Energetic effects of adsorption of C₆-C₈ hydrocarbons on hard coal samples of different metamorphism

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Abstract. The analysis of sorption equilibrium of aliphatic saturated and unsaturated hydrocarbons on low and medium rank coals were performed. Isosteric sorption enthalpy correlation with the degree of fill of sorption capacity was presented for the low rank coal. There was found a crucial role of primary pore structure in the coal grains in the process of sorption, especially in case of temperature anomalies occurrence. Hexane differently than other hydrocarbons of longer chains, represent the property of micropore penetration. Due to literature the presence of double bound in other molecules causes difficulties with penetration into porous structure of coal.

1 Introduction

The analysis of structure, chemical and physical characteristic of coal as well as organic reactivity of coal are basic research measurements. The correlation between chemical and physical structure and physicochemical properties of hard coal are significant for the determination of its usefulness in the coal processing into chemical and energy raw materials as well as in the research aimed at determination of gases accumulation in coal.

Hard coal seams can be treated as a specific collector of mine gases. Those gases are mainly: CO_2, CH_4 i N_2, its share in the seams is directed by geological history of the deposit. Seams posses different properties than typical reservoirs with porous fulfillment. Those differences are a result of coal ability to deform under the influence of external mechanical load, pressure of mine gases and water in the pores and channels of coal, as well as sorption capacity of coal substance [1]. These factors affect the permeability of the deposit, at the same time remain in close relation to the techniques of obtaining methane, predicting emissions of gas in the process of mining or uncontrolled outbursts of gases and rocks.

The sorption experiments of gases and vapors on coal, especially the analysis and interpretation of the equilibrium state of sorption process at constant temperature, carried out initially in the fifties and sixties of the last century, are still of scientists interest. It is an important source of information for describing the characteristics of various coal types with respect to their porosity, coal coalification degree, type and composition of macerals, chemical structure etc.

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Coal is a complex structure, in which sorption properties are significantly associated with the degree of coalification [2,3,4]. Multiple oxygen groups on the surface, control the degree of hydrophilicity of the coal surface. It is known that the structure of the coal to large extend represent apolar character. Therefore, coal is said to be a system of dual nature: hydrophobic and hydrophilic. The reactive groups in a very large degree influence sorption of polar substances and in a characteristic way regulate sorption of apolar substances such as methane or aliphatic hydrocarbons as well as aromatic hydrocarbons and carbon dioxide [5]. By the analysis of phenomena connected with the structure responsible for the process of sorption/desorption of gases/vapors, the occurrence of outburst of gases and rocks as well as accumulation and capturing of these gases can be explained [6,7,8,9]. Interactions sorbate - sorbent play an important role in the description and modeling of processes such as outburst of gases and rocks.

2 Materials and experimental methods

From the group of aliphatic saturated hydrocarbons there were selected sorbates: hexane, heptane, octane, and for the comparison two from alken group: 1-hexene, 1-heptene. Adsorbates selection was dictated by cognitive and practical aspects. What is important is that those substances differ in molecule structure, molecular dimensions, bonds present and the dipole moment value, but at the same time have similar physicochemical properties, particularly, the value of the vapor pressure of the examined temperatures. What's more are components of gas mixtures present in the mining gases of coal seams. Selected sorbates were of analytical grade purity. In standard conditions they were present in the liquid state.

Samples of coals of different coalification degree (ISO 11760 : 2007) from polish coal mines were selected as a basic research material:

-low rank coal – Brzeszcze coal mine (seam 325, level 430m) – **B,**
-medium rank coal – Victoria coal mine (field "Witold", seam 307) – **Vi,**
-high rank coal – Wałbrzych (field "Chrobry", seam 430) **– W.**

Above there were presented the symbols of samples, used instead of full names, which were used in this paper. Systematic of samples was proposed for clarity and readability of the work. Samples of coal were selected in the way that carbon contend would differ and that they had different average reflectivity index R_n^0. It is claimed that the value R_n^0 indicates a degree of metamorphism of the examined coal. For the study, sample of coal of grain size ϕ 1.0-1.5mm were chosen, grains were of irregular shape. Grains of this size were large enough to minimize the effect of fractioning, at the same time small enough to reach equilibrium and allow to fulfil the condition of isotherms reversibility. In addition, it was possible to use a uniform particle size distribution for all types of performed analysis, which proves the results to be comparative. Majority of sorption research on hard coal presented in literature is performed on powder samples or on samples of granulation not higher than 0,9mm. As a result of such drastic fragmentation lost of primary pore structure can be observed as well as lost of chemical character of outer coal grains surface, which can have influence on higher values of sorbed amount of gas/vapors [20,21]. In order to characterize the research material there were analysis carried out: porosimetry and densimetry analysis, helium density measurements. Furthermore Boehm method was used to determine the surface functional groups. Ultimate and proximate (Table 1) and petrographic (Table 2) analysis were taken from the literature [10,11]. Characterisation of coal samples is shown in Tables 1-4.

Table 1. Selected parameters of ultimate and proximate analysis of experimental hard coal samples [10,11]

Coal sample	Chemical composition [wt. %]			Technical analysis[wt.%]			
	C^{daf}	H^{daf}	$(O+N)^{daf}$	S^{daf}	V^{daf}	W^a	A^a
B	79.60	5.09	14.70	0.72	40.87	2.9	15.50
Vi	87.58	4.88	6.41	---	27.9	1.25	7.78
W	92.13	2.95	3.76	---	9.46	0.77	9.10

Explanation: W – moisture; A –ash; V – volatile matter;
a – analytical state; daf – dry and ash-free state

Petrographic analysis of examined coals was performed by optical microscopy method by the Coal Geology Research Group, Faculty of Geology, Geophysics and Environmental Protection, AGH. Macerals and mineral matter contents for coals studied were presented in Table 2. The organic matter was formed basically of macerals of the vitrinite group 60.7 - 55.5% vol., liptinite 0.0 - 9.6% vol. and inertinite 27.5 - 38.4% vol. This data were taken from the work [10,11]. Sample *Vi* was characterised by a low content of liptinite group maceral with a relatively high content of inertinite group.

Table 2. Macerals and mineral matter contents for studied hard coal samples coals

Petrographic analysis [vol.%]						
Coal sample	Macerals group			Clay minerals	Pyrite	Carbonates
	Vitrinite	Liptinite	Inertinite			
B	60.7	9.6	27.5	2.1	trace amount	---
Vi	56.1	4.9	31.8	7.2	1.5	2.6
W	55.5	0.0	38.4	6.1	0.2	2.0

As a complementary to ultimate and proximate analysis and petrographic measurements, porosimetric and densimetric analysis was performed. Based on the densimetric results along with porosity and total pore volume (ε i V_{dens}) it can be stated that sample *B* was characterized by high value of total pore volume and in consequence, by high value of porosity. Densimetric measurement results were presented in Table 3. To give more detailed view on the structure of analyzed coals the pore volume distribution measured with the use of porosimetry was presented.

Analysis of porosimetric data was limited to macropores r>25 nm due to the significant compressibility of the coal in higher pressures.

As complementary analysis for characterizing the samples of coal, surface coal functional groups were determined by Boehm method [12]. This method is successfully used for adsorbents such as activated carbons or soot. Multiple measurements of functional groups for selected coals, even at ten time larger analytical samples gave differentiated results. Therefore, the paper presents the arithmetic average of this measurements. For accurate estimation of content of these groups, other methods, based on different principles should be used. The results were shown in Table 4. Based on the experimental data, in all hard coals there were quantified very small amounts of carboxylic, phenolic and lactonic groups. Coal of high degree of metamorphism was characterized by a very low content of the lactone group. With the increase of coal coalification degree, decrease in the amount of lactone groups was observed and to a lesser extend phenolic groups.

Table 3. Comparison of high pressure porosimetric and densimetric measurements

Sample		B	Vi	W
d_{He}[g/cm³]		1.38	1.41	1.45
d_{Hg}[g/cm³]		1.23	1.30	1.32
ε[%]		10.86	7.80	8.96
$V_p·10^2$[cm³/g]		8.83	6.00	6.79
$V_{mac}·10^2$[cm³/g]		1.20	3.39	0.81
$(V_{mic}+V_{mes})·10^2$[cm³/g]		7.63	261	5.98
V_{mac}/V_p[%]		13.6	43.5	11.9
V·10² [cm³/g] in ranges [nm]	25 − 100	0.39	0.7	0.26
	100 − 2500	0.72	2.21	0.53
	2500 − 7500	0.09	0.48	0.02

Where V_p, V_{mac}, V_{mes}, V_{mic}, volume of pores, volume of macro-, meso- and micropores.
Real coal density d_{He} was determined using the automated apparatus Accu Pyc 1330 (Micrometrics).
Apparent coal density d_{Hg} was determined using the apparatus Pascal 440 CE Instruments.

Table 4. The results of determination of oxygen functional groups with the use of Boehm method on the hard coal samples of different coalification degree

	Carboxylic pK=6.37	Lactonic pK=10.75	Phenolic pK=15.47	Sum
	[μmol/g]			
B	36.2	16.3	112.4	164.9
Vi	86.8	6.8	89.4	186.0
W	27.5	2.5	74.4	104.4

3 Results of sorption experiments

Prior to the sorption measurements hard coal samples were subjected to long-term coal degasification process until the vacuum 10^{-3} Pa was reached. In order to accelerate the degassing of samples, process of "helium flushing" took place. In this process the sample was left in the atmosphere of helium for 24 h. The helium atoms themselves do not adsorbed on the adsorbent surface, but provided the necessary kinetic energy to the molecules of adsorbed vapors and gases, in this way removed it from the surface of the sorbent [13]. After each "helium flushing" samples were again degassed. As prepared samples were subjected to sorption experiments.
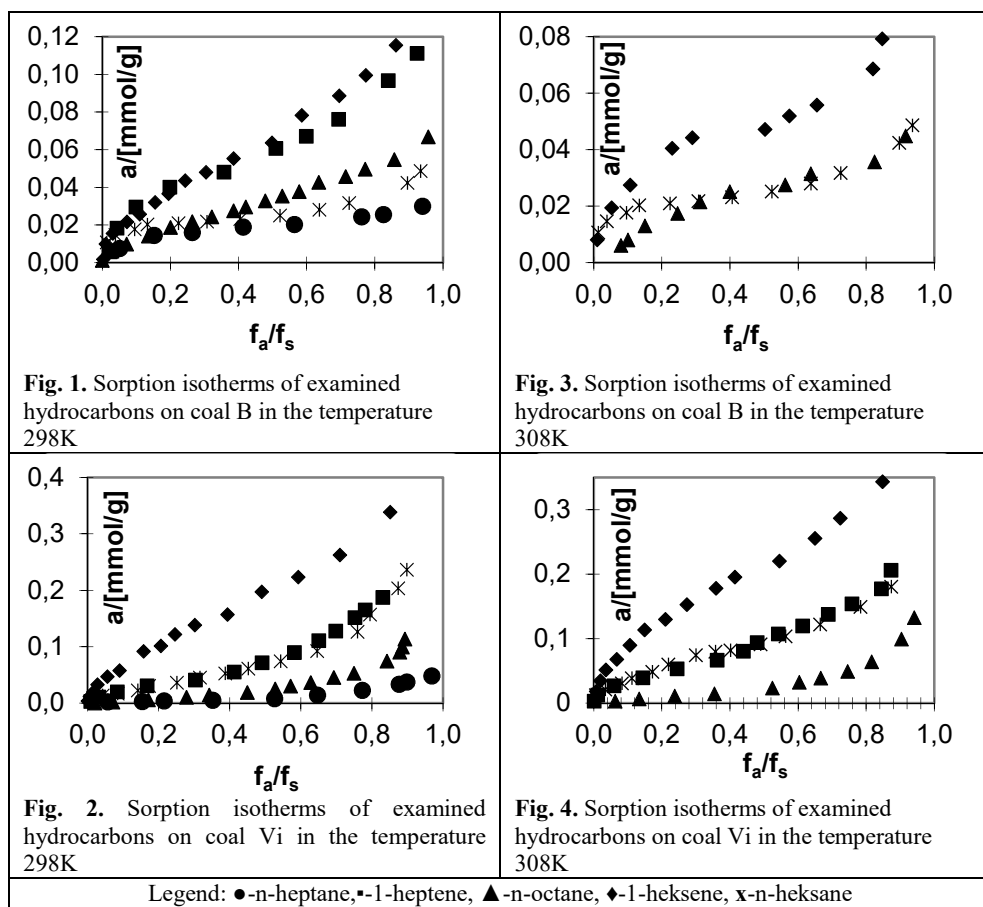
Sorption properties in a coal – sorbate configuration and obtaining sorption isotherms can be considered in terms of static and dynamic methods. For this sorption studies static method–microburette liquid, using volumetric apparatus was selected [14]. Consecutive points of the isotherms were measured by dosing the sorbate vapor portion by opening the mercury valve, so producing a simultaneous increase in the pressure in the sorption space. Estimation of the amount of sorbed hydrocarbon was determined on the basis of the vapor pressure measured before dosing, after dosing and after reaching the sorption equilibrium. Measurements were performed in the temperatures of 298, 303, 308 K.

Hydrocarbons vapors may derive from ideal gas laws as a result of intermolecular interactions (even in low pressure conditions). Therefore the derivations of hydrocarbons vapors from ideal gas properties had to be included. For this purpose fugacity coefficient ϕ and fugacity f_a of analysed hydorcarbons were examined as a function of pressure. Fugacity coefficient was calculated based on Berthelot equation [16], as well as parameters of critical point, using integral formula linking compression and fugacity coefficient. Taking into account not ideality of vapors, while calculating the sorbed amount, the fugacity coefficient was included instead of pressure in the equation for *a* calculation.

3.1 Hard coal-hydrocarbons adsorption isotherm

Examples of sorption isotherms for the investigated systems were shown in Figures 1 and 2 (298K) and Figures 3 and 4 (308K). Sorption isotherms were presented as a relation between the amount of adsorbed hydrocarbon vapors and its relative fugacity. Low sorption capacity of hard coal and a slight decrease in liquid amount in dosing part of apparatus caused a large increase in pressure on the measuring side of apparatus, which may explain not accurately appointed equilibrium points and deviations of these points on the experimental isotherms. Because of the low vapor pressure, particularly in case of long-chain hydrocarbons, during the measurement the optimal time for reaching equilibrium was chosen, after which no equilibrium pressure change was noticed (two, in some cases tree days).

In Figures 1-4 sorption isotherms of saturated and unsaturated hydrocarbon on coals *B* and *Vi* were presented. Isotherms can be characterized by the type II isotherm by the Brunauer classification, except isotherms of octane on coal *Vi*. Type II isotherm is associated with the formation of a multimolecular adsorption layer [17]. Sorption isotherms of heptane and octane on coal *Vi* can be classified into rare type III isotherms.

Fig. 1. Sorption isotherms of examined hydrocarbons on coal B in the temperature 298K

Fig. 3. Sorption isotherms of examined hydrocarbons on coal B in the temperature 308K

Fig. 2. Sorption isotherms of examined hydrocarbons on coal Vi in the temperature 298K

Fig. 4. Sorption isotherms of examined hydrocarbons on coal Vi in the temperature 308K

Legend: ●-n-heptane, ■-1-heptene, ▲-n-octane, ♦-1-heksene, x-n-heksane

Analyzing the adsorption isotherms of hydrocarbons on the coal of different coalification degree, it can be found that sorption of unsaturated hydrocarbons was higher than saturated ones. This was the case for both – coal *B* and coal *Vi*. Privileged polar hydrocarbon sorption on the coal samples was probably associated with the impact of the double bond (electrons

π) with polar groups on the surface of coal. Examined hydrocarbons sorption capacity of vapors was relatively low, in particular of apolar hydrocarbons. This was most probably caused by adsorption mechanism of capturing these sorbents by hard coal.

Comparing isotherms in Figure 1 it is worth noting that coal *B* isotherms of unsaturated hydrocarbons coincided practically through the entire range of relative fugacity, while for sample Vi (Fig. 2) isotherm of 1-hexene (*a* [mmol/g]-almost three times higher) was placed above the isotherm of 1-heptene and isotherms of other sorbates. Kind of regularity was observed in case of hexane, heptane and octane isotherms on sample *Vi*.

Comparison of sorption values suggests that the porous structure of the tested hard coal samples represented the properties of molecular sieve. In general, it can be stated that the low adsorption capacity of examined coal samples was the result of pores blocking by the molecules adsorbed on the surface. This effect may suggest discoid and globular groups creation on the surface [18,19] and the incomplete hydrocarbon chain penetration into pore structure of coal.

However, based on the value of the amount adsorbed on coal test samples, it can be stated that the coal *Vi* had more than twice higher sorption capacity with respect to C_6 hydrocarbons, and several times lower in relation to heptane and octane. Sorption capacity of the two samples of coal in relation to 1 - heptene was almost the same.

Sample *W,* with a high degree of metamorphism, in respect to analyzed sorbates showed indistinguishable and practically immeasurable adsorption. This suggests adsorption on the outer surface of coal grains, which surfaces along with granules diameters of approx. 1.0 - 1.5mm, is small. As a result in this paper the sorption isotherms of coal W were not presented.

This preliminary analysis of the chosen adsorption isotherms indicated that in relation to organic sorbates of relatively long chain, the mesoporosity and macroporosity was of highest importance. The adsorption increase in the initial ranges of the relative fugacity was low (the smaller the longer the chain was). Only above f_a/f_s value of 0.5, there was observed the increase in the amount of the adsorbed molecules.

The study found that the sorption isotherms of hydrocarbon vapors on hard coal in the investigated pressures ranges and temperatures were irreversible, in each of examined cases open hysteresis loop was easily visible (the predominance of sorption processes in the microporous coal structure) [20, 21].

4. Elaboration and analysis of research results

Using the experimental adsorption data up to adsorption relative fugacity, f_a/f_s =0.3, for both hard coal samples *B* and *Vi*, experimental data was fitted using equations of adsorption isotherms. The attempt for a formal description of the experimental isotherms using the thermal sorption equation isotherms was performed along with preparation of calculated isotherms.

Thermal adsorption equation, which author used to describe the adsorption equilibrium, was derived from Jagiello and co-authors [22,23]. The experimental data were governed by the thermal equation of sorption based on an empirical fact that isosteric heat of sorption is in fact temperature-invariant in a wide range of temperatures.

The applied numerical method minimizes the deviations of the regression curves from all experimental points. That is why the results were correlated both in terms of pressure and temperature, which is of key importance when analyzing data obtained at different temperatures, enabling us to derive temperature relationships and to predict the shape of sorption/desorption isotherms at any temperature in the range of experimental data [24, 25].

The condition of temperature in variance Q_{st} is given by the formula

$$-R\left(\frac{\partial lnp}{\partial\left(\frac{1}{T}\right)}\right)_v = RT^2\left(\frac{\partial lnp}{\partial T}\right)_v = Q_{st}(v) \ (1)$$

Integrating this equation for v=const yields the general form of the equation

$$lp = -\frac{1}{RT}Q_{st}(v) + f(v) \qquad (2)$$

where f(v) is a function dependent on the amount of gas sorbed (v).
For the numerical calculations the equation (1a) was used in a form:

$$lnp = \frac{1}{T}\sum_{i=0}^{n} A_i\, v^i + \sum_{i=0}^{k} B_i v^i + zlnv \qquad (3)$$

Where $A_o...A_{ni}$ $B_o...B_k$ – best fit parameters, (n), (k) – degree of polynomials approximating the functions present in the equation, p – equilibrium pressure, v – the amount of gas adsorbed, z – parameter, which value can be 0 or 1 in accordance to the fact whether approximation data are in low fill ranges.

This equation describes well the adsorption equilibrium data of gases and vapors on different kinds of adsorbents in wide ranges of pressures and temperatures with an accuracy corresponding to the accuracy of the experiment, at a relatively small number of empirical parameters. It can be treated as the regression equation defining the value of the adsorption, depending on the pressure and temperature. It also allows for good accuracy extrapolation for other temperatures and pressures, provide crucial information about a heterogeneity of the adsorbent and about energy of adsorbate-adsorbent interactions.
The quality of fit is given by the formula

$$\sigma = \sqrt{\frac{1}{N}\sum\left[ln\left(p_i^{do\acute{s}}\right) - ln\left(p_i^{obl}\right)\right]^2} \qquad (4)$$

Parameters of equation and fitting errors σ were determined. It was found that in most cases a satisfactory fit was obtained for $n = 4$, $k = 0$ and $z = 1$.

Examples of sections generated isotherms (Fig. 5-8) were presented for the tested coal samples. On the graphs, points without fill represented experimental data points. The points with color filling represented isotherms calculated according to the thermal adsorption equation. The aim of this fitting, in the relative pressures, was to determine isosteric heat of adsorption. The graphs did not show the full range of adjustment, but illustrated only the most probable course of isotherms in the low fills. Very often it differed from the experimental points shown as examples, what was caused by parameters obtained in the full fit range.

The presented isothermal sections allowed to draw only qualitative conclusions. It was visible that isotherms for coal *B* had rather regular shape and the increase in temperature lead to a reduction of sorption value. Isotherms of non-typical shape can be observed for coal *Vi*. With the increase in temperature the amount of water vapor adsorbed increased, what for adsorbent of rigid structure is unlikely to happen. Furthermore, with increasing hydrocarbon chain length, the isotherms changed its shape. The porous structure of a sample *Vi* presented the dominant share of mesopores with radious in the ranges of 100-2500 [nm] (see. Tab. 3), thus raising the temperature would lead to increase of the molecule kinetic energy and the pore diameters enlargement. This might increased penetration of the sorbate in the pore system and consequently increased sorption value.

The relatively large diameter of coal grains should also be taken into account (1.0-1.5mm), as they might contain closed pores which might "open" with rising temperature. The increase in the chain length reduced this effect to the extent that, in the case of octane isotherms, in the initial range isotherms, were virtually indistinguishable. Increase in octane sorption at a temperature of 298 K was observed at pressures corresponding to the beginning of capillary condensation process in mesopores. Similar effects were caused by the presence of a double bond. This was most likely result of the double bond reactions with the functional groups present on the surface of the macropores, hence blocking access to the interior of the particles capillaries.
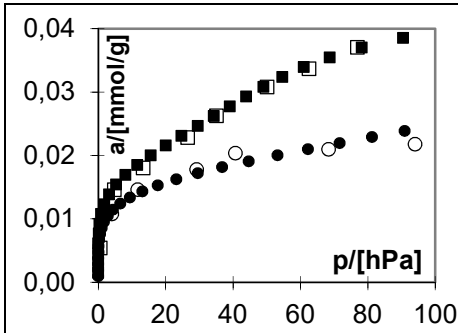
Fig. 5. Experimental and calculated sorption isotherms in B cola – n-heksane system
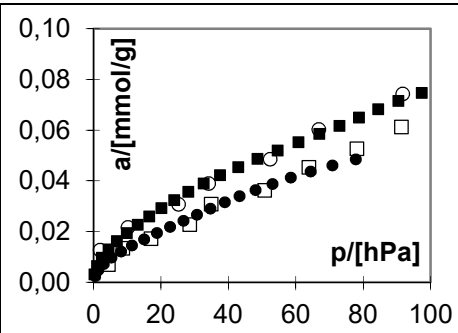
Fig. 7. Experimental and calculated sorption isotherms in Vi coal – n-heksane system
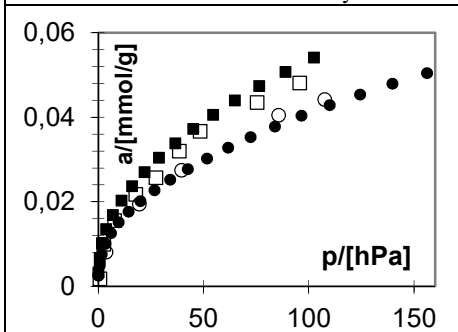
Fig. 6. Experimental and calculated sorption isotherms in B coal – 1-heksene systems
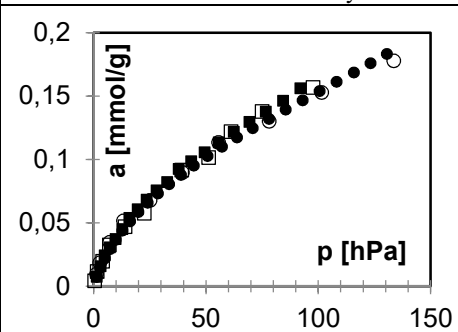
Fig. 8. Experimental and calculated sorption isotherms in Vi coal– 1-heksene systems

Legend: □ 298K; ○ 308K; ■, ● - calculated isotherms

4.1. Energetic effects of sorption process

Research on the energetic effects of the sorption process allowed for quantitative and qualitative characteristics of the binding forces between the hydrocarbon and coal surface. Isosteric heat of adsorption plays important role in the deliberations on energetic effects of adsorption process. By definition it is the thermal effect associated with a virtual moving of 1 mol of gas from volume to adsorption phase at constant temperature and pressure.

The knowledge of thermal sorption equation parameters (3) allows for numerical calculation of isosteric heats of adsorption in a function of fill due to equation (5):

$$Q_{st}(v) = -R \cdot \left(\frac{\partial \ln p}{\partial (1/T)} \right)_v = -R \sum_{i=0}^{n} A_i v^i \qquad (5)$$

A_0 constant from equation (5) allows for calculation of boundary values of isosteric heat of adsorption with $v \rightarrow 0$.

$$Q_{st}^0 = -R \cdot A_0 \qquad (6)$$

By definition isosteric heat of sorption Q_{st} is equal to sorption enthalpy ΔH_{st} with opposite sign:

$$Q_{st} = -\Delta H_{st} \qquad (7)$$

Comparing discussed above method for determining isosteric heat of adsorption with the use of the classical method based on plotting isotheres, it should be noted that the numerical method in addition to its convenience and time saving, has another advantage. It is based on the minimization of deviations from the regression curves of all experimental points, as a result data are correlated in case of pressure and temperature at the same time. This is important for the analysis of data obtained at different temperatures (families of isotherms) and allows for the preparation of temperature dependencies.

Table 5. Isosteric heat of sorption calculated with the use of (5) and (6) equations

Hydrocarbon	Q^0_{st} [kJ/mol]	Ranges of filling [dm³/kg]	Q_{st} for V_{min} [kJ/mol]	Q_{st} for V_{max} [kJ/mol]	$\Delta Q_{st}/\Delta v$ [(kJ·dm³)/mol]
Coal B					
n-Hexane	115.9	0.291–0.515	97.1	92.8	19.19
n-Heptane	81.7	0.089–0.538	81.2	77.8	7.57
n-Octane	66.5	0.067–0.672	66.3	64.4	3.14
1-Hexene	54.5	0.045–1.367	53.7	43.5	7.71
1-Heptene	62.0	0.291–1.098	59.7	55.7	4.95

Table 5 presented the values of hydrocarbons isosteric heat of sorption for coal *B* which calculation was based on isotherms determined using thermal adsorption equation. Q^0_{st} values (determined from extrapolation) characterized direct interaction of sorbate molecules with the surface of coal. In the last column of Table 5 there was shown index characterizing the average slope of curves shown in Figure 9 in relation to the axis of fill. Index provided information how the value of isosteric heat changed with increasing by 1 mol amounts adsorbed and was a measure of the distance between isotherms determined at different temperatures along with increase in filling.

The heat of adsorption as a function of filling, calculated using equation (1) was presented by a constant line in Figure 9 for sample *B*. Presented dependencies were of declining character, with increasing values of sorption once the values of isosteric heat of sorption decrease, however values were not reaching the heat of condensation. Isosteric heat values may indicate the physical nature of the hydrocarbons molecules interaction with hard coal [22]. Isosteric heat of sorption curves as a function of filling the surface may suggest energy heterogeneity of the studied coal adsorbents.
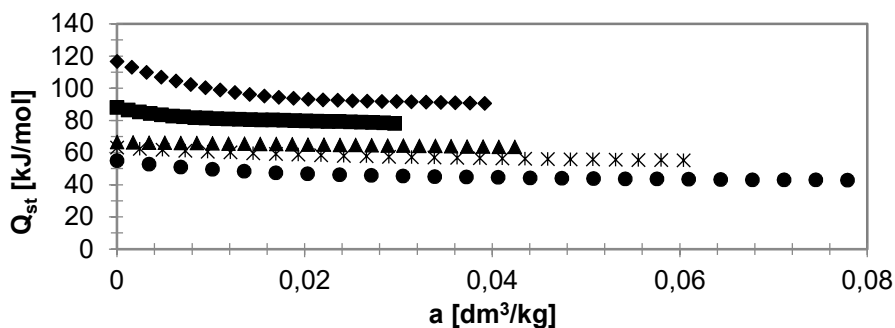

Fig. 9. Dependence of isosteric sorption heats on the amounts of sorbed hydrocarbons on the studied coal *B*((Legend: ●-n-heptane, ▪-1-heptene, ▲-n-octane, ♦-1-hexene, x-n-hexane)

Taking into consideration the values of isostheric heat of adsorption Q^0_{st} of sorbates, once there was no fill (for example sample *B*) it can be noted that the highers value of energy of

sorption was represented by the system hexane-coal. This fact may suggest that porous structure of coal *B* was of the best availability for hexane molecules. This high energy of sorption may imply that capturing of hexane molecules took place in micropore structure. For the remaining saturated hydrocarbons examined energy of adsorption was clearly lower.

5 Conclusions

In conclusion it can be stated that the isotherms of sorption depend on the kind of vapors and the type of coal:

• It can be said that in case of examined systems sorption took place mainly on the macropores surface of hard coal;

• Samples *Vi* and *B* represented much higher sorption of polar sorbate. As the molecules dimensions (in group: saturated, unsaturated hydrocarbon) were practically uniform, the differences were most probably related to association possibilities of unsaturated hydrocarbons on the surface of macropores;

• It can be expected that in case of unsaturated hydrocarbons interconnections adsorbate-adsorbate system played more important role than of adsorbate-adsorbent. Explanation to this could be stronger interconnections of unsaturated hydrocarbons and surface polar groups of hard coals *Vi* and *B*.

The investigation of energetic effects of sorption process enabled quantitative and qualitative characteristic of bounds of hydrocarbons with the surface of coal. While considering the energy aspects of the adsorption, isosteric heat of adsorption played very important role. The knowledge of thermal adsorption equation parameters allowed for numeric calculation of the isosteric heat of sorption value in a function of filling. In case of system coal/hexane high value of boundary adsorption enthalpy was observed, which can indicate penetration of this hydrocarbon into the microporous structure. For the remaining sorbates distinguishably lower values of terminal adsorption enthalpy were fund, what proves that hydrocarbons didn't penetrate in to the micropores.

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