditions. Because propane molecules diffuse too slowly along the micropore network, they are strongly adsorbed since they find themselves surrounded by the potential field generated by the pore walls. The propane molecules collide with the micropore walls much more frequently than with each other, and they are momentarily adsorbed and then released in random directions (diffusively reflected). Next, the adsorbate molecules desorb and diffuse out of the micropores, indicating the dominant effect of diffusion on the rate of establishment of the adsorption equilibrium of propane. The wall "resistance", which causes a delay as a result of both the diffuse reflection and the finite time the molecule is adsorbed, leads to a reduction in the molecular flux. This is known as "Kundsen diffusion". Kinetic theory provides the following relationship for Kundsen diffusion in gases in straight round micropores [20,21]:

$$\begin{aligned} D_K &= \frac{2}{3} \cdot r_m \bar{u} \\ &= \frac{2}{3} \cdot r_m \sqrt{\frac{8RT}{\pi M_{C_3H_8}}} = 9700 r_m \sqrt{\frac{T}{M_{C_3H_8}}} \end{aligned} \quad (6)$$

where $\bar{u} = \sqrt{\frac{8RT}{\pi M_{C_3H_8}}}$ is the mean molecular velocity, according to gas kinetic theory.

It has been assumed that the micropore radius, r_m , is equal to the half-widths of the micropore entrances, x_0 (in nm):

$$r_m = x_o = \frac{(13.028 - 1.53 \cdot 10^{-5} E_o^{3.5})}{E_o} \quad (7)$$

The values of the Kundsens diffusion coefficient for the active carbon tested chromatographically were $1.58 \times 10^{-3} < D_{K(C_3H_8)} \text{ (cm}^2/\text{s)} < 2.27 \times 10^{-3}$, and for the adsorbent tested under static conditions were $1.11 \times 10^{-3} < D_{K(N_2)} \text{ (cm}^2/\text{s)} < 1.35 \times 10^{-3}$. Prasetyo and Do have observed that the experimental diffusivities are much lower than those calculated from the Kundsens equation (for Ajax Activated Carbon, type 976), suggesting the flow in the micro-pore is not of Kundsens origin, but rather is an activated process with an energy less than the heat of adsorbate adsorption [21]. An account was taken of the effect of the adsorbate diffusion in the active carbon on adsorption according to Dollimore et al. [22].

For non-Gaussian peaks, it is often difficult or impossible to find analytical expressions for the concentration profile, but comparatively easy to obtain expressions for the various moments. The n th statistical moment, m_n , is defined by the equation:

$$m_n = \frac{\int_0^{\infty} t^n c(t) dt}{\int_0^{\infty} c(t) dt} \quad (8)$$

where $c(t)$ is the concentration of adsorbate observed at the detector at time t after the injection of the known amount of adsorbate into the column. The first moment corresponds to $n=1$ and is clearly the elution time of the centre of gravity of the peak, since it is obtained by weighting the elution time of each point in the peak by its concentration.

3. Results and discussion

The chromatographic peaks obtained were asymmetric in shape (i.e. non-Gaussian with a sharp front and diffuse rear boundary), the retention times of their maxima and centres of gravity depended on the size of the sample injected and with superposition of the diffuse rear boundaries of the peaks. The

peak-shapes obtained show that axial dispersion was negligibly small with the kinetic rate of mass transfer being infinite (i.e. the column efficiency was infinite under the chromatographic conditions applied), the concentration of propane on the adsorbent surface under equilibrium conditions being no longer proportional to its concentration in the mobile phase (helium) [2].

The peak profile method was used for calculating the propane adsorption isotherms, chromatographic measurements being carried out for different volumes of propane injected onto the column to check if the calculated C_3H_8 -isotherms represent the same equilibrium partition isotherm of the adsorbate between the adsorbent surface and the mobile phase. The convex-upward isotherms were obtained, which were superimposed for different amounts of propane injected onto chromatographic column. For a convex-upward isotherm, the adsorbate concentration at equilibrium on the active carbon surface increased less rapidly than the adsorptive concentration in the mobile phase.

The propane adsorption isotherms calculated on the basis of asymmetric peaks were described with the cubic B-spline function, and next differentiated with respect to the propane equilibrium pressure, p . The cubic B-spline curve can be described by parametric equations. Around the point with coordinates $X_i(p)$, $Y_i(p)$, it takes the form:

$$X_i(p) = \frac{1}{6} \cdot \{(-p^3 + 3p^2 - 3p + 1)X[i-1] + (3p^3 - 6p^2 + 4)X[i] + (-3p^3 + 3p^2 + 3p + 1) \times X[i+1] + p^3 X[i+2]\} \quad (9a)$$

$$Y_i(p) = \frac{1}{6} \cdot \{(-p^3 + 3p^2 - 3p + 1)Y[i-1] + (3p^3 - 6p^2 + 4)Y[i] + (-3p^3 + 3p^2 + 3p + 1) \times Y[i+1] + p^3 Y[i+2]\} \quad (9b)$$

where $2 \leq i \leq n-2$. This cubic B-spline is continuous up to second-order derivative.

The first derivative obtained was positive, $\left(\frac{da}{dp}\right)_T > 0$, and its values decreased monotonically with propane equilibrium pressure. The second derivative was negative, $\left(\frac{d^2a}{dp^2}\right)_T < 0$, and its absolute

values decreased monotonically with equilibrium pressure. The first and the second derivatives calculated for different amounts of propane superimposed, respectively, similar to the diffusive sides of the propane peaks and the propane adsorption isotherms from which they were previously calculated. The variations of the first and second derivatives with equilibrium pressure are depicted in Figs. 1 and 2, respectively.

The superimposition of the first and second derivatives calculated for different amounts of propane injected onto the chromatographic column is an additional criterion of ideality or not of the chromatographic process. In an ideal chromatographic process, infinity of the column efficiency is assumed, or in other words, the axial dispersion is negligibly small and the rate of the mass transfer kinetics is infinite. In ideal chromatography, the adsorbent internal surface is constantly at equilibrium with the adsorbate which percolates through the adsorbent particle bed. Under such conditions, the peak profiles are controlled only by thermodynamics of phase equilibria. The achievement of the ideality of the

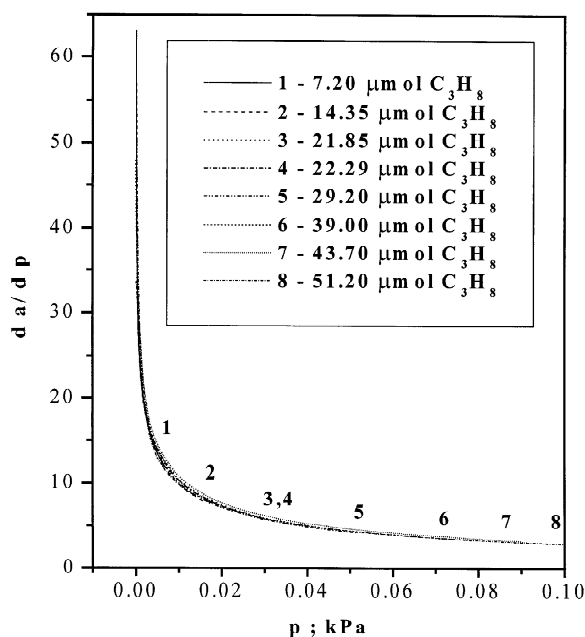


Fig. 1. The variations of the first derivatives with equilibrium pressure, $\left(\frac{da}{dp}\right)_T$, for different amounts of propane injected onto the chromatographic column with the P50 active carbon at 303 K.

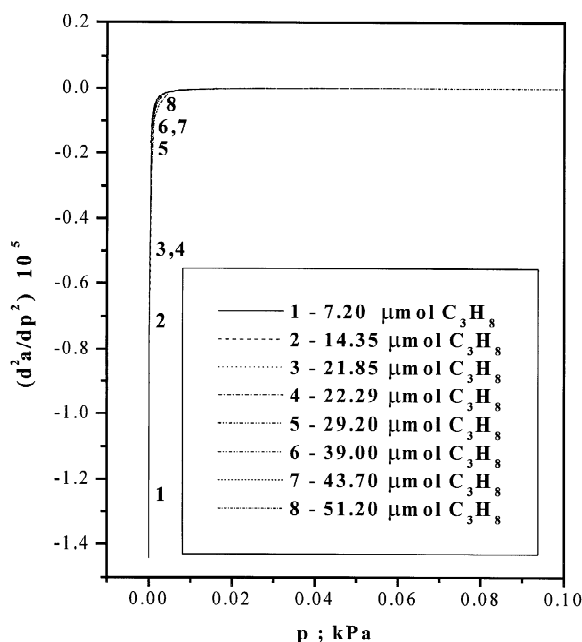


Fig. 2. The variations of the second derivatives with equilibrium pressure, $\left(\frac{d^2a}{dp^2}\right)_T$, for different amounts of propane injected onto the chromatographic column with the P50 active carbon at 303 K.

chromatographic process is possible but rather difficult when the microporous adsorbents are used, because the influence of axial dispersion on the rear profile of a peak does exist, due to the finite rate of the mass transfer kinetics and the axial diffusion.

As applied to the real chromatographic adsorption process, Henry's law is a linear relationship of the amount of adsorbate in the gaseous phase to the amount in the surface phase, for the case of ideal, non-linear chromatography. As the amount of adsorbate in each phase can be expressed in various units, Henry's constant can take several different forms [23]:

$$H_{a,c}^o = \lim_{c \rightarrow 0} \left(\frac{\partial a}{\partial c} \right)_{S,T} \quad (10)$$

$$H_{\Gamma,c}^o = \lim_{c \rightarrow 0} \left(\frac{\partial \Gamma}{\partial c} \right)_{S,T} \quad (11)$$

$$H_{\Gamma,p}^o = \lim_{p \rightarrow 0} \left(\frac{\partial \Gamma}{\partial p} \right)_{S,T} \quad (12)$$

where a is the number of moles of adsorbate in the surface layer; c the concentration of adsorbate in the

gas phase; Γ , the amount of adsorbate per unit area of the surface layer; p , the equilibrium pressure of adsorbate in the gas phase; the index $^{\circ}$ refers to zero surface coverage.

Using the following equations: $p = cRT$ and $\Gamma = \frac{a}{Sm}$ (S is the BET specific surface area of the adsorbent and m is the total mass of adsorbent in column), Henry's constants are interrelated by:

$$H_{\Gamma,p}^{\circ} = \frac{H_{\Gamma,c}^{\circ}}{RT} \quad (13)$$

$$H_{\Gamma,c}^{\circ} = \frac{H_{a,c}^{\circ}}{Sm} \quad (14)$$

$$H_{\Gamma,c}^{\circ}(Sm) = H_{\Gamma,p}^{\circ}(RTSm) = V_{g(T)}^{\circ} \quad (15)$$

In inverse gas chromatography, the specific retention volume referred to the column temperature and to zero coverage of the adsorbent surface with adsorbate, $V_{g(T)}^{\circ}$, depends on the value of the specific surface area of the adsorbent. In this case the $V_{g(T)}^{\circ}$ value one has to refer to the specific surface area obtaining the net retention volume, $V_{S(T)}^{\circ}$, being a physicochemical constant:

$$H_{\Gamma,c}^{\circ}(m) = H_{\Gamma,p}^{\circ}(RTm) = V_{S(T)}^{\circ} \quad (16)$$

When the theoretical link between chromatographic elution process and its thermodynamics is the concept of the specific retention volume, $V_{g(T)}^{\circ}$, so the adsorption second virial coefficient, B_{2S}° , would have the same physical meaning. These parameters are directly proportional to the limiting slope of the adsorption isotherm of one adsorbate:

$$V_{g(T)}^{\circ} = B_{2S}^{\circ} = RTSm \cdot \lim_{p \rightarrow 0} \left(\frac{\partial \Gamma}{\partial p} \right)_{S,T} \quad (17)$$

The adsorption second virial coefficients can be employed for the general characterization of the attractive and repulsive interactions between the outermost layer of adsorbent atoms and adsorbate molecules. The coefficient values should also be referred to zero coverage of the adsorbent surface with adsorbate:

$$B_{2S}^{\circ} = \lim_{v \rightarrow 0} B_{2S}(v) \quad (18)$$

where v is the amount of adsorbate injected onto the column.

The B_{2S}° values calculated in the proposed manner are linked to the same partition isotherm and the same adsorption isotherm for the chromatographed adsorbates at the interface.

Taking into account the (13)–(15) dependencies, one can write for unity of S and m :

$$H_{\Gamma,c}^{\circ} = H_{\Gamma,p}^{\circ} RT = V_{g(T)}^{\circ} = B_{2S}^{\circ} \quad (19a)$$

and

$$H_{a,c}^{\circ} = H_{\Gamma,c}^{\circ} \quad (19b)$$

Hence, for $S \neq 1$ and $m \neq 1$ and for $S > 0$, $m > 0$:

$$H_{\Gamma,p}^{\circ} = \frac{B_{2S}^{\circ}}{T} \cdot \frac{1}{RSm} \quad (20a)$$

and

$$\ln H_{\Gamma,p}^{\circ} = \ln \left(\frac{B_{2S}^{\circ}}{T} \cdot \frac{1}{RSm} \right) \quad (20b)$$

Regarding the dependency [23]:

$$\Delta G = -RT \ln H_{\Gamma,p}^{\circ} = \Delta H - T\Delta S \quad (21)$$

the Antoine-type (i.e. hyperbolic-type) equation can be obtained:

$$\ln \frac{B_{2S}^{\circ}}{T} = \frac{-\Delta H_{\text{ads}}^{\circ}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\text{ads}}^{\circ}}{R} + \ln(RSm) \quad (22)$$

The dependency (22) has practically the same form as that commonly applied in chromatographic calculations [1]:

$$\ln \frac{V_{g(T)}^{\circ}}{T} = \frac{-\Delta H_{\text{ads}}^{\circ}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\text{ads}}^{\circ}}{R} + \ln(RSm) \quad (23)$$

so it can be seen that the physical meaning of the adsorption second virial coefficient is very akin to the specific retention volume. The plots corresponding to Eqs. (22) and (23) are depicted in Fig. 3.

The differential isosteric enthalpy term (the first term in Eqs. (22) and (23)) represents the energy involved when the adsorbate molecule interacts specifically and non-specifically with the adsorbent atoms (mainly with the outermost layer of adsorbent atoms, but not only!). However, when the adsorbate molecule interacts with the adsorbent atoms it also suffers a change in freedom of movement. So, the

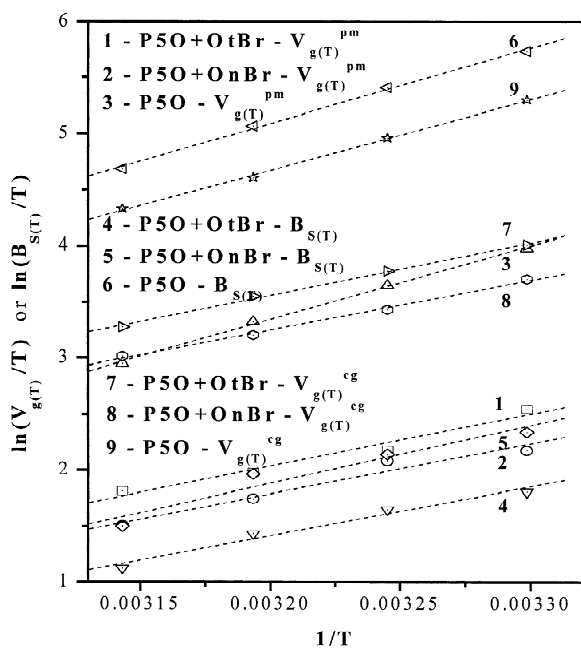


Fig. 3. The variations of the plots: $\ln\left(\frac{V_{g(T)}}{T}\right) = f_1\left(\frac{1}{T}\right)$ and $\ln\left(\frac{B_{s(T)}}{T}\right) = f_2\left(\frac{1}{T}\right)$ for different chromatographic data.

magnitude of the differential entropy term (the second and third terms in Eqs. (22) and (23)) is just a measure of the loss of freedom or randomness that an adsorbate molecule has when migrating from one phase to the other. A large entropy change indicates that the adsorbate molecules are more restrained with

less random movement along the tree-like porous structure of an activated carbon.

The differential isosteric enthalpies and entropies of adsorption were assumed to be independent of temperature in the range encompassed by the chromatographic measurements. The values were calculated on the basis of the retention times of peaks and their centres of gravity as well employing Eq. (22). The values obtained are compared with the results calculated on the basis of the adsorption second virial coefficient applying Eq. (23). The values of the aforementioned quantities are summarized in Table 1. The values of the differential isosteric enthalpy calculated for the centres of gravity are lower in comparison with the peak maxima values. The aforementioned values calculated on the basis of the retention times of centres of gravity are akin to the results obtained on the basis of the adsorption second virial coefficient for the Tóth equation parameters.

The values of the differential isosteric enthalpies and entropies of propane adsorption determined by chromatographic and static methods on different adsorbents at different temperatures are summarized in Table 2 in order to compare with the results reported here. The values of the isosteric enthalpies of adsorption obtained on more graphitised carbon blacks are lower in comparison with the results obtained on the active carbons. These values obtained on the *Carbograph 4* ($S = 129 \text{ m}^2/\text{g}$ [24]) and *Carbograph 5* ($S = 233 \text{ m}^2/\text{g}$ [24]) graphitised car-

Table 1

The comparison of the values of the isosteric enthalpies of adsorption and entropies of adsorption calculated on the basis of the adsorption second virial coefficient “B” and the specific retention volumes “V” by different methods (i.e. calculated on the basis of the peak maxima—*pm* and centres of gravity—*cg*)

Parameter	Equation	Sample		
		P5O	P5O+OnBr	P5O+Otert.Br
$-\Delta H_{(V)}^{pm}$; kJ/mol		54.9±0.3	40.4±0.2	44.6±0.3
$-\Delta H_{(V)}^{cg}$; kJ/mol		52.5±0.2	37.3±0.1	39.2±0.1
$-\Delta S_{(V)}^{pm}$; J mol ⁻¹ K ⁻¹		261.8±2.5	230.2±3.1	241.9±1.4
$r_{(pm)}^2$		0.97–0.99	0.94–0.96	0.94–0.97
$-\Delta S_{(V)}^{cg}$; J mol ⁻¹ K ⁻¹		188.9±2.1	151.6±2.8	154.5±1.8
$r_{(cg)}^2$		0.98–0.99	0.95–0.98	0.95–0.97
$-\Delta H_{(B)}$; kJ/mol	Tóth	52.8±0.2	39.8±0.2	38.7±0.3
	Unilan	54.6±0.3	43.1±0.2	36.4±0.1
$-\Delta S_{(B)}$; J mol ⁻¹ K ⁻¹	Tóth	169.8±2.1	158.9±1.9	151.4±2.6
	Unilan	201.5±3.1	181.6±1.9	180.8±1.4
r^2	Tóth	0.94–0.96	0.96–0.98	0.94–0.95
	Unilan	0.96–0.99	0.97–0.98	0.95–0.96

Table 2

The values of the differential isosteric enthalpies and entropies of propane adsorption determined by chromatographic (chrom.) and static (stat.) methods on different adsorbents at different temperature ranges

Adsorbent	Method	Temp. range (K)	$-\Delta H_{\text{ads}}$ (kJ/mol)	$-\Delta S_{\text{ads}}$ (J mol ⁻¹ K ⁻¹)	Reference
<i>Carbopack B</i> graphitised carbon black	Chrom.	–	30.1	37.2	[30]
<i>Carbopack B</i> graphitised carbon black	Chrom.	273.2–373.2	26.6	–	[18]
<i>Carbopack B</i> graphitised carbon black and heat-treated in H ₂	Chrom.	–	29.3	–	[30]
<i>Carbopack C</i> graphitised carbon black	Chrom.	223–340	22.2	88.9	[31]
<i>Carbopack C</i> graphitised carbon black	Chrom.	273.2–373.2	23.6	–	[18]
<i>Carbopack C</i> graphitised carbon black	Chrom.	–	25.5	25.1	[28]
<i>Carbopack C</i> graphitised carbon black and heat-treated in H ₂	Chrom.	–	28.5	–	[30]
<i>Carbopack F</i> graphitised carbon black	Chrom.	–	24.3	31.8	[29]
<i>Graphon</i> graphitised carbon black	Chrom.	–	35.1	63.2	[32]
<i>Graphon</i> graphitised carbon black and heat-treated in H ₂	Chrom.	–	24.7	39.8	[32]
<i>Sterling FTG</i> graphitised carbon black	Chrom.	–	25.5	40.2	[32]
<i>Sterling FTG</i> graphitised carbon black and heat-treated in H ₂	Chrom.	–	25.7	40.6	[32]
<i>Sterling MT 3100</i> graphitised carbon black	Chrom.	218–269	24.8	–	[33]
	Stat.	258.2–296.7	27.2	–	
<i>Sterling MT 3100</i> graphitised carbon black					[34,35]
	Chrom.	296.5–372	26.2	–	
<i>Carbograph 4</i> graphitised carbon black	Chrom.	–	37.2	73.2	[26]
<i>Carbograph 5</i> graphitised carbon black	Chrom.	–	42.3	73.2	[26]
<i>R-2 Ekstra</i> active carbon	Chrom.	413–453	46.9	–	[36]
<i>S2</i> active carbon	Chrom.	413–453	37.7	–	[36]
<i>Saran</i> active carbon	Chrom.	–	40.6	–	[37]
<i>Carbosieve B</i> carbon molecular sieve	Chrom.	–	49.5	–	[38]
<i>CC1</i> high burn off charcoal cloth	Chrom.	–	44.3	–	[38]
<i>CC2</i> high burn off charcoal cloth	Chrom.	–	46.2	–	[38]
<i>5A</i> zeolite	Stat.	278–463	35.2	–	[39]

–, denotes the lack of unambiguous temperature range and entropies of adsorption data.

bon blacks are comparable with the results obtained on the *S2* active carbon and the *5A* zeolite or higher than on the *Saran* active carbon. The *5A* zeolite is the synthetic zeolite with the ability, already noted, to separate *n*-paraffins from other hydrocarbons when in its *Ca*-exchanged form (size limit ≈ 490 pm [17]). Graphitised carbon black is commonly shown to be an adsorbent which has a homogeneous surface and can therefore be used to determine basic information about the nature of adsorbate–adsorbent interactions. However, Sing pointed out that the graphitised carbon black surface is also heterogeneous [25]. Mastrogiacomo and Pierini confirmed Sing's idea [26]. They covered the *Carbograph 4* surface with a different amount of squalane and determined chromatographically the differential iso-

stERIC enthalpy of adsorption. The variation of the differential isosteric enthalpy of propane adsorption (after smoothing Mastrogiacomo and Pierini's chromatographic data [26] by B-spline curve) is depicted in Fig. 4. On the non-covered *Carbograph 4* surface (0% coverage with squalane) the differential isosteric enthalpy of adsorption is the highest, and it may be related to the strong adsorption forces existing between the very active adsorbent sites and propane molecules. At low coverages of surface with squalane, the enthalpy of propane decreases because of deactivation by squalane molecules of the most active sites on the adsorbent surface. After these sites have been deactivated by squalane molecules, one should expect the enthalpy of propane adsorption to be on a constant level, i.e. corresponding to the

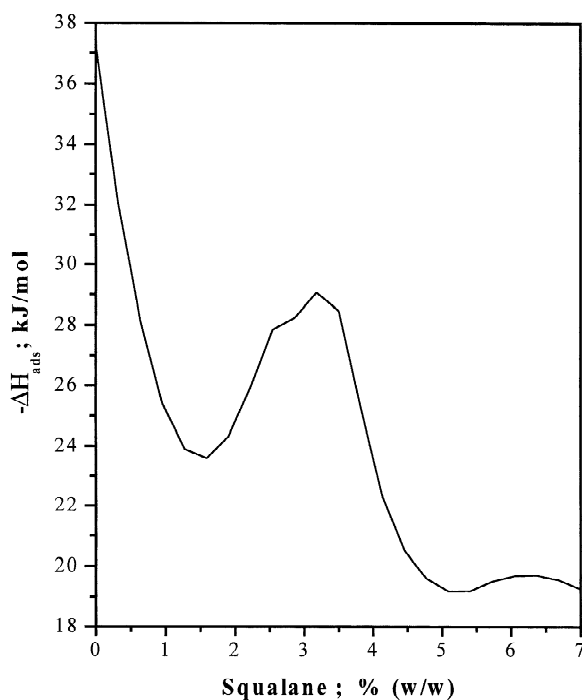


Fig. 4. The variation of the differential isosteric enthalpy of adsorption of propane versus percentage (w/w) of squalane on *Carbograph 4* (after smoothing Mastrogiacomo and Pierini's chromatographic data [26] by B-spline curve).

values given by adsorption on the real homogeneous surface. However, the isosteric enthalpy change is quite the contrary, it increases to a broad maximum and next decreases to a constant level. The existence of the maximum indicates the presence of many structural irregularities on the graphitised carbon surface, which were observed by Donnet [27]. The curve depicted in Fig. 4 is very akin to that obtained by Bruner et al. [28] for *Carbopack C*, but quite different for the *Sterling FT*, hydrogen-treated *Carbopack C* and *LS* graphitised carbon blacks [29,30]. The existence of the maximum is due to the lateral interaction with molecules of squalane. The presence of irregularities is related to the shape of the maximum breadth, and poorly accentuated and to the absence of a second peak in correspondence to the second monolayer.

Active carbon is generally considered to consist of rigid clusters of microcrystallites, with each microcrystallite made up of a stack of graphite planes. Each carbon atom within a particular plane is bonded

to three adjacent carbon atoms, with carbon atoms at the edges of the carbon planes having highly reactive radical sites. Adsorption occurs at these sites and so they have a decisive influence on adsorbate elution.

Taking the values of the differential isosteric enthalpy of adsorption presented in Table 2 into account, it may be stated that they are higher on the graphitised carbon blacks heat-treated in hydrogen in comparison with the results obtained on the non-treated ones. The $-\Delta H_{\text{ads}}$ values for the *Graphon* and *Carbopack B* graphitised carbon blacks are the exception to the rule. It is necessary to emphasize that the $-\Delta H_{\text{ads}}$ magnitudes determined:

- (i) chromatographically and statically in different temperature ranges on the *Sterling MT 3100* graphitised carbon black differ only by 1 kJ/mol;
- (ii) on the same graphitised carbon black but at different laboratories are significantly different.

The $-\Delta H_{\text{ads}}$ values obtained are comparable with the results obtained on the active carbons by other authors (Tables 1 and 2). The entropy of adsorption is also comparable with the other authors' results in the case of values calculated on the basis of the peak maxima data, but the $-\Delta S_{\text{ads}}$ values calculated on the basis of the retention times of gravity centres of peaks are significantly higher.

4. Conclusions

The analysis of the results obtained reveals the following:

- (i) A derived simple dependency between the $-\Delta H_{\text{ads}}$ and $-\Delta S_{\text{ads}}$ magnitudes and experimental data through the Antoine-type equation enables the $-\Delta H_{\text{ads}}$ and $-\Delta S_{\text{ads}}$ magnitudes to be calculated from adsorption second virial coefficients, B_{2S} , calculated on the basis of chromatographically determined adsorption isotherm data.
- (ii) The values of the adsorption second virial coefficients found empirically varying linearly with reciprocal column temperature, T , akin to the specific retention volumes.
- (iii) The agreement of Tóth and Unilan equations for the differential isosteric enthalpy of adsorption at the limit of zero surface coverage, $-\Delta H_{\text{ads}}^0$ is

a sensitive test of the accuracy of the adsorption second virial coefficients.

- (iv) If there is a large discrepancy between the two values of the adsorption second virial coefficients, or if one of them is negative, the values obtained for the differential isosteric enthalpy of adsorption and the adsorption second virial coefficients should be disregarded, of course.
- (v) The three parameter equations employed, i.e. the Tóth and Unilan are confirmed to be the best all-round equations for the description of the chromatographic adsorption data on the microporous active carbons.

References

- [1] H. Grajek, Z. Witkiewicz, H. Jankowska, J. Chromatogr. A 782 (1997) 87.
- [2] G. Guiochon, S. Golshan-Shirazi, A.M. Katti, *Fundamentals of Preparative and Non-linear Chromatography*, Academic Press, Boston, MA, 1994.
- [3] *Nomenclature for Non-linear Chromatography (IUPAC Recommendations 1996)*, Pure Appl. Chem. 68 (1996) 1591.
- [4] Z. Witkiewicz, H. Grajek, J. Choma, J. Chromatogr. 556 (1991) 441.
- [5] H. Grajek, S. Neffe, Z. Witkiewicz, J. Chromatogr. 600 (1992) 67.
- [6] J. Tóth, W. Rudziński, A. Waksmundzki, M. Jaroniec, S. Sokółowski, Acta Chim. Acad. Sci. Hung. 82 (1974) 11.
- [7] D.P. Valenzuela, A.L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice-Hall, Englewood Cliffs, NJ, 1989.
- [8] W. Rudziński, D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.
- [9] J. Tóth, Acta Chim. Acad. Sci. Hung. 69 (1971) 311.
- [10] J. Tóth, in: A. Dąbrowski (Ed.), *Adsorption and Its Application in Industry and Environmental Protection*, Vol. I, Applications in Industry, Elsevier, Amsterdam, 1999, p. 485.
- [11] J.M. Honig, L.H. Reyerson, J. Phys. Chem. 56 (1952) 140.
- [12] J.A. Korver, Chem. Weekblad 46 (1950) 301.
- [13] H. Grajek, Z. Witkiewicz, J. Chromatogr. A 969 (2002) 87.
- [14] H.P. Böehm, Carbon 32 (1994) 759.
- [15] H. Grajek, Adsorp. Sci. Technol. 18 (2000) 347.
- [16] H. Grajek, Adsorp. Sci. Technol. 19 (2001) 303.
- [17] R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978.
- [18] J.F. Parcher, P.J. Lin, Anal. Chem. 53 (1981) 1889.
- [19] T. Nakahara, P.S. Chappellear, R. Kobayashi, Ind. Eng. Chem. Fundam. 16 (1977) 220.
- [20] W. Benzinger, K.J. Hüttinger, Carbon 34 (1984) 1465.
- [21] I. Prasetyo, D.D. Do, AIChE J. 45 (1999) 1892.
- [22] D. Dollimore, G.R. Heal, D.R. Martin, J. Chromatogr. 50 (1970) 209.
- [23] D. Atkinson, G. Curthoys, J. Chem. Educ. 55 (1978) 564.
- [24] A.R. Mastrogiacomo, M.F. Ottaviani, E. Pierini, M. Cangioti, M. Mauro, F. Mangani, Chromatographia 55 (2002) 345.
- [25] K.S.W. Sing, Carbon 32 (1994) 1311.
- [26] A.R. Mastrogiacomo, E. Pierini, Chromatographia 53 (2001) 437.
- [27] J.-B. Donnet, Carbon 32 (1994) 1305.
- [28] F. Bruner, G. Bertoni, P. Ciccioli, J. Chromatogr. 120 (1976) 307.
- [29] F. Mangani, F. Bruner, J. Chromatogr. 289 (1984) 85.
- [30] G. Crescentini, F. Mangani, A.R. Mastrogiacomo, P. Palma, J. Chromatogr. 392 (1987) 83.
- [31] Z. Krawiec, M.-F. Gonnord, G. Guiochon, J.R. Chretien, Anal. Chem. 51 (1979) 1655.
- [32] A. DiCorcia, R. Samperi, J. Phys. Chem. 77 (1973) 1301.
- [33] E.V. Kalaschnikova, A.V. Kiselev, R.S. Petrova, K.D. Shcherbakova, Chromatographia 4 (1971) 495.
- [34] S. Ross, J.P. Olivier, *On Physical Adsorption*, Wiley-Interscience, New York, 1964.
- [35] S. Ross, J.K. Saelens, J.P. Olivier, J. Phys. Chem. 66 (1962) 696.
- [36] A. Betti, F. Dondi, G. Blo, S. Coppi, G. Cocco, G. Bighi, J. Chromatogr. 259 (1983) 433.
- [37] T.H. Gvozdoich, A.W. Kiselew, J.I. Jaszyn, Neftekhimija 8 (1968) 476.
- [38] X.L. Cao, B.A. Colenutt, K.S.W. Sing, J. Chromatogr. 555 (1991) 183.
- [39] W. Schirmer, G. Meinert, A. Grossmann, Monatsberichte 11 (1969) 886.