

APARATURA

BADAWCZA I DYDAKTYCZNA

The characteristic of the adsorption and energetic properties of the oxidised and reduced graphene

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ABSTRACT

The interaction of the selected atoms and molecules with the surfaces of oxidised and reduced graphene samples have been characterised. Moreover, the adsorption and acceptor-donor properties have been analysed. The equations of the Lennard-Jones (12-6) and (10-4) and the Steele (10-4-3) potential functions have been employed for the characterisation of the interactions. The parameters of the pore structure have been determined by means of the α_s comparative method on the basis of the N₂ low-temperature adsorption data at 77 K. The N₂ adsorption data on the Carbopack F and Cabot BP280 graphitised carbon blacks have been used as the reference adsorption data. The characteristics of the surface energetic properties of the tested graphene have encompassed the determination of the specific component of the surface energy and the acceptor-donor properties. The oxidised graphene has been characterised by the electron-acceptor properties, whereas the reduced graphene by the electron-donor properties.

Charakterystyka właściwości adsorpcyjnych i energetycznych utlenionego i zredukowanego grafenu

Słowa kluczowe: grafen, odwrócona chromatografia gazowa, rentgenowska spektrometria fotoelektronów

STRESZCZENIE

Scharakteryzowano oddziaływanie wybranych atomów i cząsteczek z powierzchniami próbek utlenionego i zredukowanego grafenu. Ponadto analizowano właściwości adsorpcyjne i akceptorowo-donorowe grafenu. Do charakterystyki oddziaływań zastosowano równania funkcji potencjalnych Lennarda-Jonesa (12-6) i (10-4) oraz funkcję potencjalną Steele (10-4-3). Na podstawie danych niskotemperaturowej (77 K) adsorpcji N_2 wyznaczono metodą porównawczą α_s parametry struktury porowatej badanego grafenu. Jako adsorpcyjne układy odniesienia zastosowano dane adsorpcji N_2 na sadzach grafityzowanych Carbopack F i Cabot BP280. Charakterystyka energetycznych właściwości powierzchniowych badanego grafenu obejmowała chromatograficzne wyznaczenie wartości składowej specyficznej swobodnej energii powierzchniowej oraz właściwości akceptorowo-donorowych. Grafen utleniony charakteryzował się właściwościami elektrono-akceptorowymi, natomiast zredukowany elektrono-donorowymi.

1. THEORY

Graphene is an allotrope of carbon. Since the discovery of graphene the intensive investigations concerning both the characteristics of its properties and the possibilities of their changes in order to endow it with the desirable features. One of the employed methods is doping with elements of surface functionalisation. As a result a very precise control of the electrochemical properties of the doped graphene, which is very important, of whether it can be employed in electronics.

The materials having similar acceptor-donor properties and demonstrating a very similar structure with graphene are graphene oxide and reduced graphene oxide. Graphene oxide is a chemically modified graphene plane, being a large aromatic macromolecule having reactive functional groups on the surface as well as on the edges, for example in the epoxyd, hydroxyl and carboxylic groups. Since it was discovered that π electrons in aromatic molecules graphene and graphene oxide have been tested as a solid phase in the microextraction of analytes from an aquatic sample and soil [1]. Graphene oxide is an amorphous compound with a non-stoichiometric composition, whose structure is not yet fully known. It has been produced via the isolation of single atomic planes of graphite oxide from oxi-

dised graphite. Graphite oxide has mainly been manufactured from crumbled graphite via the addition of strong oxidisers to graphite flakes [2]. Graphite oxide prepared in such a way has next been poured into a high hydrophilicity solvent and placed in an ultrasonic washer. Due to the energy of ultrasonic radiation each oxidised graphene planes have split up, thereby a colloidal suspension, with single graphene oxide flakes of strong hydrophilic properties, has been produced [3].

The reduced graphene oxide, RGO, can be prepared by reducing the graphene oxide, GO. The reaction has been initiated by the preparation of colloidal suspension of the graphene oxide and the addition of hydrazin hydrate and heating the mixture for 24 hours at 100°C. The reduced graphene oxide precipitates as a black solid surface. Graphene oxide and reduced the graphene oxide obtained in this way have opposite 100°C acceptor-donor properties to be accurately characterised. Such a possibility gives inverse gas chromatography.

2. EXPERIMENTAL

2.1 XPS tests

The XPS tests of the graphene samples have been performed by means of the UHV multichannel system Prevac. Prior to the analysis the tested

samples were not treated chemically. The samples have been degassed at room temperature to the stable pressure, c.a. 5×10^{-4} Pa, in the sluice loading of the UHV system. Then after placement in the analysis chamber of the UHV system the specific XPS analysis was conducted. As a source of the excitation X-ray radiation from the Al anode.

During the acquisition of the XPS spectra, the samples were simultaneously irradiated with low-energy electrons from the Electron Flood Gun ($E=2$ V, $I_e=200$ μ A) in order to eliminate the electrostatic charge of the sample. The pressure in the analysis chamber was maintained at 2×10^{-4} Pa. The XPS acquisition parameters were as follows:

- the survey spectrum: Pass Energy: 200, step: 300 meV,
- the high-resolution spectrum: Pass Energy: 50, step: 100 meV.

For the XPS spectra processing and calculations of the surface composition of the tested materials the CasaXPS software was used. In order to normalise the spectroscopic measurements the x-axis (bonding energy, BE) in the XPS spectra was calibrated for the carbon neutral peak C1s (BE = 284.7 eV). The results of the analysis are collated in Table 1. They have been the basis of the interactions characteristic in static and dynamic adsorption.

2.2 Static adsorption tests

In order to characterise the interactions of atoms and molecules with the tested graphene samples, occurring at static and dynamic conditions, the following potential functions have been employed: Lennard-Jones (12-6), Lennard-Jones (9-3) and Steele 10-4-3 [4].

The Lennard-Jones (12-6) potential function in a relatively simple way describes the repulsive

and attractive interactions of atom-atom, atom-molecule and molecule-molecule. It is expressed via the following equation:

$$V(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \quad (1)$$

The parameters in the expression are:

ε – is the depth of the potential well depth, r_0 – is the point at which the potential function is zero, $V(r_0)=0$.

The Lennard-Jones (10-4) potential function, is described via the expression:

$$V_{10-4}(r) = 2\pi\rho_A r_0^2 \varepsilon \left[\frac{2}{5} \left(\frac{r_0}{r} \right)^{10} - \left(\frac{r_0}{r} \right)^4 \right] \quad (2)$$

where ρ_A is the surface density, i.e., the parameter characterising the number of atoms on the unit area, expressed in [$1/\text{nm}^2$] [5].

The Lennard-Jones (9-3) potential function describes the interactions of molecules with the spatial structure of the material and it is expressed as [5]:

$$V_{9-3}(r) = 2\pi\rho_s r_0^3 \varepsilon \left[\frac{2}{45} \left(\frac{r_0}{r} \right)^9 - \frac{1}{3} \left(\frac{r_0}{r} \right)^3 \right] \quad (3)$$

where ρ_s is the volume density, which is connected with the material structure, expressed in [$1/\text{nm}^3$].

It has been proven that the Lennard-Jones (9-3) potential function weakly describes the interaction of fluids with crystal materials and the real potential of such an interaction is actually the function of both the distance of the interacting atoms (and/or molecules) as well as the distance between the graphite lattice planes. The aggregate interaction is likely to be a well-defined function that sums the impact of the first layer of material and a homogeneous volume space behind it.

Table 1 The values of the parameters characterising the GO and RGO graphene samples determined by means of the XPS method

Orbital of the element	Maximum energy position, eV	GO sample		RGO sample	
		Atomic conc., % _{at}	Mass conc., % _{mas}	Atomic conc., % _{at}	Mass conc., % _{mas}
C 1s	286.5	66.4	58.81	88.7	85.95
O 1s	532.2	31.67	37.37	7.92	10.22
N 1s	401.4	0.4	0.41	3.38	3.82
Si 2p	102.6	0.69	1.44	-	-
S 2p	168.3	0.83	1.97	-	-

The result of such reasoning was the obtaining of the Steele (10-4-3) [6], which has the following form:

$$V_{10-4-3}(r) = 2\pi\rho_s\Delta r_0^2\varepsilon \left[\frac{2}{5}\left(\frac{r_0}{r}\right)^{10} - \left(\frac{r_0}{r}\right)^4 - \frac{r_0^4}{3\Delta(r+\alpha\Delta)^3} \right] \quad (4)$$

In comparison with the aforesaid functions, the equation (4) additionally contains the α constant, which Steele specified as equal to 0.61 and the Δ parameter being the distance between the graphite lattice plane in the spatial space [5].

The calculations of the values of the interaction potentials, atom-molecule and molecule-molecule, for the tested graphene-like materials have been done for the distances ranged from 100 to 1000 pm, with the step of 5 pm. The results are presented in Figures 1-2, whereas the values of the parameters characterising the potential functions employed are collated in Table 2.

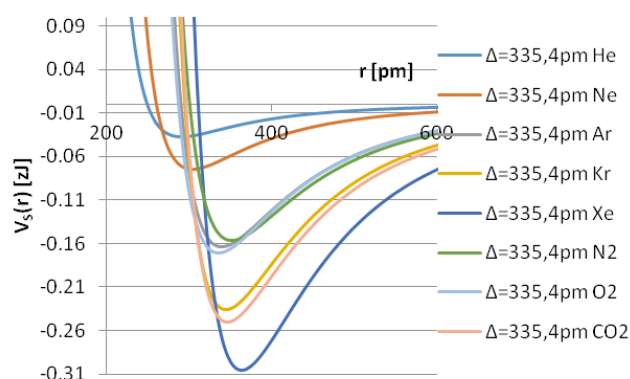


Figure 1 The variation of the Steele potential function for the interactions of graphene oxide with atoms or molecules of selected gases

2.3 Static adsorption measurements

The interactions of atoms and molecules with the GO and RGO graphene samples have been taken into account in the interpretation of the N_2 low-temperature adsorption data. The N_2 low-temperature adsorption isotherms at 77 K have been determined twice and for the characterisation of the adsorption properties of graphene samples by the α_s comparative method the average adsorption values have been used. The adsorption

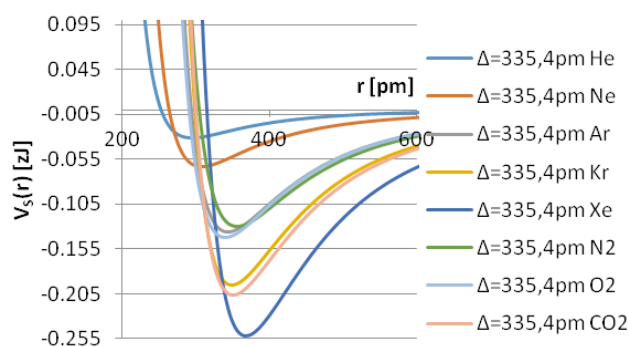


Figure 2 The variation of the Steele potential function for the interactions of reduced graphene oxide with atoms or molecules of selected gases

data obtained in such a way have been referred to as the reference adsorption data of N_2 on the graphitised carbon blacks: Carpack F ($S_{BET} = 6,8 \text{ m}^2/\text{g}$), so far rarely employed for the calculation of the N_2 reduced adsorption data on carbon adsorbents [8] and Cabot BP280 ($S_{BET} = 41 \text{ m}^2/\text{g}$) [7], which are very often employed for the N_2 reduced adsorption data on active carbons. The GO and RGO graphene samples have the specific surface area values, S_{BET} , estimated on the basis of the N_2 low-temperature data determined at 77 K in the relative pressure range

$$0.05 < \frac{p}{p_s} < 0.35, \text{ are equal c.a. } 27.6 \text{ and } 71.5 \frac{\text{m}^2}{\text{g}}.$$

The comparison of the specific surface area values of the reference adsorbents for the GO and RGO, from the impression, that in this case the N_2 adsorption data at 77 K on the Cabot BP280 graphitised carbon black are less appropriate, because in comparison to the GO and RGO graphene samples it has too high a value of the S_{BET} value, especially in the case of the GO sample. The changes of the N_2 reduced adsorption isotherms at 77 K determined on the GO and RGO samples with respect to the N_2 reduced adsorption data on the Cabot BP280 and Carpack F are presented in Figures 3 and 4, whereas the values of the parameters characterising the adsorption properties of the GO and RGO are collated in Tables 3 and 4.

Table 2 The values of the parameters characteristic for the interactions of atoms and molecules with the structures of graphene oxide and reduced graphene oxide

Sample	He	Ne	Ar	Kr	Xe	N_2	O_2	CO_2	Parameter
GO	292.6	305.8	341.6	347.2	366.7	354.3	337.9	348.9	$r_0^* [\text{pm}]$
	0.319	0.574	0.977	1.355	1.545	0.856	1.044	1.415	$\varepsilon^* [\text{zJ}]$
RGO	295.1	308.7	344.6	350.2	369.8	357.5	340.9	352.1	$r_0^* [\text{pm}]$
	0.262	0.470	0.794	1.100	1.251	0.695	0.848	1.150	$\varepsilon^* [\text{zJ}]$

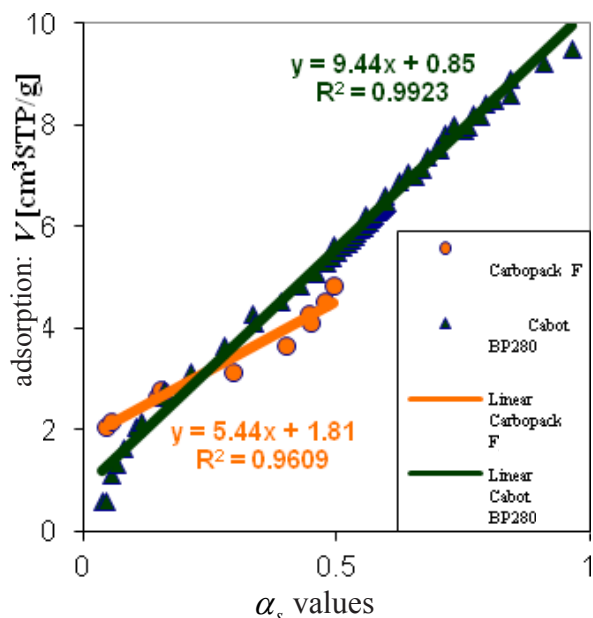


Figure 3 The variation of the $V[\text{cm}^3\text{SPT/g}] = f(\alpha_s)$ dependencies for the GO sample in the range $0.046 < \alpha_s < 0.96$ in the case of employing the N_2 reduced reference adsorption data on the Cabot BP280 graphitised carbon black in the range $0.046 < \alpha_s < 0.496$ in the case of the Carbopack F adsorbent

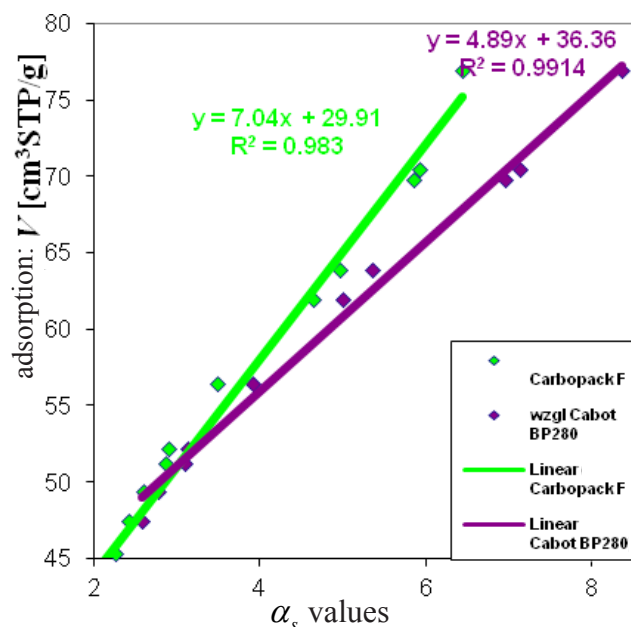


Figure 4 The variation of the $V[\text{cm}^3\text{SPT/g}] = f(\alpha_s)$ dependencies for the RGO sample in the range $2.1 < \alpha_s < 8.36$ in the case of employing the N_2 reduced reference adsorption data on the Cabot BP280 and Carbopack F graphitised carbon blacks

Table 3 The values of the parameters characterising the tested GO and RGO graphene samples calculated on the basis of the N_2 low-temperature adsorption isotherm at 77 K

Grafene samples	$S_{BET};$ m^2/g	$S_m;$ cm^2/g
GO	27.6	112
RGO	71.5	469

2.4 Chromatographic measurements

The inverse gas chromatographic tests have been performed by means of the UNICAM type 610 gas chromatograph equipped with the flame-ionisation detector (FID) working at the High sensitivity mode. The UNICAM 4880 Chromatography Data Handling System has been employed as the AD

converter for the change the analogue-to-digital signal. In order to obtain the infinite dilution conditions the probes vapours of 0.5 mm^3 have been injected several times by means of the Hamilton type 7000.5KH syringe, and the average values, taken from the sets of eight most similar retention times, have been taken for further calculations.

Every chromatographic peak has been acquired at the sampling rate of 25 Hz and described by two mathematical functions: Exponentially-Modified Gaussian (denoted as EMG, Eq. 5) and also Pearson IV (denoted as P4, Eq. 6), which the most precisely described the peaks profiles and the values of the nonlinear regression coefficients r^2 , which were the highest [9]:

$$c(t) = \frac{h_{\max} w \sqrt{2\pi}}{2s} \exp\left(\frac{t_R^{\text{sc}} - t}{s} + \frac{w^2}{2s^2}\right) \left[\frac{s}{|s|} - \text{erf}\left(\frac{t_R^{\text{sc}} - t}{\sqrt{2}s} + \frac{w}{\sqrt{2}s}\right) \right] \quad (5)$$

Table 4 The values of the parameters characterising the tested GO and RGO graphene samples calculated by using of the α_s comparative method

Reference adsorbent	GO sample				RGO sample			
	$S_c;$ m^2/g	$S_{zew};$ m^2/g	$V_{mi};$ cm^3/g	$V_{me};$ cm^3/g	$S_c;$ m^2/g	$S_{zew};$ m^2/g	$V_{mi};$ cm^3/g	$V_{me};$ cm^3/g
Cabot BP280 $S_{BET} = 41 \text{ m}^2/\text{g}$	26.3	5.1	0.0013	0.024	67.3	13.6	0.0025	0.0053
Carbopack F $S_{BET} = 6.8 \text{ m}^2/\text{g}$	13.9	7.5	0.0028	0.018	40.1	18.0	0.0028	0.0463

$$c(t) = \frac{h_{\max} \left[1 + \frac{\left(t - \frac{ws_2}{2s_1} - t_R^{sc} \right)^2}{w^2} \right]^{-s_1} \exp \left\{ -s_2 \left[\frac{1}{\tan \left(\frac{t - \frac{ws_2}{2s_1} - t_R^{sc}}{c} \right)} + \frac{1}{\tan \left(\frac{s_2}{2s_1} \right)} \right] \right\}}{\left(1 + \frac{s_2^2}{4s_1^2} \right)^{-s_1}} \quad (6)$$

where: $c(t)$ – is the ordinate of the function, i.e., the function of changes of concentration of adsorbate in time or the dependent variable;
 t – is the acquisition time of adsorbate detection, i.e., the abscissa of the function, or the independent variable;

h_{\max} – is the amplitude of the elution peak;

t_R^{sc} – is the retention time of the centre of gravity of the elution peak;

w – is the parameter which is mainly related to the width of the peak. It is necessary to emphasise that for different functions the w value may be related to the width at different heights of the elution peak [9];

s , s_1 and s_2 – are the parameters which is mainly related to the symmetry of the elution peak [9].

The effect of the interactions of atoms and/or molecules with the surfaces of oxidised and reduced graphene samples can be successfully characterised on the basis of the potential functions parameters. However, the total energetic effect of interactions of all atoms and/or molecules, which were introduced to the carrier gas flow at the time of injection is characterised by means of the molar differential enthalpy $[\Delta H_{ads}]$ and the molar differential of the entropy of adsorption $[\Delta S_{ads}]$. The values of the aforesaid thermodynamic functions can be estimated on the basis of the hyperbolic dependency of the specific retention volume (referred to the column temperature, the unit mass and the specific surface area of the column filling) and the column temperature $[V_{g(T)}^{(lg)}]$ [10]:

$$\ln \left(\frac{V_{g(T)}^{(lg)}}{T} \right) = \frac{\Delta H_{ads}}{R} \frac{1}{T} + \frac{\Delta S_{ads}}{R} + \ln(RS_{BET}m_{ads}) \quad (7)$$

where: $V_{g(T)}^{(lg)}$ – is the specific retention volume referred to the unit mass of graphene sample in column;

T – is the column temperature;

R – is the universal gas constant;

ΔH_{ads} – is the molar differential enthalpy of adsorption;

ΔS_{ads} – is the molar differential entropy of adsorption;

S_{BET} – is the specific surface area of the tested graphene material;

m_{ads} – is the mass of the tested graphene material in column.

3. RESULTS AND DISCUSSION

A very precise estimation of the values of the molar differential enthalpy and entropy of adsorption has been the result from the chromatographic tests performed at the ideal nonlinear conditions.

The absolute values of the molar differential enthalpy and entropy of adsorption rise with the number of carbons in the n-alkanes molecules ($C_5 - C_8$). It has been proven that the existence of the 'thermodynamic compensation effect' that is the dependency between the molar differential enthalpy of adsorption and the molar differential entropy of adsorption for n-alkanes ($C_5 - C_8$).

The obtained effect suggests a stronger adsorption of n-alkanes with a longer chain, which is accompanied by a stronger interaction of an adsorbate molecule with the atoms and/or functionalities of the graphene plane and it satisfies of the basic chromatographic rule that a stronger probe – adsorbent interaction results in a longer retention time.

The obtaining of the linear $(-\Delta S_{ads})=f(-\Delta H_{ads})$ dependencies confirms that n-alkanes interact nonspecifically with the graphenes surfaces. This means that the 'thermodynamic compensation effect' is accomplished for the tested adsorption systems with graphene samples and n-alkanes as probes. It should be noted, that the obtained dependencies, characterising the thermodynamic compensation effect, can only be interpreted for the ideal nonlinear chromatographic mechanism of elution of the testing substances from the beds of oxidised and reduced graphenes.

It is commonly known that some kinds of specific interactions exist, known as hydrophilic. Some kinds of nonspecific interactions, known as dispersive or hydrophobic, are also in existence [11]. The interactions connected with the existing the hydrogen bond and the π bonds are the steric effects of the molecular orbitals and the acceptor-donor interactions. However, the dispersive component of the free surface energy, known also as the London component characterises the properties, which are essential in the prediction

of the behaviour of the nonpolar adsorbents like carbon materials exposed to hydrogen.

The specific interactions appear in the case of the creation of the hydrogen bond the acid-base interactions, the interactions of the π orbitals and the steric effects.

It was confirmed that the more precisely the interactions were described the most thoroughly with the $\Delta G_{\text{ads}}^{\text{SP}}$ and $\Delta G_{\text{ads}}^{\text{vdW}}$.

For the reference lines obtained for all the tested systems the standard deviation values σ can be characterised by:

- the plausibility of the values of the molar differential enthalpy and entropy of adsorption determined on the basis of the $V_{\text{g(T)}}^{(\text{lg})}$ values,
- the correctness of the physicochemical parameters chosen for the calculations of the so called physicochemical descriptor (in this work it was the value of the molar deformation polarisation, P_D).

In order to estimate the acceptor-donor interactions between the adsorbent and the probe molecules of the testing substances with a precise definition of the acceptor-donor properties are injected onto the chromatographic column.

The relationship between the adsorbate-adsorbent interactions and the acceptor-donor properties of the adsorption system has a special meaning in the case of carbon materials. All the intermolecular forces occurring between the parts of the probe molecule and the graphene surface must be regarded as the impact of which significantly determine the properties of the system as a whole, and they are described by the retention time of the centre of gravity of the testing substance. The $\Delta G = f(P_D)$ dependencies are presented in Figures 5 and 6.

Taking into account the retention times and the values of the Gibbs free energy for the adsorbates used, they can be classified on the basis of their interactions forces with atoms and functionalities present on the surfaces of the graphene samples:

1. molecular probes, for which the interaction forces are very small, i.e., n-alkanes;
2. apolar probes, for which the interaction forces are of the average power: dichloromethane, trichloromethane, tetrachloromethane and benzene;
3. polar probes, for which the interaction forces are strong: acetonitrile, diethyl ether, ethyl acetate, n-propyl acetate and n-butyl acetate.

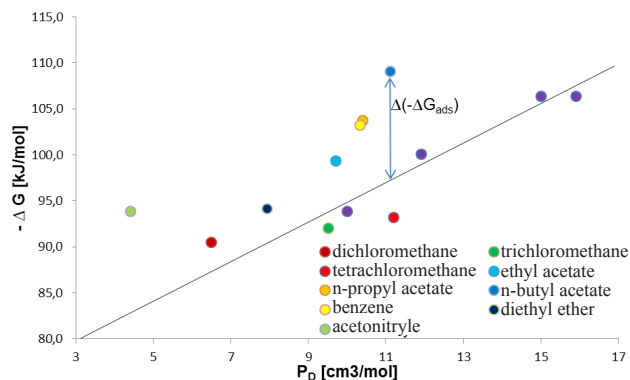


Figure 5 The variation of the molar free enthalpy of adsorption, ΔG_{ads} , for the peaks of the testing substances described by means of the P4 mathematical function, eluted from the RGO bed

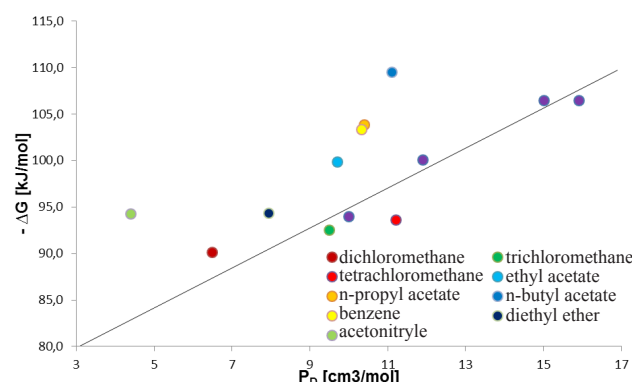


Figure 6 The variation of the molar free enthalpy of adsorption, ΔG_{ads} , for the peaks of the testing substances described by means of the EMG mathematical function, eluted from the RGO bed

The aforesaid classification is based on the methodology of the contribution estimation of the specific energy of adsorption, which cannot be isolated from the others kinds of the adsorbates molecules interactions, having different acceptor-donor properties, with the graphene sheets of the tested samples [12].

Apart from that, one may take into account that according to the hard and weak acids and bases principle of the Pearson oxygen atom in a carbonyl group is a hard base, because it has four lone valence electrons [13]. However ethyl acetate, n-propyl acetate and n-butyl acetate molecules demonstrate amphoteric properties.

To characterise of the acceptor-donor properties of the surfaces of the graphene samples tested by means of the IGC method, it is necessary to evaluate of the specific interactions between the tested adsorbent surface and two models of adsorbates. One of them is a substance being the electron donor (Lewis' base) DN, and the other

is a substance with the electron acceptor (Lewis' acid) AN. The theory introduced by Gutmann and extended by Riddle and Fowkes, concerning the AN* and DN numbers is useful in testing solids by the IGC method, however it has not been introduced to that end [14, 16]. The AN* and DN values which are necessary for the calculations are collated in Table 5.

The properties of different adsorbents are characterised among other things by the K_A and K_D parameters calculated on the basis of the thermodynamic functions determined by means of the IGC method. The aforementioned parameters are an empirical scale of the tendency of atoms for accepting electrons (K_A – parameter characterising of the acceptor properties) and their donating (K_D – parameter characterising their donor properties). The values of the K_A and K_D parameters can be estimated on the basis of the following dependency:

$$\Delta H_{\text{ads}}^{\text{SP}} = K_A \cdot \text{DN} + K_D \cdot \text{AN}^* \quad (8)$$

where:

- $\Delta H_{\text{ads}}^{\text{SP}}$ – is the molar differential enthalpy of adsorption for the specific interactions,
- DN – is the donor number in a scale proposed by Gutmann [13],
- K_A – is the parameter characterising the acceptor number,
- AN* – is the acceptor number in a scale proposed by Riddle and Fowkes [15],
- K_D – is the parameter characterising the donor properties.

It is necessary to emphasise that the value of the enthalpy of adsorption for the specific interactions, $\Delta G_{\text{ads}}^{\text{SP}}$, can be estimated by employing the following dependency:

$$\Delta G_{\text{ads}}^{\text{SP}} = \Delta H_{\text{ads}}^{\text{SP}} + T \cdot \Delta S_{\text{ads}}^{\text{SP}} \quad (9)$$

where:

- $\Delta G_{\text{ads}}^{\text{SP}}$ – is the value of the Gibbs molar free energy of adsorption for the specific interaction,
- $\Delta H_{\text{ads}}^{\text{SP}}$ – is the value of the molar enthalpy of adsorption for the specific interaction,
- $\Delta S_{\text{ads}}^{\text{SP}}$ – is the value of the molar entropy of adsorption for the specific interaction,
- T – is the column temperature.

It is presupposed that during the elution of the testing substances the values of the K_A and K_D parameters calculated in this way are theoretically independent on the column temperature.

Table 5 The AN* and DN values for the adsorbates employed [13, 14]

Adsorbate	DN [kJ/mol]	AN* [kJ/mol]
dichloromethane	0	16.3
trichloromethane	0	22.6
ethyl acetate	71.6	6.3
diethyl ether	80.4	5.9
acetonitrile	59	19.7

The K_A , K_D and K_A/K_D values for the tested samples:

1. without taking into consideration the entropic effect:

$$\frac{(-\Delta H_{\text{ads}}^{\text{SP}})_i}{\text{AN}_i^*} \approx K_A \frac{\text{DN}_i}{\text{AN}_i^*} + K_D \quad (10)$$

2. taking into consideration the entropic effect:

$$\frac{(-\Delta G_{\text{ads}}^{\text{SP}})_i}{\text{AN}_i^*} \approx K_A \frac{\text{DN}_i}{\text{AN}_i^*} + K_D \quad (11)$$

where subscript i denotes the probe employed.

On the basis of the analysis results collated in Table 6 one can state, that the K_A and K_D results strongly depend on the determination method employed.

All the properties of both the surface functionalities and the groups existing in adsorbate molecules have an essential influence on the K_A , K_D and K_A/K_D values obtained. The K_A and K_D parameters reflect the behaviour of the tested surfaces of the graphene samples as acceptors and donors of electrons. In order to characterise the acceptor-donor properties of the solid surface the following scale is taken into consideration:

$$\frac{K_A}{K_D} \geq 1.1 \quad (12)$$

acidic surface

$$0.9 < \frac{K_A}{K_D} < 1.1 \quad (13)$$

amphoteric surface

$$\frac{K_A}{K_D} \leq 0.9 \quad (14)$$

basic surface

Table 6 The K_A , K_D and K_A/K_D values calculated for the graphene samples tested

Adsorbent	Mathematical function	Eq. 10			Eq. 11		
		K_A	K_D	K_A/K_D	K_A	K_D	K_A/K_D
RGO	P4	0.0322	0.0738	0.4363	0.0459	0.1699	0.2702
	EMG	0.0682	0.0909	0.7503	0.0495	0.1731	0.2860
GO	P4	1.1372	0.4292	2.6485	1.0762	0.4950	2.1729
	EMG	0.0790	0.0023	34.3478	0.4040	0.1470	2.7502

Analysing the results obtained for the graphene samples one can state that the RGO surface have electron-donor properties, whereas the GO surface have electron-acceptor properties.

Although the differences are not significant, one may set up that both samples, during the elution of the analytes mixtures with different electron-donor and electron-acceptor properties, and this will demonstrate both acidic and basic properties. The most important results of the tests of the acid-base properties of carbon materials by means of the IGC method, is the possibility of unambiguous determination of the properties of their surfaces.

4. CONCLUSIONS

Although the chemical structure of the tested graphene samples seems to be relatively simple but the description of the intermolecular interactions between adsorbates molecules and surface atoms or functionalities have been very difficult. The following conclusions can be drawn from the tests of the oxidised and reduced graphene materials:

1. The obtaining of the linear dependencies confirms the existing of the ideal linear chromatographic conditions for n-alkanes at their infinitive dilutions.
2. The results have confirmed, that the IGC method is a good tool for the testing of the acceptor-donor properties of graphene materials.
3. The combination of the IGC results with XPS ones and the results of the low-temperature N_2 adsorption compliment one another very well and to get to know the essence of the physical adsorption occurring at dynamic conditions on the graphene surfaces and their chemical properties.
4. On the basis of the K_A and K_D parameters values and their quotients the following conclusions can be formulated:

a) the amphoteric and basic probes, having relatively low AN^* values and relatively high DN values, have been eluted from the beds of graphene ma-

terials during the longest time, however, the neutral and acidic probes having relatively high AN^* values and the DN ones equal to zero, i.e., methylene chloride and chloroform behave quite contrary to the previous group,

b) the calculated K_A and K_D parameters values, their quotients and the surface composition data compliment one another very well and enabling a more precise interpretation of the acid-base properties of the tested graphenes surfaces,

c) the suggested characteristic of the acceptor and donor properties of the tested graphene materials as adsorbents can be employed only in the case of weak probe-adsorbent surface interactions, which occurring during the chromatographing of probes in graphene bed in column, since the strong probe-adsorbate interactions cannot be tested by means of the IGC method.

5. The errors committed during the determination of the values of the specific component of the free energy of adsorption, ΔG_{ads}^{SP} , have been cumulative in character and have a decisive influence on the obtained values of the K_A and K_D parameters and their ratios, K_A/K_D .

6. The specific interactions of the graphene materials with the probes characterised by the different acidic and basic properties significantly depended on the kind of surface functionalisation and on the electron density distribution in the molecular orbital of these probes.

The results of the chromatographic tests of the adsorption properties of the oxidised and reduced graphene samples presented in the paper have enabled an unambiguous characteristic of the surface acceptor-donor properties of these materials. The explanation of the way in which electrons have been exchanged between the atoms of the functionalities located in the structures of the graphene materials and the active sites of probes now is not possible to elucidate.

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