Жидкие кристаллы и их практическое использование. 2021. Т. 21, № 4. С. 89–93
Liquid Crystals and their Application. 2021. Vol. 21, № 4. P. 89–93
ISSN 1991–3966 (print), 2499–9644 (online)

Short communication
DOI: 10.18083/LCAppl.2021.4.89

SUPRAMOLECULAR PLANAR LIQUID CRYSTAL SYSTEMS ON CARBON SURFACE AS UNIVERSAL ISOMER-SELECTIVE ADSORBENTS

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Abstract. *The features of the monolayer structure of supramolecular liquid crystals (LC) and «supramolecular LC − β-cyclodextrin» bilayers placed on a flat carbon surface are presented. The application possibility of these materials in gas-adsorption chromatography is discussed. It is shown that self-organizing ordered planar structures of these modifiers on the adsorbent-carrier carbon surface provide high meta-/para- and ortho-/para-selectivity as well as enantioselectivity to non-polar and polar optical isomers.*

Key words: *supramolecular liquid crystals, carbon substrate surface, monolayers, β-cyclodextrin, bilayers, gas-adsorption chromatography, selectivity*

For citation: Bykov E.S., Kopytin K.A., Onuchak L.A. Supramolecular planar liquid crystal systems on carbon surface as universal isomer-selective adsorbents. *Liq. Cryst. and their Appl.*, 2021, **21** (4), 89–93. **DOI**: 10.18083/LCAppl.2021.4.89.

Краткое сообщение
УДК 544.723.23

СУПРАМОЛЕКУЛЯРНЫЕ ПЛАНАРНЫЕ ЖИДКОКРИСТАЛЛИЧЕСКИЕ СИСТЕМЫ НА УГЛЕРОДНОЙ ПОВЕРХНОСТИ КАК УНИВЕРСАЛЬНЫЕ ИЗОМЕРСЕЛЕКТИВНЫЕ АДСОРБЕНТЫ

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Аннотация. *Обсуждаются особенности строения монослоев супрамолекулярных жидких кристаллов (ЖК) и бислоев «супрамолекулярный ЖК − β-циклодекстрин» на плоской углеродной поверхности и возможности их применения в газо-адсорбционной хроматографии. Показано, что самоорганизующиеся упорядоченные планарные структуры этих модификаторов на углеродной поверхности адсорбента-носителя обеспечивают высокую мета-/пара- и орто-/пара-селективность, а также энантиоселективность как к неполярным, так и полярным оптическим изомерам.*

Ключевые слова: *супрамолекулярные жидкие кристаллы, углеродная подложка, монослои, β-циклодекстрин, бислои, газо-адсорбционная хроматография, селективность*

Для цитирования: Bykov E.S., Kopytin K.A., Onuchak L.A. Supramolecular planar liquid crystal systems on carbon surface as universal isomer-selective adsorbents. *Liq. Cryst. and their Appl.*, 2021, **21** (4), 89–93. **DOI**: 10.18083/LCAppl.2021.4.89.

Introduction

Advances in the use of liquid crystal (LC) sorbents are associated with the highly selective separation of structural isomers in the form of distribution gas-liquid chromatography (GLC) [1, 2]. The use of supramolecular LC capable of forming chain associates or dimers due to the specific interaction of proton and electron donor substituents [3−5] made it possible to increase structural selectivity significantly [6−9] in comparison with traditional sorbents. In addition to individual supramolecular LC, their mixtures with chiral macrocyclic compounds (cyclodextrins and their derivatives) have recently attracted interest as sorbents for GLC. Due to the complexation of organic molecules with a chiral macrocycle, the resulted composite sorbents are capable of selective sorbing both structural and optical isomers using GLC [10−12]. The determining factor for the demonstration of enantioselectivity is the absence of the «LC − macrocycle» complexation. Interest in gas-adsorption chromatography (GAC) with mono- and bilayers of supramolecular LC and macrocycles has increased recently. This happened because the absence of bulk LC phase in GAC reduces the binding possibilities of mesogen and macrocycle molecules and makes it possible to expand the temperature range of adsorbent application for separation of isomers mixtures differed markedly in boiling points. Methods for obtaining ordered surface structures by controlled self-assembly of molecules have acquired practical importance due to the possibility of formation of stable supramolecular complexes on a solid surface [13−16].

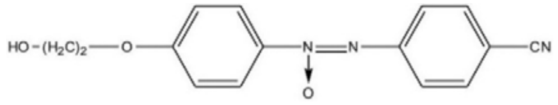
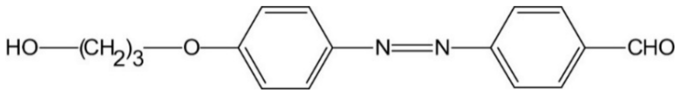
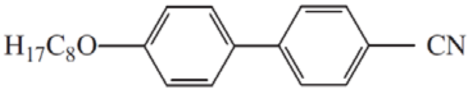
Monolayers of supramolecular LC on carbon surface

Monolayers of supramolecular LC of 4-(2-hydroxyethyloxy)-4'-cyanoazoxybenzene (HEOCAB), 4-(3-hydroxypropyloxy)-4'-formylazobenzene (HPOFAB) and 4,4'-octyloxycyanobiphenyl (8OCB) (*Sigma-Aldrich Inc.*) (Table 1) were applied from chloroform solutions on a carbon adsorbent-carrier Carbopack Y (*CpY, Supelco Inc.*) with a flat graphite-like surface. The amount of LC modifier was calculated based on the specific surface area of CpY and the value of a landing area s_1 of LC molecule, which is a projected molecule area providing the maximum coverage of flat substrate surface.

The adsorption properties of adsorbents modified with monolayers of HEOCAB, HPOFAB [17] and 8OCB were studied by gas chromatography in the temperature range 80 ÷ 180 °C. About 30 volatile and medium-volatile organic compounds of different classes with boiling points of 66 ÷ 216 °C were used as test adsorbates.

Based on a comparative analysis of the thermodynamic characteristics of adsorption (Henry's constant $K_{1,c}$, changes in internal energy $\Delta\overline{U}_1^0$ and entropy $\Delta\overline{S}_{1,c}^0$) for adsorbates with different molecular sizes and shapes, an assumption was made about the structural organization of planar LC monolayers on a carbon surface. Thus, a monolayer of the most polar nematic HEOCAB (μ = 8,69 D) forms an ordered planar structure of polymolecular associates with low defectiveness (voids) and a high ability to carry out specific interactions with adsorbate molecules.

Table 1. **Structural formulas and molecular parameters of LCs**

Structural formulas and phase transition temperatures, °*C*	Name of LC	μ, D	*l*/*d*	s_1, Å^2
 Cr 113 (Cr+N) 135 N 175 Iso	HEOCAB	8,69	3,5	96
 Cr 98 SmA 135 N 141 Iso	HPOFAB	5,82	3,6	90
 Cr 54 SmA 67 N 78 Iso	8OCB	6,85	4,4	107

μ – dipole moment, D; *l* – length of LC molecule, Å; *d* – diameter of LC molecule, Å; s_1 – landing area of LC molecule, Å^2

Smectic–nematic HPOFAB (μ = 5,82 D) forms supermolecules (associates) in a monolayer due to hydrogen bonds with defects (gaps between mesogen molecules) in size corresponding to *n*-octane molecules. Smectic-nematic 8OCB (μ = 6,85 D) forms the densest two-dimensional layer on the flat carbon surface. The layer is formed by the dimers of this mesogen molecules. There are practically no structural defects in the layer, which has been also confirmed by direct experimental data [18]. The studies of structural adsorption selectivity with respect to *para-* and *meta-*xylene isomers showed that these values are the higher, the lower the LC polarity. The selectivity increases according the following modifiers sequence: HEOCAB → 8OCB → HPOFAB. The range of values $\alpha_{p/\mathrm{m}}$ = 1,06 ÷ 1,09 exceeds even the *para-/meta-*selectivity of the unmodified CpY and graphitized carbon black ($\alpha_{p/m}$ = 1,05) confirming the associated structure of planar monolayers of the studied LCs. In comparison with the pure carbon adsorbent, the modified adsorbents also showed *ortho-/para-*selectivity ($\alpha_{o/p}$ = 1,06 ÷ 1,16).

All studied CpY/LC adsorbents with monolayers were used for the subsequent formation of «supramolecular LC − β-cyclodextrin (β-CD)» bilayers on the CpY surface.

«Supramolecular LC − β-cyclodextrin» bilayers on carbon surface

The layer-by-layer method (LbL) was used to obtain carbon adsorbents modified with the «supramolecular LC − β-CD» bilayers. β-CD is a macrocyclic oligomer consisting of 7 D-glucose residues with an average cavity diameter of 6,8 Å, containing 21 hydroxyl groups on both sides at the entrance to the cavity. The initial CpY adsorbent-carrier was successively modified with a monolayer of supramolecular LC from a chloroform solution, and then with β-CD from an aqueous-ammonia solution. It has been established that modification of CpY with polar HEOCAB and β-CD leads to formation of mixed adsorption layer due to the solvation of components, which prevents the formation of «host − guest» inclusion complexes during adsorption from gas phase [19]. For two other adsorbents (CpY/HPOFAB/β-CD and CpY/8OCB/β-CD [20]), the layer-by-layer assembly was used to obtain bilayer structures with alternating LC and macrocycle monolayers on CpY surfaces with an approximate calculated bilayer thickness of 13−20 Å, depending on the orientation of β-CD molecules relatively to the planar premonolayer of the LC orientant.

Isomers of *p-* and *m-*xylene, optical isomers of terpene hydrocarbons $C_{10}H_{16}$ (limonenes, camphenes), terpenoids (menthols, borneols), as well as butanediols-1,3 and butanediols-2,3 were used as model adsorbates.

Separation factors for isomers $\alpha_{\mathrm{I/II}}$ were calculated as the ratio of their Henry's adsorption constants $K_{1,c}$, which are equal to the ratio of the reduced retention times of adsorbates t_R':

$$\alpha_{\mathrm{I/II}} = \frac{K_{1,c\,(\mathrm{I})}}{K_{1,c\,(\mathrm{II})}} = \frac{t'_{R\,(\mathrm{I})}}{t'_{R\,(\mathrm{II})}}, \qquad (1)$$

and isomer I elutes from the column after isomer II.

Analysis of the separation factors $\alpha_{\mathrm{I/II}}$ makes it possible to characterize the structural organization of bilayer adsorbents obtained by the LbL method (Table 2). The increased values of $\alpha_{\mathrm{I/II}}$ indicate the availability of a cavity or free hydroxyl groups of macrocyclic β-CD for outer-sphere or inner-sphere complexation, respectively, with adsorbate molecules. All studied CpY/LC/β-CD adsorbents have structural *para-/meta-*selectivity to test xylene isomers, and for the bilayer modifiers based on HEOCAB and HPOFAB, the selectivity is lower ($\alpha_{p/m}$ = 1,06; 90 ºC) that based on 8OCB ($\alpha_{\mathrm{p/m}}$ = 1,13; 90 °C).

Table 2. **Separation factors $\alpha_{\mathrm{I/II}}$ of isomers for adsorbents with the "supramolecular LC - β-cyclodextrin" bilayers**

Adsorbates	$\alpha_{\mathrm{I/II}}$		
	CpY/HEOCAB/β-CD	CpY/HPOFAB/β-CD	CpY/8OCB/β-CD
p/*m*-Xylenes	$\alpha_{p/m}$ = 1,06; 90 °C	$\alpha_{p/m}$ = 1,06; 90 °C	$\alpha_{p/m}$ = 1,13; 90 °C
(±)-Camphenes	$\alpha_{\mathrm{I/II}} \approx 1$; 100–150 °C	$\alpha_{+/-}$ = 1,07; 120–150 °C	$\alpha_{-/+}$ = 1,09; 160 °C
(±)-Limonenes	$\alpha_{+/-}$ = 1,04; 110 °C	$\alpha_{-/+}$ = 1,05; 100 °C	$\alpha_{-/+}$ = 1,01; 180 °C
(±)-Menthols	$\alpha_{-/+}$ = 1,10; 100 °C	$\alpha_{-/+}$ = 1,01; 100 °C	$\alpha_{-/+}$ = 1,03; 100 °C
(±)-Borneoles	−	$\alpha_{+/-}$ = 1,04; 150 °C	−
(±)-Butanediols-1,3	$\alpha_{-/+}$ = 1,15; 100 °C	−	$\alpha_{+/-}$ = 1,10; 100 °C
(±)-Butanediols-2,3	$\alpha_{+/-}$ = 1,25; 150 °C	−	$\alpha_{-/+}$ = 1,12; 180 °C

Under the conditions of macrocyclic cavity blocking, the adsorbent with a mixed binary layer CpY/HEOCAB/β-CD did not show enantioselectivity towards camphene isomers and exhibited low selectivity towards limonene enantiomers. However, for the polar enantiomers of menthols, butanediols-1,3 and butanediols-1,2, very high values $\alpha_{I/II}$ were obtained for gas-adsorption chromatography, which indicate a high contribution of the outer-sphere complexation of adsorbate molecules with the preorganized structure formed by hydroxyl groups at the entrance to the β-CD cavity.

In work [21], using quantum chemical and crystal chemical methods, it was shown that on a «pure» graphene-like carbon surface, β-CD molecules are predominantly oriented «sideways» and associated, which prevents complexation with molecules of organic compounds. Moderate enantioselectivity values for the CpY/HPOFAB/β-CD adsorbent with alternating LC and macrocycle monolayers both with respect to terpene hydrocarbons (camphenes and limonene) and polar terpenoids (menthol and borneols) indicate a change in the macrocycle orientation. The polar premonolayer of HPOFAB, which forms an associated structure on the CpY surface, oriented the β-CD layer in a way, so its orientation relatively to the carbon surface became oblique. The inner-sphere complexes with β-CD are formed only by enantiomeric limonenes, which molecules have more elongated molecular shape, and by bicyclic borneols, which are capable of outer-sphere interactions with the pre-organized structure of β-CD. Weak enantioselectivity for menthol is due to sterically hindered interactions with peripheral groups of β-CD molecules.

A dense monolayer formed by the mesogen dimers of 8OCB significantly changes the orientation of the axes of β-CD molecules from horizontal on the CpY surface to almost vertical in the bilayer. This is reflected in the enhancement of not only the outer-sphere, but also the «adsorbate − macrocycle» inner-sphere interactions and provides enantioselectivity to enantiomers of non-polar camphenes with a framework form of molecules, and polar butanediols-1,3 and butanediols-2,3.

Therefore, for the three CpY/LC/β-CD bilayer adsorbents obtained by the LbL technology studied in this work, the isomer-selective properties are compared. It was found that the selectivity with respect to structural and optical isomers of different polarity increases in the series of binary modifiers: HEOCAB/β-CD → HPOFAB/β-CD → 8OCB/β-CD, which is associated with an increase in the possibility of inclusive and outer-sphere complexation of these isomers in bilayer on carbon surface.

Acknowledgments: *This work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the state assignment (Grant No. FSSS-2020-0016).*

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Contribution of the authors: *the authors contributed equally to this article.*

The authors declare no conflicts of interests.

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Поступила 26.10.2021, одобрена 10.11.2021, принята 15.11.2021
Received 26.10.2021, approved 10.11.2021, accepted 15.11.2021