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Selectivity of Chemically Modified (Architectonic) and Non-modified (Topographic) Adsorbents

Selektywność adsorbentów chemicznie modyfikowanych (architektonicznych) oraz niemodyfikowanych (topograficznych)

Селективность химически модифицированных (архитектонических) и немодифицированных (топографических) адсорбентов

Chemically modified and non-modified adsorbents are widely used in chromatography [1-4]. From the practical point of view it is important to establish correlations between surface properties of such adsorbents and their separation ability, and to study the adsorption mechanism of chromatographed substances on such adsorbents. A great facility in testing of adsorbents is provided by chromatographic methods for studying energetic heterogeneity of adsorbents [5-10], as the effects of heterogeneity play a considerable role in the process of chromatographic separation [11-16]. The surface structure of chemically modified and non-modified adsorbents is quite different. Consequently, the thermodynamic analysis of both types of adsorbents, conducted from the viewpoint of their ability to separation, should be different [8,11,15].

In this paper some problems connected with selectivity of chemically modified and non-modified adsorbents and their testing are discussed. These problems concern the establishment of the separation mechanism on such adsorbents. So far the following question: "can bonded phases be classified under adsorption or partition", is still opened, and has recently been discussed by Colin and Guiochon [17].

EXPERIMENTAL

The problem of selectivity of chemically modified and non-modified adsorbents will be discussed by comparing the separation of the sample composed of light hydrocarbons C_1-C_4 on columns packed with hydroxylated silica gel and with silica gels esterified with n-butanol and n-decanol. The surface characteristics of silica gels are given in Table 1. The specific surface areas were measured by using the method of thermal desorp-

Table 1. Surface properties of silica gels modified with aliphatic alcohols

Silica gel	Surface area, m^2/g		D.E.	% C
	S_{N_2}	S_{H_2O}		
Esterified with n-butanole	312	30	2.7	6.71
Esterified with n-decanole	106	28	2.9	6.15

tion of nitrogen [18]. The esterification degree (D.E.) was calculated from the content of carbon in the studied sample and from its specific surface by using of the equation of Ballard et al. [19]. The elementary analysis of esterified silica gels was performed on Hewelt Packard CHN, Model F and M 185 analyzer. The D.E. is a measure of the number of esterfied OH groups per $m\mu^2$ of the silica surface. Moreover, for esterified silica gels the values of specific surfaces S_{H_2O}, measured by means of water vapour adsorption at 298 K, were calculated .

The S_{H_2O} values are considered to be the approximate measure of the number of non-esterified silanole groups of the silica gel surface [20].

The problem of testing of adsorbents will be discussed on the basis of the analysis of the energy distribution functions and adsorption isotherms. As an example of such an analysis we consider the adsorption of cyclohexane, cyclohexene, n-hexane and benzene at 373.6 K on silica gel esterified with n-octanol. The values of specific surface areas of this adsorbent were S_{N_2} = 152 m^2/g and S_{H_2O}= 45 m^2/g. A detailed description of the method of measurement and the relevant calculations are given in the earlier papers [6-8].

Separation of the hydrocarbons C_1-C_4 mixture was performed on Giede 18.3 chromatograph with a detector of thermal conductivity. In all measurements columns 1 m long and 4 mm I.D. were used. Moreover, adsorption isotherms of cyclohexane and cyclohexene were measured on hydroxylated silica gel of the specific surface area S_{N_2} = 597 m^2/g and on silica gels, esterified with aliphatic alcohols from n-pentanol to n-decanol. The preparation of these adsorbents was described in refs. [11] and [21]. The surface characteristics of these adsorbents are summarized in Table 2. The results obtained for esterified silica

Table 2. Characterization of surface properties of silica gels modified with aliphatic alcohols from C_5 to C_{10}

Silica gel	Heats of adsorption, kcal/mole		Surface area, m^2/g		D.E.	% C
	C_6H_{12}	C_6H_{10}	S_{N_2}	S_{H_2O}		
Non-modified	8.7	9.6	597			
Esterified with n-pentanole	7.7	8.8	118	44	0.31	0.3
Esterified with n-hexanole	8.8	8.8	378	80	0.20	0.9
Esterified with n-heptanole	7.2	8.2	115	72 :	0.34	0.56
Esterified with n-octanole	7.9	8.8	318	87	0.55	2.8
Esterified with n-nonanole	7.2	8.6	131	67	0.44	1.04
Esterified with n-decanole	-	-	493	55	0.41	2.39

gels are compared with those obtained for silanized sil-
ica gels and for complex carbon-silica adsorbents (carbo-
sils). Carbosils were obtained by pyrolisis of n-octanol (carbo-
sil A) and benzyl alcohol (carbosil B) on the silica gel
surface [22,23].

RESULTS AND DISCUSSION

Graphitized carbon black is one of better adsorbents for
the gas chromatography. The basic factor allowing graphite to be
a universal adsorbent is a proper topography of its adsorp-
tion centers. The distances between the energetic centers of
graphite are approximately the same as the lenghts of chemical
bonds of hydrocarbons molecules, so that the direct dispersion
interactions between the particular components of the adsorb-
te molecule and the energetic centers of the graphite may oc-
cur. Owing to such interactions it is possible to separate ge-
ometrical isomers of hydrocarbons on graphite [24,25]. Differ-
ent adsorption energies of geometrical isomers of hydrocar-
bons result from different distances between energetic centers
of their molecules and energetic centers of the "flat" graph-
ite surface.

In case of other non-modified adsorbents, the distances
between adsorption centers are much greater than the lenghts of
chemical bonds in hydrocarbons molecules, for example, the dis-
tances between hydroxyl groups of silica gels range from 2.5
to 5 Å [1]. Through chemical modification of adsorbents with
organic substances new energetic centers are formed. The dis-
tances between these centers are similar to those between ener-
getic centers of adsorbate molecules. Therefore, on chemically
modified adsorbents, there exist more favourable conditions for
the occurrence of direct interactions between energetic centers
of the adsorbate and adsorbent. However, the condition of the
preparation of the adsorbent and the kind of the used modifica-

tor should be chosen in order to obtain a good adsorbent for
separation of a given type of the sample. It is connected with
the necessity of forming a proper system of energetic centers
on the surface [8,9,15,26]. As an example illustrating   the
effect of distribution of energetic centers of adsorbent on
its separation ability, we consider the chromatograms presen-
ted in Figs. 1 and 2. The separation of C_1-C_4 hydrocarbons on
esterified silica gels depends on the kind of alcohol used for
modification and on D.E. [11,21,26]. However, in case of
hydroxylated silica gels, it is determined by porosity and by
the content of free and bound hydroxyl groups [1,3]. A good
separation of C_1-C_4 hydrocarbons mixture was obtained on hy-
drixylated silica gel, as seen in Fig. 1A. Modification of sil-
ica gel with alcohols improved the separation of these   sub-
stances (cf.Figs. 1B and 2). However, this separation depends
on the kind of alcohol used for esterification. It can be seen
from the data given in Table 1 that silica gels modified with
n-butanol and n-decanol are characterized by similar values of
D.E. and S_{H_2O} . Surface silanole groups of incompletely esteri-
fied silica gel play an important part in the separation of analyzed
mixture [27] by causing a suitable orientation of adsorbate mol-
ecules with respect to the surface. Silica gel esterified
with n-butanol possesses the specific surface almost three
times greater than silica gel modified with n-decanol. Due to
this difference, on the column packed with the first adsorbent
there should exist a greater possibility of differentiating of
dispersion interactions of hydrocarbons, and thus, of their sep-
aration . In practice, however, the adsorbent modified with n-
-decanol appeared more selective (see Fig.2). A higher selectiv-
ity of this adsorbent results from the fact that on its sur-
face there exists a more favourable distribution of energetic
centers CH, CH_3 and OH groups for differentiation of adsorption
energies of the substances analyzed than on silica gel esterified
with n-butanol.

Fig. 3 shows hypothetical and simplified schemes of inter-
actions of molecules of butylen isomers with the silica gel
surface esterified with alcohols. Configuration of alcoxyl
groups on the silica gel surface depends on the D.E., length of
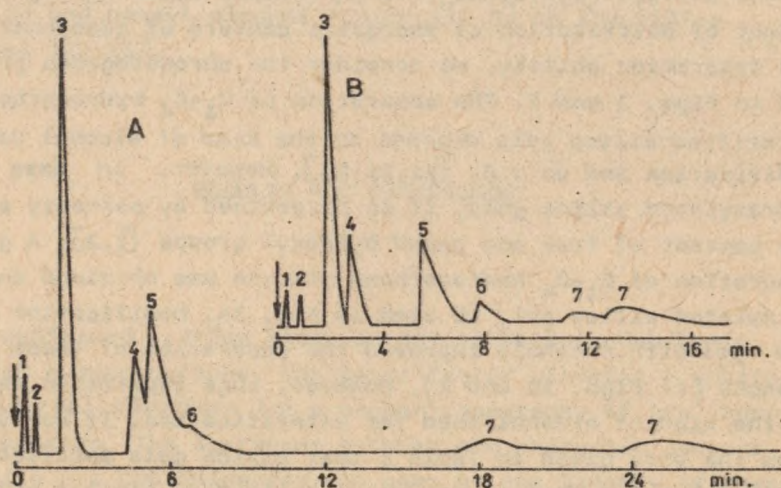the alcoxyl chain and column temperature [8,11,28]. It can be

Fig. 1. Chromatograms of the separation of light hydrocarbons
at 30°C on hydroxylated (A) and esterified with n-butanole (B)
silica gels. Peaks: 1 - methane, 2 - ethane, 3 - n-propane,
4 - propene, 5 - iso-butane, 6 - n-butane, 7 - butenes (butene-
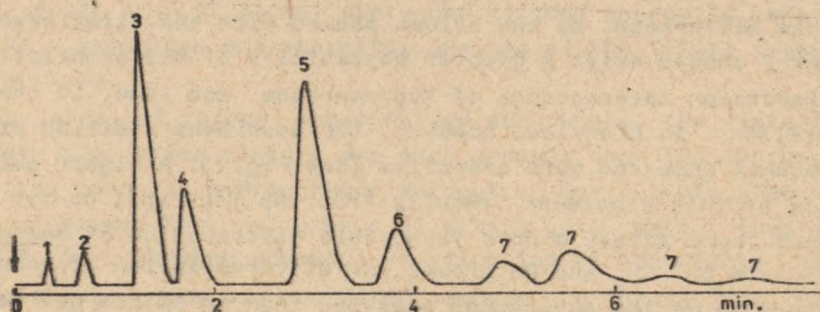-1, cis- and transbutenes, 2-methylpropene)

Fig. 2. Chromatograms of the separation of light hydrocarbons
at 30°C on esterified with n-decanole silica gel. Peaks: 1 -
methane, 2 - ethane, 3 - n-propane, 4 - propene, 5 - isobutane,
6 - n-butane, 7 - butenes (butene-1, cis- and transbutenes,
2-methylpropene)

seen in Fig. 3 that in the adsorption process of hydrocarbons, there may occur effects of spatial interactions between atoms of hydrocarbon molecule and energetic centers of modified adsorbents ("energetic stereoeffects"). They may occur both dur-
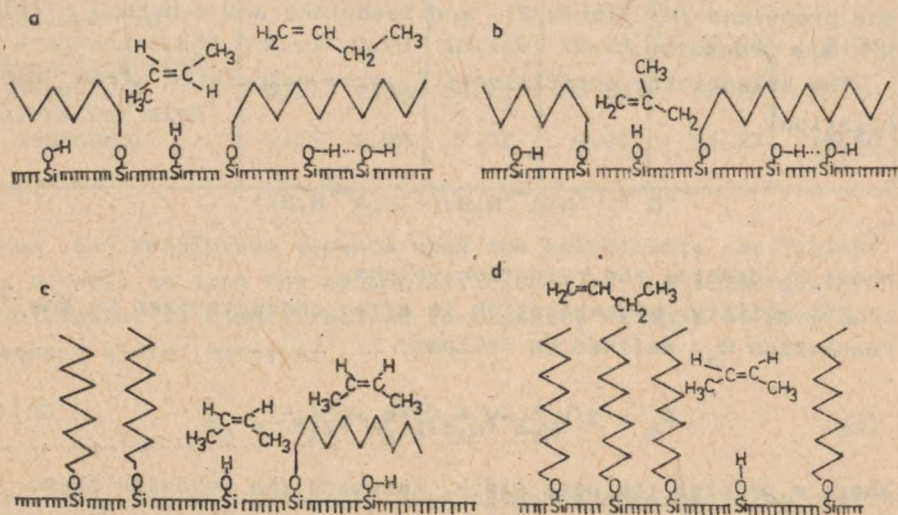

Fig. 3. Schemes illustrating the interactions of molecules of butylen isomers with silica gel surface esterified with ali - phatic alcohols. In Figs. a-d various configurations of alcoxyl chain are shown. These configurations depend on the degree of esterifications, on the temperature of adsorption system and on lenght of chain of alcoxyl radicals: a,b - small esterification and low temperature; c,d - hight esterification. In Figs. c,d the energetic stereoeffects are shown.

ing adsorption of hydrocarbons molecules on OH groups and during the movement of molecules towards non-esterified OH groups between the standing chains of the radical. Energetic stereoeffects are subtle effects, but they may decide about the separation. The magnitude of these effects will depend on the length and configuration of the alcoxyl chain as well as on the size and spatial structure of adsorbent. In case of both silica gels discussed here the effects of spatial interactions will be stronger on the surface of silica gel esterified with n-decanol, because of greater length of the chain of the decyl group. Thus, the tract of the adsorbate molecule

towards the silanole group will be longer in this case   than
in case of silica gel esterified with n-butanole.

The above suggestions are confirmed by the data presented
in Tables 3 and 4, where some constants characterizing the
ability to separation of the mixture composed of isobutane (A)
and propylene (B) (Table 3), and isobutane and n-butane (Table
4), are presented.

The selectivity coefficients k_c were calculated   from   the
relation:

$$k_c = (V_{N,A} - V_{N,B})/(V_{N,A} + V_{N,B}),   \tag{1}$$

where V_N denotes the retention volume.

The ability of separation is often characterized by the
resolution R_s, defined as follows:

$$R_s = 2(V_{N,A} - V_{N,B})/(w_A + w_B),   \tag{2}$$

where w denotes the peak width. Assuming the gaussian shape
of peaks and that the number of theoretical plates n does not
depend upon a kind of chromatographed compound, the last   re-
lation is reduced to:

$$R_s = \sqrt{n}\, k_c/2.   \tag{3}$$

Table 3. Some constants characterizing the separation of bu-
tane (A) and propylene (B)

Silica gel	K_c	R_s	K_A	K_B	$K_A^s \cdot m^{-1}$ $\cdot 10^{-3}$	$K_B^s \cdot m^{-1}$ $\cdot 10^{-3}$
Hydroxylated /non-modified/	0.066	0.51	12.125	10.62	7.65	6.70
Esterified with n-butanol	0.36	2.0	14.71	6.86	7.86	3.66
Esterified with n-decanol	0.31	2.99	7.17	3.78	11.27	5.94

Table 4. Some constants characterizing the separation of iso-
butane (A) and n-butane (B)

Silica gel	K_c	R_s	K_A	K_B	$K_A^s \cdot m^{-1} \cdot 10^{-3}$	$K_B^s \cdot m^{-1} \cdot 10^{-3}$
Hydroxylated /non-modified/	0.13	0.78	12.125	15.75	7.65	9.94
Esterified with n-butanol	0.17	1.39	14.71	20.86	7.86	11.14
Esterified with n-decanol	0.16	1.89	7.17	9.86	11.27	15.50

Thus, the resolution depends upon the selectivity coefficient k_C as well as upon the column efficiency n. The selectivity coefficient is simply related to capacity rations of both subsequent eluted species:

$$k_C = (K_A^s - K_B^s)/(K_A^s + K_B^s). \qquad (4)$$

In case of energetically heterogeneous adsorbent the coefficient K_i^s is given by:

$$K_i^s = \alpha \int \chi_i \, (\varepsilon) \quad \exp \, (-\varepsilon)/kT \, d\varepsilon \qquad (5)$$

where χ_i is the distribution function for i-th component, and α is a constant connected with the partition functions of the adsorbate molecules in adsorbed and gaseous phases.

Because the resolution depends much strongly on k_C than on n (cf.eq.3) and on K^s, the changes in the value of this parameter reflect, first of all, the changes of selectivity and capacity (see Tables 3 and 4); although the improving of the separation of the propylene and isobutane on silica gel esteri - fied with n-decanole, in comparison with the silica gel modified with n-butanole, is rather due to improving of the column efficiency - cf. (Table 3). The problem of determination of the number of theoretical plates and its dependence upon the kind of alcohol used in esterification, was discussed previously [21]. We have observed that esterification causes the increase of n in comparison with non-esterified adsorbent.

In case of silica gels modified with n-butanole and n-
-decanole differences between coefficients K_A^s and K_B^s (see Tables
3 and 4) follow from different energies of adsorption, and
consequently, because both these adsorbents are characterized
by very similar values of D.E. and S_{H_2O} (cf. Table 2), these
differences are connected with the energetic stereoeffects.

It can be concluded from the above discussion that testing
of chemically modified adsorbents will be a more complex problem
than in case of non-modified ones. Fig. 4 presented the
energy distribution functions for n-hexane, cyclohexane, cyc -
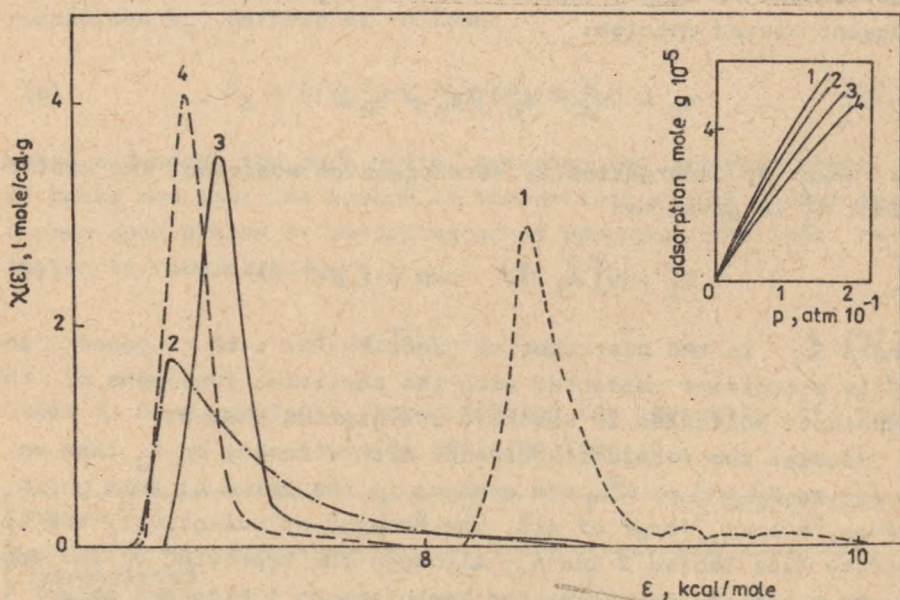lohexene and benzene adsorbed on silica gel esterified with n-
-octanol.

Fig. 4. The energy distribution functions and isotherm of ad-
sorption of benzene (1), cyclohexene (2), cyclohexane (3) and
n-hexane (4) on silica gel modified with n-octanole

On this adsorbent at least two types of adsorption centers can
be distinguished, i.e. non-esterified OH groups and alcoxyl
groups. Two types of adsorption centers can be distinguished
on the curve in Fig. 4. One of them can be attributed to narrow

peaks in the region of lowest adsorption energies. These cen-
ters constitute alcoxyl groups chemically bound with the sil-
ica gel surface. The tails of the peaks which occur in   the
range of highest energies can be attributed to non-esterified
silanole groups.

It is interesting to compare the mean energies and values
of adsorption of the tested substances on the studied silica
gel and hydroxylated silica gels. Mean adsorption energies on
silica gel esterified with n-octanol are 6.9,7.0,7.2 and 9.6
kcal/mole, respectively. These energies were calculated from
energy distributions:

$$q^o_{st} \cong \bar{\varepsilon} = \int_0^\infty \chi(\varepsilon)\, \varepsilon \, d\varepsilon \Big/ \int_0^\infty \chi(\varepsilon)\, d\varepsilon \qquad (6)$$

where q^o_{st} denotes the isosteric heats of adsorption in the ze-
ro coverage limit. Thus, the adsorption energies of the tested
solutes change in the direction: $\bar{\varepsilon}_{C_6H_6} > \bar{\varepsilon}_{C_6H_{10}} > \bar{\varepsilon}_{C_6H_{12}} >$
$\bar{\varepsilon}_{C_6H_{14}}$. In the same way change the values of adsorption (see
Fig. 4.) However, for hydroxylated silica gels the sequence of
these changes is [29]: $\bar{\varepsilon}_{C_6H_6} > \bar{\varepsilon}_{C_6H_{14}} > \bar{\varepsilon}_{C_6H_{10}} > \bar{\varepsilon}_{C_6H_{12}}$, and
for graphitized carbon black adsorption energies _of the ad-
sorbates studied here change in the sequence [2]: $\bar{\varepsilon}_{C_6H_{14}} >$
$\bar{\varepsilon}_{C_6H_6} > \bar{\varepsilon}_{C_6H_{10}} > \bar{\varepsilon}_{C_6H_{12}}$. As can be seen, the sequence of changes
of mean adsorption energies on esterified silica gel is simi-
lar to that characteristic of graphite, whereas in case
of hydroxylated silica gel is quite different. This is likely
to be caused by a high D.E. of the esterified adsorbent, the
effect of which is the formation of new energetic centers on
the surface, such that the distances between them are sim-
ilar to those which occur on graphite surface.

Figs. 5 and 6 present adsorption isotherms of cyclohexa-
ne and cyclohexene on silica gels esterified with alipha -
tic alcohols from C_5 to C_{10}, and on hydroxylated silica
gel. Adsorption of cyclohexane at a given pressure p increases
with the   increase of surface area of silica gel (Fig. 5) Si-
lica gel esterified with n-decanol is an exception. How-
ever, adsorption of cyclohexane on silica gels esterified
with n-hexanol, n-octanol and n-decanol is higher than on hy-
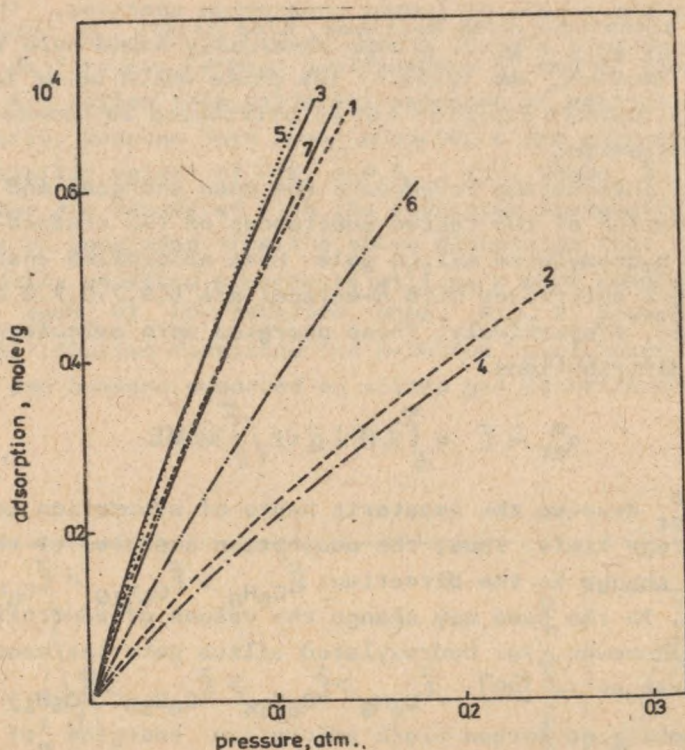droxylated silica gel despite the fact that these adsorbents

Fig. 5. The adsorption isotherms of cyclohexane on silica gels:
hydroxylated (1) and esterified with n-pentanole (2), n-hexano-
le (3), n-heptanole (4), n-octanole (5), n-nonanole (6) and n-
decanole

possess the largest surface. The above anomalies can be inter-
preted by steric effects connected with the orientation of al-
coxyl groups on the surface of esterified silica gels. Such
effects were discussed in the previous papers [8,21,28].

An excellent example illustrating influence of architectu-
re of energetic centers on ability to separation and on   ad-
sorption properties are modified and non-modified carbosils.
Fig. 7 compares IR spectrum of some selected non-modified and
modified with octadecylotrichlorsilane ODS and hexamethylene-
disilane HNDS carbosils. Surface characteristics of these
adsorbents are presented in Table 5.

The analysis of the data given in Fig. 7 shows that all in-
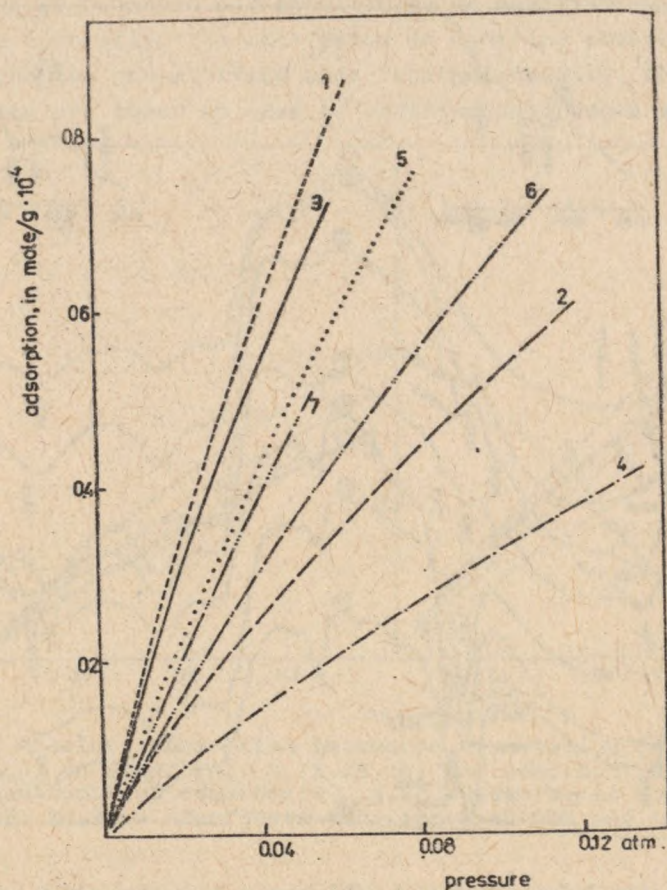vestigated adsorbents are heterogeneous. We can distinguish

Fig. 6. The adsorption isotherms of cyclohexene on silica gels: hydroxylated (1), and esterified with n-pentanole (2), n-hexa - nole (3), n-heptanole (4), n-octanole (5), n-nonanole (6) and n-decanole (7)

here distinc peaks on the IR curves: the peak at 3740 cm^{-1} is attributed to free OH groups, the band 3700 - 3000 cm^{-1} - to bound OH groups and to physically adsorbed water, the band from 2860 cm^{-1} to 2960 cm^{-1} is characteristic of alkil groups and the band at 3060 cm^{-1} is attributed to vibrations of phenyl rings. The detailed analysis of IR spectrum was presented in refs. [22, 23]. The surface of carbosils is mosaic: besides sur- face OH groups there are "patches" of polymeric carbon [30].

After silanization, the surface OH groups are substituted by radicals of ODS and HNDS, consequently the obtained adsorb-
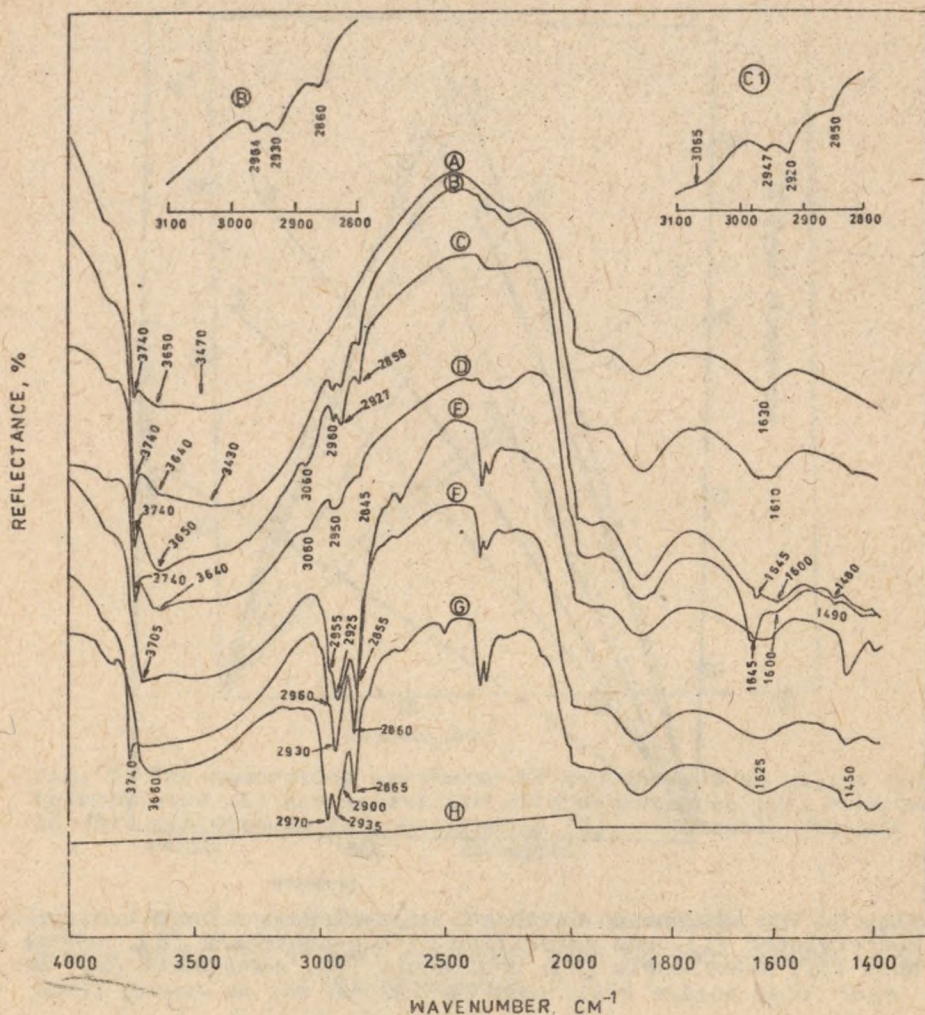
Fig. 7. Infrared spectra of the following adsorbents; A non-
-modified silica gel (adsorbent A in Table 5); B,C - carbosils
obtained by covering adsorbent A with a carbon layer formed by
the pyrolysis of n-heptanol (B), (adsorbent B in Table 5) and
benzyl alcohol (C); C 1 - adsorbent C modified with hydrogen;
D - carbosil obtained by pyrolysis of mixture of both alcohols;
E - adsorbent A silanized with ODS; F - adsorbent B silanized
with ODS; G - adsorbent A silanized with ODS and then HMDS;
H - carbon-silica adsorbent containing pure pyrogenic carbon.
Data from the paper [23]

ents are topographic-architectonic. Fig. 8 presents adsorption isotherms of n-hexane and chloroforme on modified and on non-modified carbosils. The adsorption on modified adsorbents is higher than on non-modified ones. Instantaneously, the heats of adsorption are lower in case of modified adsorbents see (Table 6).
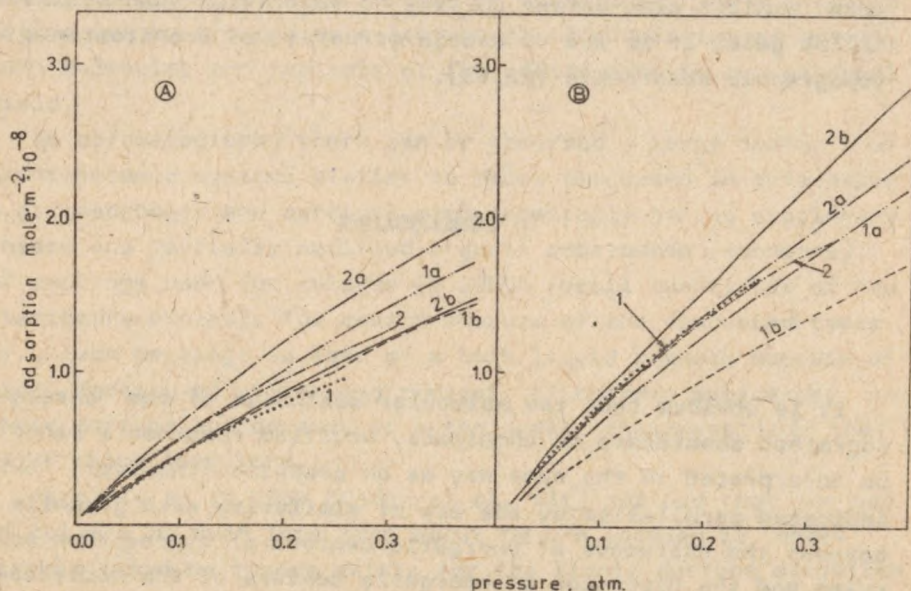

Fig. 8. Absolute adsorption isotherms of n-hexane (A) and chloroform (B) on adsorbent A (1,1a,1b) and adsorbent B (2,2a,2b). 1,2 - non-modified adsorbents; 1a,2a - adsorbents modified with ODS; 1b,2b - adsorbents modified with ODS and then HMDS

Table 5. Properties of partially dehydroxylated silica gel(adsorbent A) and carbon-silica adsorbent (adsorbent B) silanized with ODS (I) and with ODS + HMDS (II)

Adsorbent	Elemental analysis, % w/w		Heats of adsorption, kcal/mole	
	% C	% H	n-hexane	chloroform
Adsorbent A	-	0.70	9.1	10.2
Adsorbent A I	9.36	2.16	7.4	6.1
Adsorbent A II	11.82	2.60	7.0	7.5
Adsorbent B	2.30	0.72	9.2	8.9
Adsorbent B I	2.80	0.74	7.1	7.5
Adsorbent B II	6.10	1.42	6.7	6.1

Thus increasing of adsorption on modified adsorbents is the result of a formation of an appropriate architectonic structure. Owing to such structure, chemically modified adsorbents exhibit better ability to separation. Moreover, the modified adsorbents exhibit also better ability to separation than modified silica gels. It is due to mosaic structure of architectonic - topographic adsorbents [22,23].

CONCLUSIONS

It is obvious that the molecular mechanism of the chromatographed substances on chemically modified adsorbents cannot be interpreted in the same way as on graphite. However, the indicated parallelism by the way of similarity with graphite - between the distances of energetic centers of hydrocarbon molecules and the distances of energetic centers of the modificator molecules, seems to be significant.

The surface of chemically non-modified adsorbents can be considered "flat", two-dimensional, and they can be characterized by means of the topography of adsorption centers. "Surfaces" of modified adsorbents, however, should be treated as three-dimensional. The energetic centers are here spatially distributed, forming an architectonic construction [8,11,28]. The characteristic of chemically modified adsorbents only by means of $\chi(\varepsilon)$, or by isotherm, or adsorption heats, is not adequate for a complete description of their surfaces. Function $\chi(\varepsilon)$ describes only global heterogeneity of the adsorbent surface without giving any information about the topography of adsorption centers. As to adsorption, it is rather a qualitative characteristic of the surface, whereas adsorption heats give information only about the average energetic properties of the adsorbent. The surfaces of chemically modified adsorbents should be additionally characterized by means of the architecture of adsorption centers, i.e. by configuration of chemisorbed

radicals and distances between energetic centers. Also,   the
thermodynamic description of non-modified and modified adsor -
bents will be different. In the first case, the adsorbed phase
can be treated as a gas in an external potential field. How-
ever , in case of architectonic adsorbents, the adsorption
system can be treated as a lattice fluid consisting of adsorb-
ate molecules and radicals of the modificator in an external
field.

In chromatography there can be observed a large number   of
architectonic systems similar to those discussed in this paper,
e.g. adsorbents and carriers with chemically bonded stationary
phases and partially modified organic substances (monomers),
or packings used for columns in GSLCh (small quantities of the
stationary phases). The common feature of the discussed types
of column packings is lack of a bulk liquid phases, because of
small density of chains and radicals of organic substances   on
their surface and because of a too small "thickness" of   the
layer which they form.

As early as in 1969 Conder at al. [31] noticed that the use
of columns of much less than about 5% w/w loading is unde-
sirable since no theory exists for the liquid surface situation
in the absence of a bulk phase.

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STRESZCZENIE

    Rozważano zagadnienie selektywności w chromatografii adsor-
bentów chemicznie modyfikowanych oraz niemodyfikowanych. Dys-
kutowano również problem testowania takich adsorbentów. W tym
celu analizowano korelacje pomiędzy odpowiednimi charakterys-
tykami powierzchniowymi (izotermami adsorpcji, widmami IR, che-
miczną naturą centrów adsorpcyjnych oraz ich topografią) adsor-
bentów chemicznie modyfikowanych (alkoholami alifatycznymi i
silanami)oraz niemodyfikowanych i ich zdolnością rozdzielczą.
Stwierdzono zasadnicze różnice w molekularnym mechanizmie ad-
sorpcji i retencji na obu typach adsorbentów. Na tej podstawie
proponuje się podział adsorbentów na architektoniczne (modyfi-
kowane chemicznie) oraz topograficzne (niemodyfikowane).

Резюме

    В работе рассматривается селективность в хроматографии хи-
мически модифицированных и немодифицированных адсорбентов. Кро-
ме того обсуждается проблема тестирования этого типа адсорбен-

тов. С этой целью были исследованы соотношения между соответ-
ствующими поверхностными характеристиками (адсорбционными изо-
термами, инфракрасными спектрами, химической природой адсорб-
ционных центров и их топографией) и модифицированных химически
(алифатическими спиртами и силанами) и немодифицированных ад-
сорбентов и их разделительной способностью.

Указаны существенные разницы в молекулярном механизме ад-
сорбции и удерживания на обоих типах адсорбентов. На этом осно-
вании предлагается разделение адсорбентов на архитектонические
(химически модифицированные) и топографические (немодифициро-
ванные).