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EFFECT OF SURFACE PHENOMENA ON SELECTIVE SEPARATION PROPERTIES OF LIQUID CRYSTAL STATIONARY PHASE

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The present work deals with the study on the distribution of contribution of adsorption and dissolution to retention volume of individual components in gas-liquid chromatography as dependent on the amount of liquid crystal stationary phase deposited on solid support and on the chromatographic column temperature.

INTRODUCTION

Liquid crystalline compounds have been known for nearly 120 years but the beginning of their use in gas chromatography can be attributed to 60–70-s of the last century [1, 2]. These compounds are distinguished by their properties. Due to melting of solid crystals, the liquid is formed in which molecules are located not only in parallel to each other but in the layers (smectic phase) and under further heating another liquid form is created in which molecules are arranged in parallel while layers are not formed (nematic phase). Further increase in temperature leads to a definite point of orientation loss and the liquid becomes isotropic [3]. Most frequently such mesophases are observed in aromatic compounds containing benzene and naphthalene rings. Namely the presence of these phases makes the especially selective with respect to linear molecules. Quantitative factor of the separation ability of these stationary phases is the maximum structural selectivity (MS) which is defined as the ratio of the volume retention of *para*- and *meta*-xylene. As a rule, the maximum structural selectivity appears at the temperatures close to the lower limit of presence of the nematic mesophase [4]. Smectic and nematic mesophases are used primarily for separation of isomeric alkyl and halogen substituted benzene derivatives, phenols, polycyclic aromatic compounds [1–3]. When transiting from liquid crystals to the isotropic liquid state, they lose their selectivity with respect to linear molecules and the sequence of elution of individual components in most cases is defined by their boiling points. The efficiency of stationary liquid phases in gas chromatography depends greatly on their

proper application on the surface of solid media, i.e. in the creation of a uniform liquid layer in the separation column which would screen negative impact of active adsorption centers of a nozzle as completely as possible. At the same time, it should be noted that in some cases the contribution of adsorption of the tested substance on the surface of stationary liquid-solid support is most significant for some systems ranging from several percent to tens percents of total retention [5]. Contribution of adsorption process to chromatography is significant even at high impregnation of solid carriers by stationary liquid [6]. All this as a whole lowers selectively-isolation effect of stationary fluid, worsening the maintenance and resolution ability of the chromatographic column.

EXPERIMENTAL

The present study aimed to determine the nature of distribution of contribution of adsorption and dissolution to retention volumes of definite components in gas-liquid chromatography depending on the amount of applied liquid crystal stationary liquid on solid support and the temperature of the chromatographic column. The object of the study was a liquid crystal, stationary liquid hydroquinone-bis-(*p*-heptyloxybenzoate) characterized by nematic mesophase within 120–195°C, with the polarity of 37% [4], dissolved in isopropylbenzene [7] which was applied respectively in the amounts 5, 8, 10, 15% on the Chromaton N-AW solid support of 0.250–0.315 mm graining. Application of stationary liquid on the solid support was carried out according to the technique most widely used in the practice of gas chromatography [8].

As test compounds, we used triads of isomers: *ortho*-, *meta*-, *para*-xylene and *ortho*-, *meta*-, *para*-cresol. Contributions of adsorption and dissolution to the retention volumes of some sorbates in the process of chromatography were determined at the column temperature of 100°C (when stationary phase is a solid crystal) and 160°C (when stationary liquid is characterized by the presence of mesophase).

Experiment was conducted on a Chrom-5 chromatograph. Length of the column – 3 m, diameter – 3 mm. Detector FID, carrier gas – helium, flow rate of carrier gas – 30 ml/min. Contributions of dissolution and adsorption at the interface between stationary liquid-solid support to the retention of the above organic compounds were determined by the formula [6]

$$V_g^T = \Gamma / \rho + \Gamma \Gamma_3 S_3 / 100 \Pi$$

where V_g^T – specific retention volume (cm³); g – mass of the liquid phase (g); Γ – Henry coefficient; ρ – density of the stationary liquid (g/cm³); Γ_3 – adsorption coefficient at the interface between a stationary phase-solid support (cm); S_3 – the value of the surface of solid medium (cm²/g); Π – degree of saturation (rate of impregnation, %) of solid carrier by stationary liquid.

The first part of the equation describes the contribution of dissolution (R), and the second is the contribution of adsorption (A) to the retention of the studied organic compounds. Graphics associating values V_g^T and $100/P$ were used for determination of the Γ/ρ value.

RESULTS AND DISCUSSION

The information on the distribution of contribution of dissolution and adsorption at the elution of the above mentioned organic compounds from the chromatographic column are summarized in Tables 1 and 2.

The data presented in Table 1, where the chromatography is carried out at the column temperature of 100°C prove that the share of adsorption interaction in the process of retention of investigated compounds is high and that at the increase of degree of impregnation of the solid support of the stationary liquid, this factor increases. This fact cannot be explained to the end currently, although it can be assumed that at the column temperature of 100°C liquid phase is crystallized in the form of individual solid units concentrating in the form of separate "islands" in the accessible pores or on the active centers of the solid support

Table 1. Distribution of contributions of adsorption (A) and dissolution (D) in % LC deposited on solid support Chromaton N-AW. ($t_{col.}=100^\circ\text{C}$)

Sor-bate	Rate of impregnation, %							
	5		8		10		15	
	D	A	D	A	D	A	D	A
<i>o</i> -xylene	54.5	45.5	42.4	57.6	22.5	77.5	19.6	80.4
<i>m</i> -xylene	53.5	47.5	41.9	58.1	21.0	79.0	16.4	83.6
<i>p</i> -xylene	52.3	47.7	39.7	60.3	21.1	78.9	16.8	83.2
<i>o</i> -cresol	55.1	44.9	30.3	69.7	22.5	77.5	22.1	77.9
<i>m</i> -cresol	55.4	44.6	31.3	68.7	22.6	77.4	22.4	77.6
<i>p</i> -cresol	54.9	45.1	29.8	70.2	21.7	78.3	20.9	79.1

Table 2. Distribution of contributions of adsorption (A) and dissolution (D) in % LC deposited on solid support Chromaton N-AW ($T_{col.} = 160^\circ\text{C}$)

Sor-bate	Rate of impregnation, %							
	5		8		10		15	
	D	A	D	A	D	A	D	A
<i>p</i> -xylene	30.1	69.9	42.3	57.7	47.3	52.7	47.8	52.2
<i>m</i> -xylene	32.4	67.6	45.3	54.7	51.3	48.7	52.6	47.4
<i>o</i> -xylene	34.1	65.9	48.9	51.1	53.8	46.2	54.7	45.3
<i>o</i> -cresol	40.3	59.7	52.2	47.8	58.4	41.6	60.1	39.9
<i>m</i> -cresol	43.7	56.3	55.7	44.3	60.7	39.3	62.2	37.8
<i>p</i> -cresol	44.9	55.1	57.3	42.7	62.1	37.9	63.4	36.6

while the remaining (greater) part of the surface nozzles is in the "bare" state. With the increase of a degree of saturation in this temperature interval majority of dissolved crystals separates from the solvent, having no time for fixing on the surface of solid medium and are washed out of the column. As a whole, the effect of elevation of the role of adsorption interactions is exposed equally for xylenes and for cresols.

Table 2 presents the results characterizing the distribution of above interaction in the process of chromatography of the some organic compounds at the stationary phase at the column temperature of 160°C, i.e. when the crystals are in the state of nematic mesophases.

This case shows also, though to a lesser extent, the effect of adsorption interaction

which is expected to decrease with the increase in the degree of impregnation of solid support by stationary liquid. The contribution of dissolution to retention of cresols in the process of chromatography is slightly higher than that for xylenes. Apparently, under such temperature conditions, stationary liquid is capable to create more homogeneous film on the surface of solid media on a certain part of the surface of solid support.

CONCLUSIONS

Thus, the above stationary phase in the heating mode of the column of 160°C cannot be used for separation of the triad xylene isomers because of the small difference in retention values of these components, although the sequence of their elution is characteristic of liquid crystals in the nematic phase: a *meta-ortho-para*. As to the triad of cresol isomers, this phase allows their separation at high-resolution rate, with the criteria of uniformity $\Delta=0.71$ [6] with the order of elution that is characteristic of a liquid crystal in the nematic mesophase.

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Вплив поверхневих явищ на селективно-розділові властивості рідкокристалічної нерухомої фази

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Досліджено розподіл внесків адсорбції і розчинення в утримуваній об'єм окремих компонентів у газорідинній хроматографії в залежності від кількості нанесеної на твердий носій рідкокристалічною нерухомою фази і температури нагріву хроматографічної колонки.

Влияние поверхностных явлений на селективно-разделительные свойства жидкокристаллической неподвижной фазы

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Исследовано распределение вкладов адсорбции и растворения в удерживаемый объем отдельных компонентов в газожидкостной хроматографии в зависимости от количества нанесенной на твердый носитель жидкокристаллической неподвижной фазы и температуры нагрева хроматографической колонки.