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**ISOMER-SELECTIVE PROPERTIES OF CARBON ADSORBENT MODIFIED  
BY «4-*n*-OCTYLOXY-4'-CYANOBIHENYL –  $\beta$ -CYCLODEXTRIN»  
UNDER GAS-ADSORPTION CHROMATOGRAPHY CONDITIONS**

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*The isomer-selective properties of the carbon adsorbent Carborack Y modified by successively applied immiscible monolayers of 4-*n*-octyloxy-4'-cyanobiphenyl mesogen and  $\beta$ -cyclodextrin have been studied. It has been shown that the bilayer modified adsorbent has a high selectivity to structural and optical isomers under the conditions of the gas-adsorption chromatography. Thermodynamic justification of the selectivity and its temperature dependence has been given. Compensation temperatures for the reversal of the isomer conversion from the chromatographic column have been calculated.*

**Key words:** adsorption, carbon adsorbents, modification, liquid crystal, cyclodextrin, bilayer, isomers, structure, optical properties, selectivity, gas-adsorption chromatography.

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**ИЗОМЕРСЕЛЕКТИВНЫЕ СВОЙСТВА УГЛЕРОДНОГО АДсорбЕНТА,  
МОДИФИЦИРОВАННОГО БИСЛОЕМ  
«4-*n*-ОКТИЛОКСИ-4'-ЦИАНОБИФЕНИЛ –  $\beta$ -ЦИКЛОДЕКСТРИН»  
В УСЛОВИЯХ ГАЗО-АДСОРБЦИОННОЙ ХРОМАТОГРАФИИ**

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*Изучены изомерселективные свойства углеродного адсорбента Carborack Y, модифицированного последовательно нанесенными несмешивающимися монослоями мезогена 4-*n*-октилкокси-4'-цианобифенила и  $\beta$ -циклодекстрина. Показано, что модифицированный бислоем адсорбент обладает высокой селективностью к структурным и оптическим изомерам в условиях газо-адсорбционной хроматографии. Дано термодинамическое обоснование селективности и ее температурной зависимости. Рассчитаны температуры компенсации, при которых происходит обращение выхода изомеров из хроматографической колонки.*

**Ключевые слова:** адсорбция, углеродные адсорбенты, модифицирование, жидкий кристалл, циклодекстрин, бислои, изомеры, структура, оптические свойства, селективность, газо-адсорбционная хроматография.

## Introduction

Separation and detection of isomers is the most complex task of the modern day analytical chromatography that is important for organic chemistry, biochemistry, chemical, pharmaceutical and biotechnological industries. One of the methods for obtaining universal isomer-selective sorbents (stationary phases) in gas-liquid chromatography is the use of binary systems based on achiral liquid crystals (LC) and cyclodextrins (CD) [1–3]. The LC matrix of such stationary phases facilitates the separation of structural isomers, while the cyclodextrins dissolved in it facilitate the separation of optical isomers due to the difference in the stability of the sorbate-macrocyclic binding complexes. A disadvantage of such sorbents, which are thin (~ 100–200 nm) liquid films of the mixed «LC – macrocycle» system deposited on a wide-pore solid carrier, is the increased volatility of the LC sorbent matrix under the dynamic chromatographic conditions. An investigation of the thermal stability of the LC monolayers on graphitized thermal black and its analogs has shown that strong intermolecular interactions of planar molecules of mesogen with the adsorbent carrier sharply increase the starting temperature of the thermal desorption, which is important for practical gas chromatography. Moreover, carbon adsorbents modified with LC monolayers have selectivity to structural isomers over a wider temperature range than LC stationary phases, thus, making possible faster separation of high-boiling isomers under conditions of the gas-adsorption chromatography [4–11].

Earlier, in the [12] work we studied selective properties of the carbon graphite-like adsorbent Carbpac Y (CpY) modified with a mixed adsorption layer of the associate (supramolecular) mesogen 4-(2-hydroxyethoxy)-4'-cyanoazoxybenzene (HEOCAB) and unsubstituted  $\beta$ -cyclodextrin ( $\beta$ -CD). It has been discovered that this adsorbent selectively adsorbs structural isomers and enantiomers of polar compounds from the gas phase, while the selectivity to the low polarity enantiomers is practically absent. It can be explained by the «HEOCAB –  $\beta$ -CD» solvation in the mixed adsorption layer, which prevents the formation of stable inclusion complexes of adsorbates with a low polar  $\beta$ -CD cavity.

Modification of the carbon adsorbent by alternating monolayers of the mesogen and  $\beta$ -CD under an orientation of  $\beta$ -CD molecules «favorable» to the «host – guest» inclusion complex formation on the gas

phase side can provide high selectivity to the separation of structural and optical isomers. Apparently, to obtain an adsorbent with consecutively applied monolayers of mesogen and  $\beta$ -CD it is necessary for the bilayer components to mix poorly with each other.

Thus, the purpose of this work was the experimental study of adsorption regularities from the gas phase of certain structural and optical isomers on the carbon adsorbent CpY subsequently modified by the monolayers of 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB) and  $\beta$ -cyclodextrin, as well as the determination of isomer selective properties of this adsorbent under conditions the gas-adsorption chromatography.

## Experiment

Carbon adsorbent CpY (*Supelco Inc.*) with a specific surface area of 25 m<sup>2</sup>/g was subsequently modified with the 8OCB (*Sigma Aldrich*) liquid crystal monolayer (Fig. 1) and then with the  $\beta$ -CD (*Acros Organics*) monolayer.

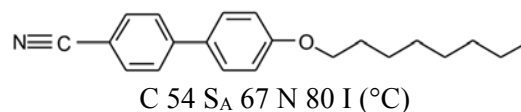


Fig. 1. Structure and phase transition temperatures of 8OCB

For this purpose, the initial CpY adsorbent-carrier with a mass of 1,5275 g was placed in a solution of 8OCB in chloroform, after which the solvent was removed by heating on a sand bath not allowing the solution to boil. The weight of the deposited 8OCB pre-monolayer was 18,2 mg, which corresponds to the formation of a monolayer in the planar orientation of the mesogen molecules on a solid surface. A  $\beta$ -CD modifier with a landing site of  $S = 107 \text{ \AA}^2$  and a mass of 25,5 mg was applied from a water solution to the adsorbent with the 8OCB pre-monolayer of 8 OCB ( $S_M = 107 \text{ \AA}^2$ ). The adsorbent with the deposited bilayer (CpY/8OCB/ $\beta$ -CD) was dried at 70 °C for several days to remove water. The modified adsorbent weighing 1,2860 g was placed in a glass column (1 m x 2 mm) and conditioned in a nitrogen stream at 150 °C for 3 hours.

The objects of the study were xylene isomers as well as optical isomers of monoterpene hydrocarbons C<sub>10</sub>H<sub>16</sub> (limonenes,  $\alpha$ -pinenes, camphenes), menthol, butanediol-1,3 and butanediol-2,3, namely: ( $\pm$ )-limonenes – (R)-1-methyl-4-isopropenylcyclohexene-1 and

(S)-1-methyl-4-isopropenylcyclohexene-1; ( $\pm$ )- $\alpha$ -pinenes – (1R,5R)-2,6,6-trimethylbicyclo[3.1.1]heptene-2 and (1S,5S)-2,6,6-trimethylbicyclo[3.1.1]heptene-2; ( $\pm$ )-camphenes – (1R)-2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane and (1S)-2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane; ( $\pm$ )-menthols – (1S,2R,5S)-2-isopropyl-5-methylcyclohexanol-1 and (1R,2S,5R)-2-isopropyl-5-methylcyclohexanol-1; ( $\pm$ )-butanediols-

1,3 – (2S)-butanediol-1,3 and (2R)-butanediol-1,3; ( $\pm$ )-butanediols-2,3 – (2S,3S)-butanediol-2,3 and (2R,3R)-butanediol-2,3 manufactured by *Sigma Aldrich*. Their structural formulas are shown in Fig. 2.

The physicochemical properties of the investigated substances (molar mass  $M_r$ , boiling point  $t_b$ , molecular volume  $V_m$ , polarizability  $\alpha$  and dipole moment  $\mu$ ) are presented in Table 1.

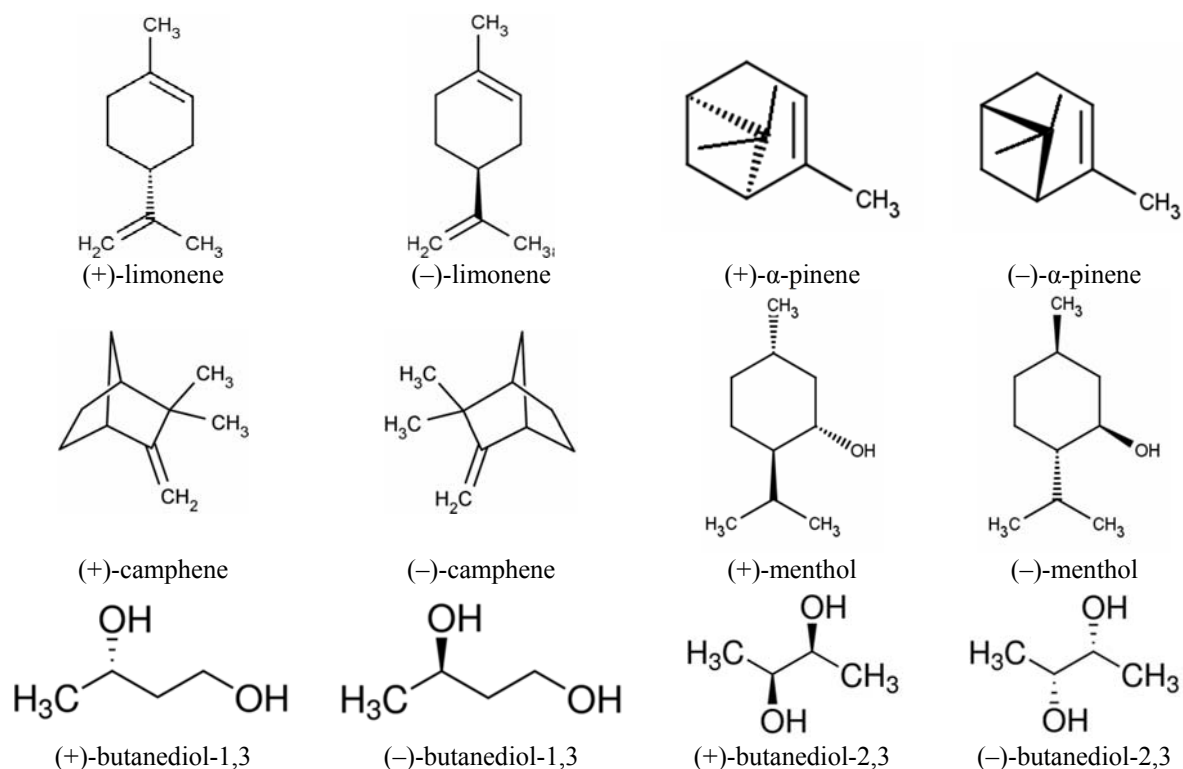


Fig. 2. Structural formulas of the studied optical isomers

Table 1. Physicochemical properties of the studied compounds

N	Adsorbates	Gross formula	$M_r$ , g/mol	$t_b$ , °C [13]	$V_m$ , Å <sup>3</sup>	$\alpha$ , Å <sup>3</sup>	$\mu$ , D [13]
1	<i>o</i> -Xylene	C <sub>8</sub> H <sub>10</sub>	106	145	182	14,1	0,62
2	<i>m</i> -Xylene			139	181		0,37
3	<i>p</i> -Xylene			138	184		0,00
4	( $\pm$ )-Limonenes	C <sub>10</sub> H <sub>16</sub>	136	178	238	18,0	0,63
5	( $\pm$ )- $\alpha$ -Pinenes			156	217	17,4	0,60
6	( $\pm$ )-Camphenes			159	233		0,70 [14]
7	( $\pm$ )-Menthols	C <sub>10</sub> H <sub>20</sub> O	156	212	258	18,9	1,55
8	( $\pm$ )-Butanediols-1,3	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	90	207,5	149	9,4	2,40 [15]
9	( $\pm$ )-Butanediols-2,3			182	123		2,13 [15]

Note: the molecule volumes  $V_m$  were calculated by the Voronoi-Dirichlet polyhedron method using the ToposPro software package [16]; the polarizability values  $\alpha$  were calculated using the SPARTAN-10 software.

The gas chromatography (GC) experiment was carried out in an isothermal regime on a gas chromatograph «Tsvet-100» with a flame ionization detector in the temperature range 90–180 °C. The carrier gas was nitrogen. The input of gaseous samples taken from the vapor phase of the researched compounds was used. Specific retention volumes (cm<sup>3</sup>/m<sup>2</sup>) per unit area of the modified adsorbent were calculated:

$$V_S^T = \frac{(t_R - t_M) \cdot F_{P_a, T_c} \cdot j_3^2}{W_a \cdot S_{sp}} = \frac{(t_R - t_M) \cdot F_{\bar{P}, T_c}}{W_a \cdot S_{sp}}, \quad (1)$$

where  $t_R$ ,  $t_M$  – the retention time of the adsorbate and the non-sorbing substance (methane),  $W_a$  – mass of the modified adsorbent,  $S_{sp}$  – its specific surface area (25 ± 1 m<sup>2</sup>/g),  $F_{P_a, T_c}$  – the volumetric flow rate of the carrier gas at the outlet of the column at the atmospheric pressure  $P_a$  and the column temperature  $T_c$ ,  $j_3^2$  – James-Martin coefficient,  $F_{\bar{P}, T_c}$  – the volumetric flow rate of the carrier gas reduced to the column temperature  $T_c$  and to the averaged (over the column length) pressure  $\bar{P}$  determined in a wide temperature range using the experimental «cold» calibration of the column method [17].

Under the conditions of the equilibrium gas-adsorption chromatography, the Henry constant of adsorption  $K_{1,c}$  is found from the experimentally determined value of the specific retention volume based on the equation:

$$K_{1,c} = \lim_{C_G \rightarrow 0} \left( \frac{\Gamma}{C_G} \right) = V_S^T, \quad (2)$$

where  $\Gamma$  – the Gibbs adsorption,  $C_G$  – the molar concentration of the adsorbate in the gas phase (the subscripts of the Henry constant indicate the initial region (1) of the adsorption isotherm (Henry region) and point that the adsorbate concentration in the gas phase is expressed as molar).

From the linear temperature dependences  $\ln K_{1,c} - 1/T$ , standard changes upon adsorption in the internal energy and entropy were determined [18]:

$$\ln K_{1,c} = -\frac{\Delta \bar{U}_1^0}{RT} + \frac{\Delta \bar{S}_1^0}{R} + 1 \quad (3)$$

$\Delta \bar{U}_1^0$  and  $\Delta \bar{S}_1^0$  show the average values (for the investigated temperature interval) of internal energy and entropy changes in the transition of 1 mol of the adsorbate with a standard concentration in the gas phase of 1 mcmol/cm<sup>3</sup> into an adsorbed state with a standard adsorption value of  $\Gamma = 1$  mcmol/m<sup>2</sup> while  $\Delta \bar{U}_1^0 = -\bar{q}_{\text{dif},1}$  where  $\bar{q}_{\text{dif},1}$  is the differential molar heat of adsorption [19].

Isomer separation factors  $\alpha_{I/II}$  were calculated as their Henry constants' relation:

$$\alpha_{I/II} = \frac{K_{1,c}(I)}{K_{1,c}(II)}, \quad (4)$$

wherein isomer I is eluted from the column after isomer II.

## Results and discussion

The choice of 8OCB and  $\beta$ -CD to obtain the modifying bilayer on the CpY surface is due to their poor mutual solubility. The fact that 8OCB is prone to dimerization not only in the bulk phase but also on the graphite surface [20] is of a great importance for the formation of a bilayer and not just a mixed adsorption layer. Strong dimer adhesion to the flat graphitized CpY surface also hinders the interaction of 8OCB with  $\beta$ -CD in the two-dimensional space of the adsorption layer. The estimated thickness of the bilayer is 13–20 nm depending on the orientation of the  $\beta$ -CD molecules relative to the 8OCB pre-monolayer.

Fig. 3 represents the dependences of the Henry constant of adsorption logarithm ( $\ln K_{1,c}$ ) of *p*-xylene from the reverse temperature obtained using three adsorbents: the original CpY modified by the monolayer (CpY/8OCB) and modified by the bilayer (CpY/8OCB/ $\beta$ -CD).

For the modified as well as for the initial CpY adsorbents linear dependences of  $\ln K_{1,c}$  from  $1/T$  are observed in a wide range of temperatures without jumps at the phase transitions temperatures of the 8OCB liquid crystal. This indicates that for the researched modified adsorbents there is an adsorption rather than a distribution retention mechanism under the GC experiment conditions.

Henry adsorption constants of *p*-xylene decrease when passing from the CpY adsorbent to the CpY/8OCB adsorbent due to the screening of the carbon adsorbent by the mesogen monolayer. At the same time, when applying the 8OCB/ $\beta$ -CD bilayer to the CpY instead of an even greater decrease in  $K_{1,c}$ , an increase of this parameter is observed. Similar patterns are observed for other xylene isomers. An increase in the adsorption constant can take place only if the contribution of the «adsorbate – macrocycle» complexation in the adsorption layer exceeds the contribution from the decrease in the adsorption potential of the carbon adsorbent-carrier by screening its surface with a bilayer.

Table 2 presents the thermodynamic adsorption characteristics of the investigated isomers on the CpY/8OCB/ $\beta$ -CD adsorbent.

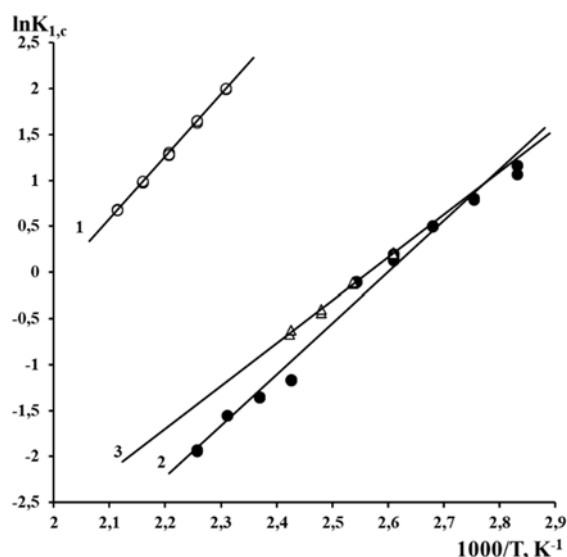


Fig. 3. Temperature dependencies of *p*-xylene:

1 – CpY adsorbent, 2 – CpY modified by 8OCB monolayer, 3 – CpY modified by the 8OCB/  $\beta$ -CD bilayer

The  $K_{1,c}$  increase in the row *m*-xylene ( $\mu = 0.37$  D)  $\rightarrow$  *p*-xylene ( $\mu = 0$  D)  $\rightarrow$  *o*-xylene ( $\mu = 0.62$  D) indicates a small contribution of orientational interactions of *m*- and *o*-xylene molecules with hydroxyl groups of  $\beta$ -CD molecules in the surface layer of the adsorbent. Apparently, for xylenes, the ability to interact with the cavity of the macrocycle is more important, which is more pronounced in *p*-xylene than in *m*- and *o*-xylenes. This is confirmed by the fact that the heat of adsorption

$|\Delta\bar{U}_1^0|$  for *p*-xylene is higher than for *m*- and *o*-xylenes (Table 2). The greater retention of *o*-xylene comparing to other isometric xylenes is due to the entropic contribution (weak localization of molecules in the  $\beta$ -CD cavity) instead of the complexation energy contribution. This is confirmed by a smaller drop in entropy upon its adsorption from the gas phase ( $\Delta\bar{S}_{1,c}^0 = -105,3$  J/mol·K) comparing with *m*- and *o*-xylenes.

Table 2. Henry constants of adsorption, internal energy and entropy changes upon adsorption of compounds on the CpY/8OCB/ $\beta$ -CD adsorbent from the gas phase

№	Adsorbate	$K_{1,c}$ (130 °C) cm <sup>3</sup> /m <sup>2</sup>	$-\Delta\bar{U}_1^0$ , kJ/mol	$-\Delta\bar{S}_{1,c}^0$ , J/mol K
1	<i>o</i> -Xylene	0,74	38,1±1,6	105,3±4,1
2	<i>m</i> -Xylene	0,62	38,0±1,9	106,5±4,7
3	<i>p</i> -Xylene	0,67	39,3±1,8	109,2±4,5
4	(+)-Limonene	2,03	45,4±1,4	115,0±3,4
5	(-)-Limonene	2,05	45,4±1,3	114,9±3,1
6	(+)- $\alpha$ -Pinene	0,78	41,6±1,3	113,7±3,3
7	(-)- $\alpha$ -Pinene	0,79	40,5±1,1	110,8±2,8
8	(+)-Camphene	0,81	41,0±3,1	111,7±8,0
9	(-)-Camphene	0,86	39,5±0,6	107,6±1,6
10	(+)-Menthol	8,53	54,6±1,7	126,0±3,8
11	(-)-Menthol	8,70	54,9±1,7	126,6±3,9
12	(+)-Butanediol-1,3	7,25	70,7±3,3	167,2±7,4
13	(-)-Butanediol-1,3	6,86	69,1±3,5	163,8±7,8
14	(+)-Butanediol-2,3	2,62	66,7±1,7	165,7±6,2
15	(-)-Butanediol-2,3	2,74	64,6±1,6	160,3±3,8

The structural selectivity of the CpY/8OCB/ $\beta$ -CD adsorbent in the investigated temperature range 90–160 °C is high ( $\alpha_{p/m} = 1,13$ , 90 °C,  $\alpha_{o/p} = 1,17$ , 160 °C) and exceeds the selectivity of both the initial CpY ( $\alpha_{p/m} = 1,10$ , 160 °C) adsorbent-carrier as well as the selectivity of the 8OCB in the gas-liquid chromatography ( $\alpha_{p/m} = 1,06$ ;  $S_A$ , 64 °C) (Fig. 4).

$\alpha_{p/m}$  decreases and  $\alpha_{o/p}$  increases with the temperature growth.

However, the study of the enantioselectivity of an adsorbent containing a monolayer of densely packed  $\beta$ -CD molecules at the boundary with the gas phase is of the most interest.

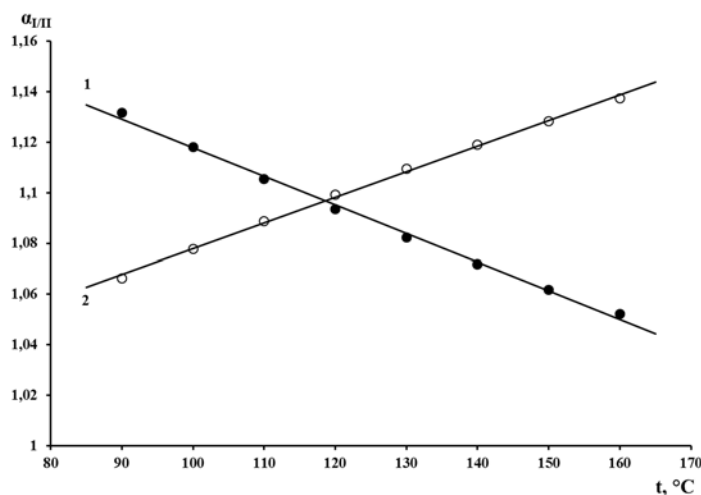


Fig. 4. Xylene isomer separation factor dependence on temperature on a column with the CpY adsorbent modified by the 8OCB/ $\beta$ -CD bilayer: 1 –  $\alpha_{p/m}$ ; 2 –  $\alpha_{o/p}$

A macrocyclic  $\beta$ -CD molecule consists of 7 residues of D-(+)-glucopyranose connected by 1,4-glycosidic bonds, has a truncated cone shape, and contains 21 hydroxyl groups at the entrance to the cavity on both sides. The volume of the  $\beta$ -CD cavity, calculated by the Voronoi-Dirichlet molecular polyhedral method [21] was 496 Å<sup>3</sup>. The volumes of the molecules of the investigated optical isomers (Table 1) are smaller than the volumes of the cavity of the  $\beta$ -CD molecule and in theory all of them can form «host – guest» inclusion complexes with isolated  $\beta$ -CD molecules in the gas phase.

In a dense  $\beta$ -CD monolayer deposited on a flat 8OCB pre-monolayer free entry of guest molecules into the cavity of the macrocycle apparently is difficult due to the self-organization of the  $\beta$ -CD molecules. For example, it has been shown experimentally [22] that the  $\beta$ -CD molecules in a monolayer on the surface of pyrolytic graphite are dimerized and oriented «sideways» to the carbon surface. There is a reason to believe that the 8OCB pre-monolayer reduces the CpY hydrophobicity and changes the structural organization of the  $\beta$ -CD monolayer. This leads to a change in the orientation of the macrocycle molecules from the

horizontal («sideways») to the inclined and to an increase in the probability of inclusive complexation with adsorbate molecules and their interaction with hydroxyl groups at the cavity entrance.

Adsorption from the gas phase of six pairs of optical isomers belonging to monocyclic and bicyclic monoterpenes as well as isomeric butanediols was studied.

On the column with the CpY/8 OCB/ $\beta$ -CD adsorbent, Henry's adsorption constants  $K_{1,c}$  increase in the  $\alpha$ -pinene  $\rightarrow$  camphenes  $\rightarrow$  limonenes  $\rightarrow$  butanediols-2,3  $\rightarrow$  butanediols-1,3  $\rightarrow$  menthols series (Table 2). This indicates a certain contribution of orientational and/or specific interactions with hydroxyl groups of  $\beta$ -CD molecules to the interaction energy with the modified adsorbent. Thus, for example, the  $K_{1,c}$  constants for the optical isomers of butanediol-1,3 are almost three times higher than the analogous values for butanediol-2,3 isomers meaning the investigated adsorbent has a very high selectivity to the isomers of the functional group position. This is apparently due to the fact that in the case of butanediol-1,3 both hydroxyl groups can interact with the surface of the modified adsorbent, whereas in the case of the butanediol-2,3

there is only one which is confirmed by the difference in the  $|\Delta\bar{U}_1^0|$  values (Table 2).

In general, an increase in the  $K_{1,c}$  adsorption constants corresponds to an increase in the boiling temperature points ( $t_b$ ) of the compounds and is less correlated with the polarizability ( $\alpha$ ), the volume ( $V_m$ ) and the dipole moment ( $\mu$ ) of the molecules (Table 1). It is important to note that for all the investigated optical isomers (except menthols) the change in the internal energy  $|\Delta\bar{U}_1^0|$  (adsorption heat) for the (+)-isomer is higher than for the (-)-isomer. A similar regularity is observed in the gas-liquid version with cyclodextrin-

containing stationary phases [23, 24]. The stronger interaction of (+)-isomers with the cavity of the  $\beta$ -CD molecule is possibly due to the fact that it is formed by a closed oligomeric D-(+)-glucopyranose chain.

Unlike the previously studied carbon adsorbent with a mixed layer of the «HEOCAB +  $\beta$ -CD» modifier, the investigated adsorbent with the modifying 8OCB/ $\beta$ -CD bilayer selectively adsorbs both: the enantiomers of low polar (camphene) and polar compounds (butanediols-2,3) (Fig. 5).

Table 3 represents experimental values of the separation factors of  $\alpha_{I/II}$  optical isomers on the researched adsorbent.

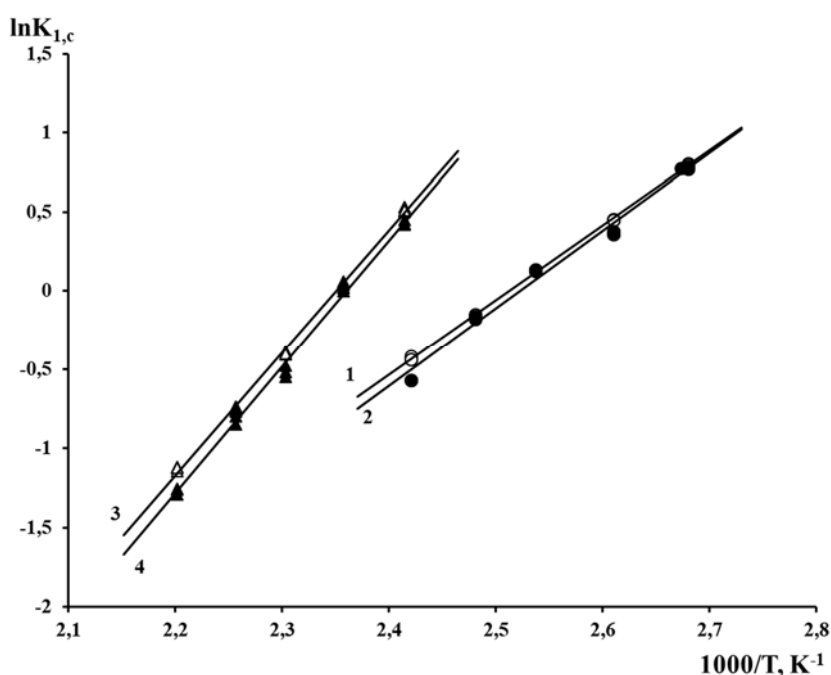


Fig. 5. Temperature dependences of Henry adsorption constant on CpY/8OCB/ $\beta$ -CD adsorbent: 1 – (-)-camphene, 2 – (+)-camphene, 3 – (-)-butanediol-2,3, 4 – (+)-butanediol-2,3

Table 3. Experimental values of the isomer separation factors, linear dependence coefficients of the logarithm of the separation factor  $\ln\alpha_{I/II}$  from  $1/T$  (equation 5), compensation temperature  $T_{com}$

Adsorbates	$\alpha_{I/II}$	$\Delta(\Delta\bar{U}_1^0)_{I/II}$ , kJ/mol	$\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$T_{com}$ , K
<i>p/m</i> -Xylenes	$\alpha_{n/m} = 1,13-1,05$ (90–160 °C)	-1,3	-2,7	488
<i>o/p</i> -Xylenes	$\alpha_{o/n} = 1,14-1,07$ (160–90 °C)	1,2	3,9	313
(±)-Limonenes	$\alpha_{-/+} = 1,01-1,008$ (180–130 °C)	0	0,1	180
(±)- $\alpha$ -Pinenes	$\alpha_{-/+} = 1,04-1,01$ (160–120 °C)	1,1	2,9	382
(±)-Camphenes	$\alpha_{-/+} = 1,09-1,01$ (160–90 °C)	1,5	4,1	358
(±)-Menthols	$\alpha_{-/+} = 1,02-1,01$ (120–180 °C)	-0,3	-0,6	514
(±)-Butanediols-1,3	$\alpha_{+/-} = 1,07-1,002$ (120–180 °C)	-1,6	-3,4	457
(±)-Butanediols-2,3	$\alpha_{-/+} = 1,12-1,03$ (180–120 °C)	2,1	5,4	376

Values of  $\alpha_{I/II}$  vary from 1,01 (limonenes) to 1,12 (butanediols-2,3), which is comparable or even higher than for commercial capillary columns with cyclodextrin-containing stationary phases [25]. However, unlike to these stationary phases, the (-)-isomers have a higher adsorption on the CpY/8OCB/ $\beta$ -CD than the (+)-isomers (with the exception of butanediol-1,3). From table 2 data it can be seen that the higher adsorption of (-)-isomers in comparison to the (+)-isomers is owed not to the energy but to the entropy factor. Indeed, the (-)-isomers interact less strongly with the semipolar plane than the (+)-isomers ( $|\Delta\bar{U}_1^0|_{(-)} < |\Delta\bar{U}_1^0|_{(+)}$ ). Consequently, the higher values of  $K_{1,c}$  for (-)-isomers are associated with a lower entropy drop during the adsorption from the gas phase ( $|\Delta\bar{S}_{1,c}^0|_{(-)} < |\Delta\bar{S}_{1,c}^0|_{(+)}$ ). Despite the fact that the last inequality for the entropy holds true for butanediols-1,3, the increased (by 1.6 kJ/mol) value of the change in the internal energy for the (+)-isomer of this diol provides its greater retention in comparison with the (-)-isomer.

Let's review the temperature dependence of the enantioselectivity of the researched adsorbent with the bilayer. It has been established that in the case of gas-adsorption chromatography on an adsorbent with a bilayer, the enantioselectivity of  $\alpha_{I/II}$  increases with the temperature growth (except for menthols and butanediols-1,3).

The temperature dependence of the enantiomer separation factor using the equation (3) is described by the following equation:

$$\ln\alpha_{I/II} = -\frac{\Delta(\Delta\bar{U}_1^0)_{I/II}}{RT} + \frac{\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}}{R}, \quad (5)$$

where  $\Delta(\Delta\bar{U}_1^0)_{I/II} = \Delta\bar{U}_1^0(I) - \Delta\bar{U}_1^0(II)$  and  $\Delta(\Delta\bar{S}_{1,c}^0)_{I/II} = \Delta\bar{S}_{1,c}^0(I) - \Delta\bar{S}_{1,c}^0(II)$  represent the differences in the changes of the internal energy and the entropy of adsorption of the optical isomers I and II (isomer I is eluted from the separation column after isomer II).

The  $\ln\alpha_{I/II}$  dependences on  $1/T$  for the investigated isomer pairs are shown in Fig. 6 (camphenes,  $\alpha$ -pinenes, limonenes,) and Fig. 7 (butanediols-2,3, butanediols-1,3, menthols).

$\Delta(\Delta\bar{U}_1^0)_{I/II}$  and  $\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}$  values calculated based on the equation (5) are presented in Table 3. Obtained  $\Delta(\Delta\bar{U}_1^0)_{I/II}$  and  $\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}$  small values do not contradict the literature data for cyclodextrin-containing stationary phases [26].

From the data presented in Table 3, it can be seen that for those pairs of optical isomers for which  $\Delta(\Delta\bar{U}_1^0)_{I/II}$  and  $\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}$  values are positive, the enantioselectivity  $\alpha_{I/II} = \alpha_{-/+}$  increases with the rising temperature ( $\alpha$ -pinenes, camphenes, butanediols-2,3). Conversely, if  $\Delta(\Delta\bar{U}_1^0)_{I/II}$  and  $\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}$  are negative, then there is a decrease in  $\alpha_{I/II}$  with the rising temperature (menthols, butanediols-1,3). For limonenes these differences are close to zero and for this pair of enantiomers the enantioselectivity is practically absent in the investigated temperature range.

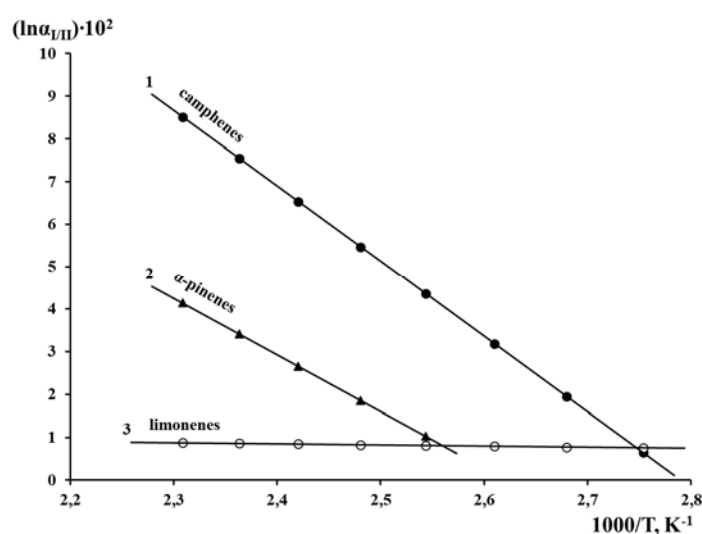


Fig. 6. Dependence of the separation factor logarithm of the optical isomers of monoterpene hydrocarbons on the reverse temperature in a column with the CpY/8OCB/ $\beta$ -CD adsorbent: 1 – camphenes, 2 –  $\alpha$ -pinenes, 3 – limonenes ( $\alpha_{I/II} = \alpha_{-/+}$ )



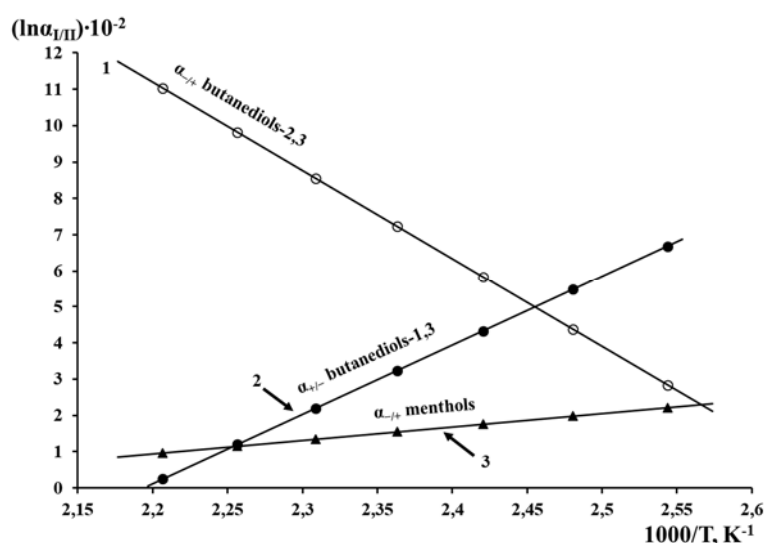


Fig. 7. Dependence of the separation factors logarithm of the optical isomers of alcohols on the reverse temperature in a column with the CpY/8OCB/β-CD adsorbent: 1 – butanediols-2,3 ( $\alpha_{-/+}$ ), 2 – butanediols-1,3 ( $\alpha_{+/-}$ ), 3 – menthols ( $\alpha_{-/+}$ )

The enthalpy-entropy compensation temperature  $T_{\text{com}}$  at which the order of the enantiomeric yield can change can be calculated from the equation (5) with  $\alpha_{I/II} = 1$ :

$$\frac{\Delta(\Delta\bar{U}_1^0)_{I/II}}{RT} = \frac{\Delta(\Delta\bar{S}_{1,c}^0)_{I/II}}{R} \quad (6)$$

Compensation temperatures are presented in Table 3. It is clear that  $T_{\text{com}}$  is higher for those isomer pairs whose selectivity decreases with the temperature rise.

### Conclusion

The premonolayer of the mesogenic 8OCB deposited on the carbon adsorbent CpY provides a «favorable» for the interaction with the adsorbates orientation of macrocyclic β-CD molecules at the gas-phase border. Under the 8OCB/β-CD bilayer forming conditions, rather than the mixed adsorption layer, the modified carbon adsorbent provides high structural selectivity and enantioselectivity to both polar and low polar optical isomers over a wide temperature range (90–180 °C).

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