

Chromatographic characterisation of acceptor–donor properties of MCMs*

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The values of the specific retention volumes of non-polar and polar adsorbates chromatographed on the ordered mesoporous silica adsorbents (MCMs) were determined under their infinite dilution conditions. Two methods were employed for the calculation of the standard free energy of adsorption, ΔG_{ads} , of the chromatographed adsorbates on the basis of the specific retention volumes. The ΔG_{ads} values were employed for the estimation of the van der Waals contribution and specific contribution of the free surface energy for the MCMs and the parameters characterising their ability to act as acceptors, K_A , and donors, K_D , of electrons.

1. INTRODUCTION

The silica adsorbents MCM41 are rated to the ordered mesoporous silica materials. These adsorbents contain hexagonal mesopores non-connected with one another and creating a honey comb structure. An essential property of the materials is the possibility during synthesis to predict and control the dimension and volume of pores in the obtained adsorbent. The MCM41 group has homogeneous pores with the dimensions ranging from 1.5 nm to 10 nm. For them, the pore volume is usually ranged from 1.0 to 1.5 cm³/g, whereas the specific surface area is ranged from 900 to 1500 m²/g. The mesopore walls are made of amorphous silica [1].

*This article is dedicated to Professor Roman Leboda on the occasion of his 65th birthday

Few papers concerning the problem of testing the acceptor–donor properties of ordered mesoporous silica materials by inverse gas chromatography have been published recently. The adsorbate–adsorbent interactions, i.e., the probe – the ordered mesoporous silica adsorbent, can be regarded as van der Waals interactions and/or specific ones. Therefore the adhesion energy must be divided into several terms corresponding to different dipole interactions (fluctuating dipole–induced dipole, induced dipole–permanent dipole and permanent dipole–permanent dipole) and acceptor–donor interactions including hydrogen bonds as their subset. To the first approximation, the adhesion energy, W_{adh} , can be simply expressed as the sum of two terms, W_{adh}^{vdW} , the van der Waals interaction per unit surface area, and W_{adh}^{SP} , the interactions of the forces called specific which represent the sum of all non van der Waals interactions. Hence,

$$W_{adh} = W_{adh}^{vdW} + W_{adh}^{SP} \quad (1a)$$

For the adsorption of an adsorbate on the tested MCM filling the column, one can write:

$$-\Delta G_{ads} = N_A \omega_p W_{adh}^{vdW} + N_A \omega_p W_{adh}^{SP} \quad (1b)$$

or as

$$-\Delta G_{ads} = -\Delta G_{ads}^{vdW} + N_A \omega_p W_{adh}^{SP} \quad (1c)$$

where: W_{adh}^{SP} – the specific work of adhesion;

N_A – the Avogadro number;

ω_p – the cross-sectional area of adsorbate molecule,

hence

$$-\Delta(\Delta G_{ads}) = -(\Delta G_{ads} - \Delta G_{ads}^{vdW}) = N_A \omega_p W_{adh}^{SP} \quad (1d)$$

where: $-\Delta(\Delta G_{ads})$ – the specific contribution of the free energy of adsorption is determined as the distance (vertical to the abscissa !) between the reference line of n-alkanes and the point for the polar probe in the plot $\Delta G_{ads} = f_1(\log P_o)$ and $\Delta G_{ads} = f_2(T_b)$, i.e. the chosen reference states:

$\log P_o$ – the logarithm of the saturation pressure at column temperature;

T_b – the boiling temperature of adsorbate.

The total standard free energy of transferring one mole of adsorbate from the gas phase to the standard state on the adsorbent surface, known as the energy of adsorption, can be calculated on the basis of the specific retention volume referred to one gram of adsorbent in the column and to the column temperature, $V_{g(T)}^{(1g)}$, as follows [2]:

$$\Delta G_{ads}(I) = -RT \ln \left(\frac{p_{s,g}}{\pi_s S_{BET}} V_{g(T)}^{(1g)} \right) \quad (3)$$

$$\Delta G_{ads}(II) = \Delta H_{ads} - T\Delta S_{ads} \quad (4)$$

$$\ln \frac{V_{g(T)}^{(1g)}}{T} = \frac{-\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} + \ln(RS_{BET}m_{ads}) \quad (5)$$

where: $p_{s,g}$ – the reference pressure equal to 1 atm (101325 N/m²);

π_s – the two-dimensional pressure for the adsorbed state, $0.338 \cdot 10^{-3}$ N/m;

ΔH_{ads} and ΔS_{ads} – the enthalpy and entropy of adsorption calculated on the basis of equation (4);

S_{BET} – the specific surface area of the tested adsorbent.

For such characterised system the $p_{s,g}$, π_s and S_{BET} parameters are constant, and equation (3) takes the following form $\Delta G_{ads} = -RT \ln V_{g(T)}^{(1g)} + const$, for which the value of the constant strongly depends on the chosen reference state of the adsorbed molecule.

2. THEORETICAL

Pearson has proposed the Hard-Soft Acid-Base (HSAB) principle for the generalized Lewis acid-base interaction to classify acids and bases according to the absolute hardness [3], whereas Lee summed up the Pearson's proposal in the following way:

- i) a hard acid contains an acceptor atom of high positive charge and a relatively small size. It does not have easily excitable outer electrons and it is not polarizable [4];
- ii) a soft acid contains an acceptor atom of low positive charge and a relatively large size. It has several easily excitable outer electrons and it is polarizable [4];

- iii) a hard base contains a donor atom of low polarizability that is hard to reduce. It is associated with empty orbitals of high energy and hence inaccessible [4];
- iv) a soft base contains a donor atom of high polarizability and low electronegativity. It is easily oxidised and associated with unoccupied low-lying orbitals [4].

Isaacs has proposed the HSAB principle for organic reactions and the frontier orbital approach to illustrate the electrophilic and nucleophilic interactions [5], whereas Lee summed up the Isaacs proposal in a similar way as he did for the Pearson's one [4]:

- i) a hard electrophile (or acid) has a high-energy lowest unoccupied molecular orbital (LUMO) and usually has a positive charge [4];
- ii) a soft electrophile has a low-energy LUMO, but it does not necessarily have a positive charge [4];
- iii) a hard nucleophilic (or base) has a low-energy (highest occupied molecular orbital) HOMO and it usually has a negative charge [4];
- iv) a soft nucleophile has a high-energy HOMO but it does not necessarily have a negative charge [4].

As it is commonly known acid-base properties of the tested solid have a decisive influence on the value of the specific contribution of the enthalpy of adsorption of the test substance:

$$-\Delta H_{ads}^{SP} = K_A \cdot DN + K_D \cdot AN \quad (6)$$

where: ΔH_{ads}^{SP} - the contribution of the specific enthalpy of adsorption of the probe on the tested surface,

K_A and K_D - the parameters characterising the ability of the tested surface to behave as an acceptor or a donor of electrons, respectively,

AN and DN - the acceptor number and donor number of probe, respectively.

Liquids can also be characterised by donor, DN , and acceptor, AN , numbers following the Gutmann acid-base approach [6]:

- the donor number characterising the basicity or electron-donor ability, which is the molar enthalpy value of the reaction between the base, viz., the electron-donor D and a reference acceptor, antimony pentachloride - $SbCl_5$, in a dilute solution of 1,2-dichloroethane [7];
- the acceptor number characterising the acidity or electron-acceptor ability, which is defined on the NMR chemical shift of ^{31}P in triethylphosphine - $(C_2H_5)_3PO$, when it is dissolved in the acceptor solvent A [8].

In chromatographic study, it is necessary to choose either a strong donor (base) character, or a strong acceptor (acid) character, and both characters (amphoteric).

The donor number (DN) was defined by Gutmann *et.al* [6, 7] as the negative of the enthalpy of formation of the adduct produced when the organic compound (i.e. the base in question) reacted with the reference Lewis acid, $SbCl_5$:

$$\Delta H_{SbCl_5-base} = DN_{base} \quad (7)$$

Gutmann has also introduced the concept of an acceptor number (AN), to supplement DN and to measure the strength of the Lewis acidity or electrophilicity of a liquid [6]. The AN_S values were determined from the magnitude of induced chemical shifts in ^{31}P NMR spectra of triethylphosphine oxide (Et_3PO) as a basic probe. Thus, both AN and DN values were scaled semiempirically, and a given acid–base interaction could be expressed by an analog to the E and C equation [9].

On account of the incompatibilities of the units of both the AN and DN numbers and the K_A and K_D Riddle and Fowkes have corrected the AN values for the van der Waals contribution to the chemical shift on the basis of the determination of the γ_S^D values from measurements of the surface and interfacial tensions of the test liquids [10]. They determined the enthalpy of formation of the adduct $SbCl_5-(C_2H_5)_3PO$ and introduced the corrected acceptor number AN^* . It enables a direct comparison of the K_A and K_D values and an estimation of the surface nature by employing the following equation [11]:

$$\frac{(-\Delta H_{ads}^{SP})_i}{AN_i^*} = K_A \frac{DN_i}{AN_i^*} + K_D, \quad (8)$$

where i denotes a probe.

The main aim of the paper is to characterize the acceptor–donor properties of the ordered mesoporous functionalized silica adsorbents by means of inverse gas chromatography.

Voelkel described in his paper another method of determining the K_A and K_D parameters by the direct use of the ΔG_{ads}^{SP} value, which introduces the contribution of the entropic term [12]:

$$\Delta G_{ads}^{SP} = \Delta H_{ads}^{SP} - T\Delta S_{ads}^{SP} \quad (9a)$$

Thus equation (8) has become the form:

$$\frac{(\Delta G_{ads}^{SP})_i}{AN_i^*} \cong K_A \frac{DN_i}{AN_i^*} + K_D \quad (9b)$$

where ΔG_{ads}^{SP} {or $-\Delta(\Delta G_{ads})$ } is the specific component of the free energy, actually it is the vertical distance between the total free energy of the polar probe and the total free energy of a hypothetical *n*-alkane on the reference line having the same value on the abscissa.

3. EXPERIMENTAL

3.1. Adsorbents and adsorbates

The characteristics of the MCMs tested were elucidated on the basis of the results obtained via low-temperature N₂ adsorption data, XPS, XRD and AFM tests, and reported earlier [13].

The following substances have been employed as adsorbates, regarding their peculiar interactions of them with the MCMs surfaces:

- i) neutral: *n*-alkanes: C₅–C₈ – 0 D and cyclohexane – 0.3 D;
- ii) acidic: dichloromethane, trichloromethane and tetrachloromethane, which have the *sp*³ hybridisation and dipole moments: 1.60 D, 1.08 D and 0 D, respectively and benzene – 0 D;
- iii) basic: acetonitrile – 3.2 D, tetrahydrofuran – 1.75 D, diethyl ether – 1.3 D;
- iv) amphoteric: acetone – 2.9 D, ethyl acetate – 1.7 D.

3.2. Chromatographic tests

The chromatographic measurements of the aforementioned probes were undertaken using a Unicam type 610 gas chromatograph fitted with an on-line Unicam 4880 chromatography data handling the system which was switched on when a sample was injected. The instrument was equipped with a flame ionization detector. The injector and detector temperatures were 396 K and 398 K, respectively. Elution peaks of the adsorbates were acquired at 343–393 K and the sampling rate 10 Hz employing helium at a flow rate equal to 20±0.1 cm³/min.

The MCM samples, degassed at 383 K, were placed in 65 cm × 0.4 cm I.D. glass columns, the length of the adsorbent bed in each column being 10–12 cm. The part of the column which was unoccupied by the MCM was filled with glass beads of 80 mesh size. The filled column was mounted in the chromatograph thermostat and heated at 423 K for 24 hours in a helium stream at a flow-rate of 40 cm³/min. The amount of the injected adsorbates onto column ranged between

0.05-0.005 μl of vapour in the case of *n*-alkanes, cyclohexane and benzene and liquid for diethyl ether and ethyl acetate.

The important part of these chromatographic tests has been the determination of the retention volume of a non-adsorbed probe, viz., the holdup. The gas holdup time, t_M , can be calculated from the dependence:

$$\ln\left[(t_{Ri} - t_M)\sqrt{M_i}\right] = a + b \cdot U(z) \quad (10)$$

where t_{Ri} are the retention times of Ar, Kr, Ne and Xe ;

M_i is the atomic mass of the aforesaid gases ;

$U(z)$ is the Kirkwood-Müller or Lennard-Jones 12-6 or 9-3 potential function ;

a and b are the coefficients.

The justification for the basic idea of calculating the t_M values was very precisely presented earlier [2].

For all the tested systems the asymmetric elution peaks were obtained, for which the retention times depended on the amount of adsorbate injected onto column. The retention times were estimated on the basis of the first statistic moment, m_1 , i.e. the centres of gravity of peaks:

$$t_R = m_1 = \frac{\int_{t_b}^{t_e} tc(t)dt}{\int_{t_b}^{t_e} c(t)dt} \quad (11)$$

The retention times corresponding to the infinitely low coverage of the MCM surface with probe molecules were determined by employing the following dependency [14]:

$$t_R^o = \lim_{v \rightarrow 0} t_R(v) \quad (12)$$

The specific retention volumes were calculated by employing the retention times determined for the infinite dilution of probe and referred to 1 gram of the MCM in the column [14]:

$$V_{g(T)}^{(1g)} = \frac{3 \left(\frac{p_i}{p_o} \right)^2 - 1}{2 \left(\frac{p_i}{p_o} \right)^3 - 1} F_o (t_R^o - t_m) \frac{T_c}{T_f} \left(\frac{p_o - p_{H_2O}}{p_o} \right) \frac{1}{m_{ads}} \quad (13)$$

In equations (11)-(13) $c(t)$ is the function of concentration with respect of time, v – is the amount of probe injected onto column, $t_R(v)$ – is the retention time of probe dependent on the amount of probe injected onto column, t_m – is the hold-up time, F_o – is the carrier gas flow-rate measured by soap flow-meter at the column temperature, T_c – is the column temperature, T_f – is the temperature of flow-meter, p_i – is the pressure at the inlet of column, p_o – is the ambient pressure, p_{H_2O} – is pressure of water vapour at the ambient temperature, m_{ads} – is the total mass of adsorbent in the chromatographic column.

4. DISCUSSION

Based on the theoretical considerations discussed earlier, the values of the K_A and K_D parameters have been calculated by employing equations (8) and (9b). They are collected in Tables 1 and 2, respectively, and the corresponding plots are depicted in Figures 1 and 2.

The values of the quotient K_A / K_D suggested that the MCMs surfaces tested here have electron acceptor properties. It is necessary to add that in the case of employing equation (8) the K_A values are lower than 0 (see Figure 1), but in the case of using equation (9b) the values of both parameters are above 0 (see Figure 2). It can be observed that the entropic effect has a decisive influence on the chromatographically determined K_A and K_D parameters.

The other problem is that there are no sets of probes for these tests, like the Grob test. Lowering the number of probes employed will have a decisive influence on the results obtained.

Tab. 1. The comparison of the dependencies for equation (8), (every dependence is characterised by the values of linear regression coefficient, r , and the standard deviation values for linear regression, SD).

Adsorbent	Parameter	$\Delta G_{ads}(I)$	$\Delta G_{ads}(II)$
C16	logPo	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.46 + 0.05 \frac{DN}{AN^*}$ $r=0.9995$ $SD=0.21$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.45 + 0.09 \frac{DN}{AN^*}$ $r=0.9996$ $SD=0.20$
	Tb	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.45 + 0.21 \frac{DN}{AN^*}$ $r=0.9991$ $SD=0.28$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.43 + 0.25 \frac{DN}{AN^*}$ $r=0.9991$ $SD=0.28$
C16-SH	logPo	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.44 - 0.19 \frac{DN}{AN^*}$ $r=0.9973$ $SD=0.49$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.43 - 0.19 \frac{DN}{AN^*}$ $r=0.9969$ $SD=0.51$
	Tb	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.43 - 0.03 \frac{DN}{AN^*}$ $r=0.9973$ $SD=0.50$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.41 - 0.03 \frac{DN}{AN^*}$ $r=0.9967$ $SD=0.51$
C16-NH ₂	logPo	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.45 - 0.07 \frac{DN}{AN^*}$ $r=0.9989$ $SD=0.36$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.47 - 0.16 \frac{DN}{AN^*}$ $r=0.9989$ $SD=0.36$
	Tb	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.44 + 0.07 \frac{DN}{AN^*}$ $r=0.9978$ $SD=0.49$	$\frac{-\Delta H_{ads}^{SP}}{AN^*} = 0.46 - 0.01 \frac{DN}{AN^*}$ $r=0.9983$ $SD=0.45$

The acceptor–donor properties of the tested MCMs have been characterised on the basis of the recommended values of the K_A / K_D quotient:

$$\frac{K_A}{K_D} \leq 0.9 \quad \text{basic (donor)}$$

$$0.9 < \frac{K_A}{K_D} < 1.1 \quad \text{amphoteric}$$

$$\frac{K_A}{K_D} \geq 1.1 \quad \text{acidic (acceptor)}$$

Tab. 2. The comparison of the dependencies for equation (9a), every dependence is characterised by the values of linear regression coefficient, r , and the standard deviation values for linear regression, SD .

Adsorbent	Parameter	T	$\Delta G_{ads}(I)$	$\Delta G_{ads}(II)$
C16	logP _o	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.06 + 0.17 \frac{DN}{AN^*}$ $r = 0.9993$ SD= 0.57	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.07 + 0.17 \frac{DN}{AN^*}$ $r = 0.9993$ SD= 0.33
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.07 + 0.18 \frac{DN}{AN^*}$ $r = 0.9994$ SD= 0.53	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.07 + 0.18 \frac{DN}{AN^*}$ $r = 0.9994$ SD= 0.37
	T _b	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.05 + 0.17 \frac{DN}{AN^*}$ $r = 0.9995$ SD= 0.49	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.05 + 0.17 \frac{DN}{AN^*}$ $r = 0.9995$ SD= 0.33
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.07 + 0.18 \frac{DN}{AN^*}$ $r = 0.9995$ SD= 0.48	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.06 + 0.18 \frac{DN}{AN^*}$ $r = 0.9995$ SD= 0.37
C16-SH	logP _o	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.01 + 0.16 \frac{DN}{AN^*}$ $r = 0.9980$ SD= 0.15	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.02 + 0.16 \frac{DN}{AN^*}$ $r = 0.9981$ SD= 0.15
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = -0.01 + 0.18 \frac{DN}{AN^*}$ $r = 0.9987$ SD= 0.14	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.01 + 0.17 \frac{DN}{AN^*}$ $r = 0.9985$ SD= 0.15
	T _b	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = -0.005 + 0.16 \frac{DN}{AN^*}$ $r = 0.9983$ SD= 0.14	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.005 + 0.16 \frac{DN}{AN^*}$ $r = 0.9983$ SD= 0.14
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = -0.02 + 0.17 \frac{DN}{AN^*}$ $r = 0.9988$ SD= 0.13	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.003 + 0.17 \frac{DN}{AN^*}$ $r = 0.9986$ SD= 0.14
C16-NH ₂	logP _o	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.12 + 0.19 \frac{DN}{AN^*}$ $r = 0.9992$ SD= 0.12	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.12 + 0.18 \frac{DN}{AN^*}$ $r = 0.9991$ SD= 0.13
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.11 + 0.20 \frac{DN}{AN^*}$ $r = 0.9990$ SD= 0.15	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.11 + 0.20 \frac{DN}{AN^*}$ $r = 0.9991$ SD= 0.14
	T _b	120	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.11 + 0.18 \frac{DN}{AN^*}$ $r = 0.9994$ SD= 0.11	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.11 + 0.18 \frac{DN}{AN^*}$ $r = 0.9993$ SD= 0.11
		100	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.11 + 0.20 \frac{DN}{AN^*}$ $r = 0.9992$ SD= 0.14	$\frac{-\Delta G_{ads}^{SP}}{AN^*} = 0.10 + 0.20 \frac{DN}{AN^*}$ $r = 0.9993$ SD= 0.13

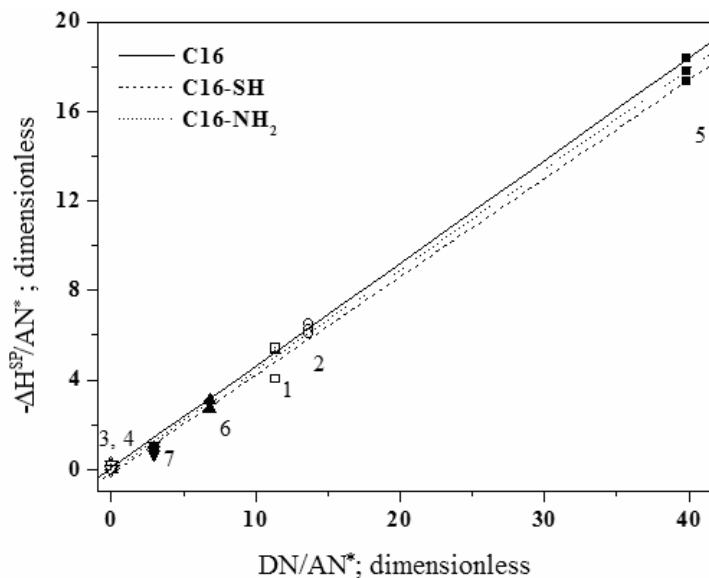


Fig. 1. The plots for the tested MCMs and the employed probes corresponding to equation (8), where: 1 – ethyl acetate, 2 – diethyl ether, 3 – methylene chloride, 4 – chloroform, 5 – tetrahydrofuran, 6 – acetone, 7 – acetonitrile.

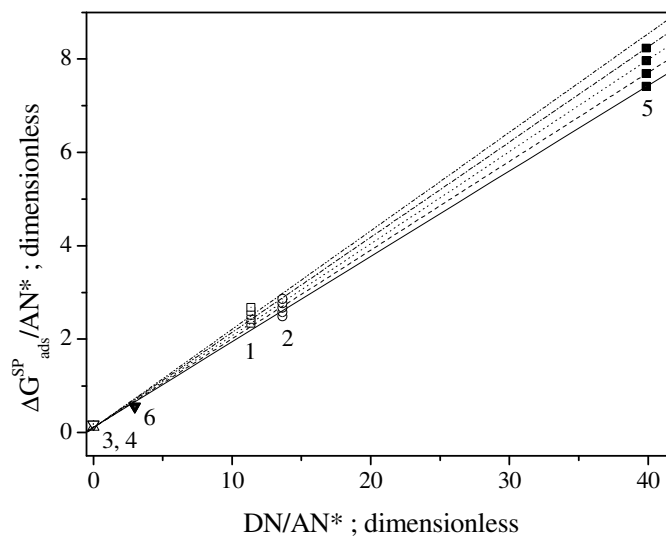


Fig. 2. The plots for the tested MCMs and the employed probes corresponding to equation (9b), where: 1 – ethyl acetate, 2 – diethyl ether, 3 – methylene chloride, 4 – chloroform, 5 – tetrahydrofuran, 6 – acetone, 7 – acetonitrile.

As the results of the analysis it has been found that all the tested adsorbents have acceptor properties. It seems obvious in the case of C16 and C16-SH because of strong acceptor properties of –OH and –SH groups, whereas the well-founded doubts come from the values of the K_A / K_D quotient for the C16-NH₂ adsorbent.

5. CONCLUSIONS

The employed IGC method gives more plausible results taking the $-\Delta(\Delta G_{ads})$ values into account, on the basis of which it is possible to characterize the acceptor–donor properties of the MCMs surfaces.

A good correlation between the XPS and IGC results has been obtained in the case of the acceptor–donor characteristics. It suggests, that the specific adsorbate–adsorbent interactions are strongly dependent on the percentage of elements in the surface layers of the tested MCMs.

It is necessary to work out the set of probes for these tests for unambiguous interpretation of the acceptor–donor properties.

6. REFERENCES

- [1] V. R. Choudhary, K. Mantri, *Langmuir*, 16, 7031 (2000).
- [2] H. Grajek, J. Paciura-Zadrożna, Z. Witkiewicz, *J. Chromatogr. A*, 1194, 118 (2008).
- [3] R. G. Pearson, *Hard and Soft Acids and Bases*, Dowden, Hutchinson and Ross, Inc., Stroudsburg, 1973.
- [4] L. -H. Lee, *Progr. Colloid Polym. Sci.* 82, 337 (1990).
- [5] N. S. Isaacs, *Physical Organic Chemistry*, (2nd Ed.), Longman Scientific and Technical Longman House, Harlow Essex, 1995.
- [6] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978.
- [7] V. Gutmann, A. Steininger, E. Wychera, *Monatsh. Chem.* 97, 460 (1966).
- [8] U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* 106, 1235 (1975).
- [9] A. P. Marks, R. S. Drago, *J. Am. Chem. Soc.*, 97, 3324 (1975).
- [10] F. L. Riddle, Jr., F. Fowkes, *J. Am. Chem. Soc.*, 112, 3259. (1990)
- [11] C. Bilgiç, F. Tümsük, *J. Chromatogr. A*, 1162, 83 (2007).
- [12] A. Voelkel, *Crit. Rev. Anal. Chem.* 22, 411 (1991).
- [13] H. Grajek, J. Paciura-Zadrożna, Z. Witkiewicz, *J. Chromatogr. A*, 1194, 118 (2008).
- [14] H. Grajek, *J. Chromatogr. A*, 1145, 1 (2007).