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ARTICLES

Using Adsorbents with Immobilized Metal Chelate Layers for the Gas-Chromatographic Separation of Aromatic Hydrocarbons

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Abstract—Adsorbents based of Silipor 200 silica with immobilized layers of nickel acetylacetonate, ethylacetoacetate, and malonate are synthesized. The retention of arenes on the modified phases is studied; that the applicability of these adsorbents to the separation of complex mixtures of aromatic hydrocarbons is demonstrated.

Keywords: gas chromatography, adsorbents, metal chelates, aromatic hydrocarbons

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Study of chemically immobilized surface layers is one of the most promising trends in chelate-containing adsorbents. Interest in these chromatographic materials is well understood: a change in the nature of the modifying chelate offers an opportunity to vary to a certain extent the characteristics of the intermolecular adsorbate–adsorbent interaction and thereby substantially extends the applicability of these materials to the analytical separation and preconcentration of a large number of compounds [1–3].

The chromatographic properties of adsorbents modified with metal chelate layers are dependent on a number of factors, the most significant of which are the nature of the metal and ligand, and electron density distribution in the structure of the complex [4]. The simultaneous existence of multiple active sites in a single molecule and a partial compensation of an electron deficient metal atom through its inclusion in the chelate ring create the possibility of various specific interactions between these molecules and adsorbates of different types. In some cases, one can separate mixtures that are difficult to separate using conventional gas-chromatographic methods [5, 6].

Polycyclic aromatic hydrocarbons and alkyl-substituted benzenes are widely used in industry because of their active biological properties. Therefore, these substances may be present in various environmental samples and food. Monitoring of toxicant concentrations is currently one of the most important tasks of analytical chemistry [7]. Despite the large number of adsorbents, liquid stationary phases, and analytical columns of different types used in gas chromatography for arenes, the development of new chromatographic materials for a variety of applications in the separation and determination of aromatic hydrocarbons is an actual problem.

In this work, we studied the gas chromatographic separation of mixtures of alkyl-substituted benzenes and condensed aromatic hydrocarbons using silica adsorbents modified with nickel acetylacetonate, ethylacetoacetate, and malonate.

EXPERIMENTAL

Chelate-containing materials for gas chromatography were prepared based on Silipor 200 silica characterized by high thermal and mechanical stability. The adsorbent was prepared by sequential assembly through the chlorination of silica gel, followed by the synthesis of nickel acetylacetonate, ethylacetoacetate, and malonate at its surface by the procedure presented in [8]. The chelate structure and surface morphology were studied by IR spectroscopy and scanning electron microscopy [9].

The parameters of specific surface area and the porosity of the adsorbents were assessed using a TriStar II automated gas-adsorption analyzer and the volumetric adsorption method. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method in the automatic mode after evacuation at 200°C for 2 h by the low-temperature nitrogen adsorption isotherm.

The thermal stability of chromatographic adsorbents was determined by the results of thermal analysis with the use of a Netzsch STA 449 C instrument in the temperature range of 25–1000°C in air. The adsorbents were conditioned in a flow of inert carrier gas (helium) for at least 4 h, raising the temperature from 50 to 250°C.

Chromatographic separation of aromatic hydrocarbons was carried out in a Chrom 5 gas chromatograph with a flame ionization detector in an isother-

Table 1. Specific surface area, porosity, and thermal stability of the studied adsorbents

Adsorbent	S_a, m²/g	Total pore volume, cm³/g	Average pore size, nm	T_{max}, °C
Silipor 200	200*	1	0.7	–
Silipor 200 after chlorination	198*	1	0.8	–
Silipor 200 + nickel acetylacetonate	173*	1	0.7	300
Silipor 200 + nickel malonate	169*	1	0.7	220
Silipor 200 + nickel ethylacetonate	174*	1	0.8	210

* Relative error is ±10%.

mal mode and under the temperature rise from 150 to 250°C at a rate of 10 K/min. Helium was used as a carrier gas at a flow rate of 30 mL/min. Packed glass columns 1.2 m in length and 3 mm in inner diameter were used in the experiments.

RESULTS AND DISCUSSION

To study the characteristics of the adsorbents, the values of specific surface area and porosity were determined. The modification of the Silipor 200 surface with chelate complexes leads to a decrease in specific surface area, which is associated with fact that the complexes are held by the edges of large pores, while fine pores are filled by the chelate and closed (Table 1). The data of thermal analysis, presented in Table 1, indicate that the synthesized materials can be used for gas-chromatographic studies at rather high temperatures without failure of the modifying complex.

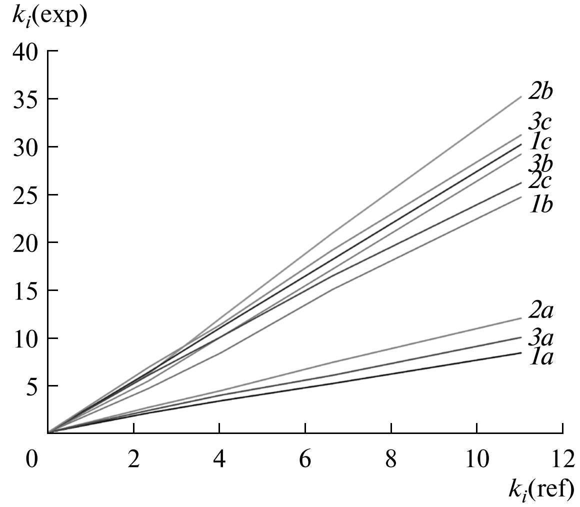

Fig. 1. Correlation of the capacity factors of (*a*) alkanes, (*b*) arenes, and (*c*) alcohols at the adsorbents modified with (*1*) nickel acetylacetonate, (*2*) nickel ethylacetoacetate, and (*3*) nickel malonate and at unmodified Silipor 200.

The chromatographic retention of standard mixtures of *n*-alkanes (C_5–C_9), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *m*-xylene, and mesitylene), and aliphatic alcohols (C_1–C_4) at the synthesized materials was studied at 150°C. The selectivity in homologous series was assessed based on the slopes of linear dependences of the column capacity factor, k_i (exp), on the same characteristics for the column with unmodified Silipor 200, adopted as a reference k_i (ref) (Fig. 1). The highest selectivity of the separation between the classes of organic compounds is achieved using columns with a maximum distance between the correlation dependences of capacity factors, which is confirmed by the findings of the regression analysis [10]. The comparison of the slopes led to the conclusion that the phases of nickel malonate and nickel ethylacetoacetate had the best separation properties with respect to arenes; all modified adsorbents are promising for the separation of mixtures of hydrocarbons and alcohols.

The values of relative retention times and the selectivity coefficients are presented in Table 2; they characterize the samples obtained as more selective for aromatic hydrocarbons as compared to the initial silica. Adsorbents with immobilized layers of nickel chelates exhibit high selectivity for polyaromatic hydrocarbons (PAHs), which improves the separation performance and reduces the duration of gas-chromatographic determination.

The polarity of the studied adsorbents in the modification process was assessed using the Kovats retention indices (**RI**) and the Rohrschneider polarity coefficients with respect to Carbopack B [11]. Further-

Table 2. Relative retention times with respect to benzene (t'_{rel}) and selectivity coefficients (σ_r) of some aromatic hydrocarbons

Compound	Silipor 200		Silipor + nickel acetylacetonate		Silipor + nickel ethylacetonat		Silipor + nickel malonate	
	σ_r	t'_{rel}	σ_r	t'_{rel}	σ_r	t'_{rel}	σ_r	t'_{rel}
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Toluene	1.86	1.86	1.91	1.91	1.89	1.89	1.86	1.86
p-Xylene	1.84	3.42	1.82	3.47	1.75	3.31	1.84	3.41
m-Xylene	1.86	3.48	1.79	3.41	1.79	3.38	1.80	3.35
o-Xylene	2.55	4.73	2.43	4.64	1.91	3.62	2.42	4.50
Mesitylene	1.88	6.53	1.65	5.62	1.69	5.72	1.65	5.52
Naphthalene	1.00	9.49	1.00	4.84	1.00	6.58	1.00	4.85
Anthracene	1.83	17.30	1.87	9.68	1.98	13.10	1.84	9.63
Phenanthrene	1.67	15.85	1.71	9.51	1.73	12.93	1.69	9.46

Table 3. Retention indices (RI) and polarity coefficients (*X*, *Y*, *U*, and *Z*) of the test substances obtained for the studied adsorbents at 150°C

Adsorbent	Benzene		2-Butanone		Nitromethane		Ethanol		Σ
	RI	*X*	RI	*Z*	RI	*U*	RI	*Y*	
Silipor 200	730	1.69	1154	6.78	1059	7.01	1075	7.79	23.27
Silipor + nickel acetylacetonate	712	1.54	1120	6.44	915	5.57	952	6.56	20.11
Silipor + nickel ethylacetonate	722	1.61	1135	6.59	923	5.65	986	6.90	20.75
Silipor + nickel malonate	728	1.67	1144	6.68	946	5.88	998	7.02	21.25

more, a total polarity index was used, defined as the sum of coefficients *X*, *Y*, *U*, and *Z* (Table 3). The results obtained indicate that nickel chelates immobilized at the surface of Silipor 200 reduce the overall polarity and change the polarity of the adsorbents toward different classes of organic compounds. In particular, after the modification of the initial adsorbent with nickel acetylacetonate, the contribution of donor interactions (*Z* and *U*) and π-complexation (*X*) decreases, which occurs, probably, due to the shielding of the nickel ion, having deficient electron density, with chelate ligands. Note that Silipor 200 modified with nickel malonate demonstrates the largest total polarity with respect to all the test substances. This adsorbent has a high ability to form hydrogen bonds ($Y = 7.02$) and is capable of donor–acceptor ($Z = 6.68$) and π–π interactions ($X = 1.67$), which leads to a stronger retention of arenes, alcohols, nitro compounds, aldehydes, and ketones.

The adjusted retention times of aromatic hydrocarbons, obtained in the mode of temperature rise from 150 to 250°C at a rate of 10 K/min are listed in Table 4. It is seen that in the case of Silipor 200, there is an overlap of the chromatographic peaks of *o*-, *m*-, and *p*-xylenes and ethylbenzene; *p*-cymene, and *tert*-butylbenzene; naphthalene and durene; mesitylene and pseudocumene, as well as some PAHs (acenaphthene and fluorine; anthracene and stilbene), which have similar retention parameters.

A common feature of adsorbents with immobilized layers of nickel complexes is a stronger retention of alkyl-substituted benzenes, which is associated with

Table 4. Adjusted retention times (t', min) of aromatic hydrocarbons at the studied adsorbents

Compound	Silipor 200	Silipor + nickel acetylacetonate	Silipor + nickel ethylacetonate	Silipor + nickel malonate
Benzene	0.98	1.64	1.21	1.69
Toluene	2.25	2.84	2.52	2.52
p-Xylene	3.47	4.64	4.21	4.19
m-Xylene	3.76	5.00	4.44	4.45
o-Xylene	3.58	4.67	4.30	4.35
Ethylbenzene	3.75	4.34	4.10	4.11
Mesitylene	7.58	6.17	5.85	5.87
Pseudocumene	8.08	6.50	6.09	6.29
tert-Butylbenzene	9.42	6.83	6.27	6.41
p-Cymene	9.75	7.17	6.69	6.73
Decalin	6.75	5.97	5.52	5.57
Naphthalene	11.42	9.17	9.25	9.29
Durene	11.91	11.17	10.77	10.84
Diphenyl	13.58	12.84	12.69	12.75
Acenaphthene	16.92	13.34	13.35	13.40
Fluorene	17.27	16.27	15.60	15.69
Phenanthrene	19.65	18.00	18.19	18.36
Anthrecene	21.55	18.44	18.64	18.69
Stilbene	21.87	18.85	18.97	18.98
Fluoranthene	23.51	21.35	21.89	21.86

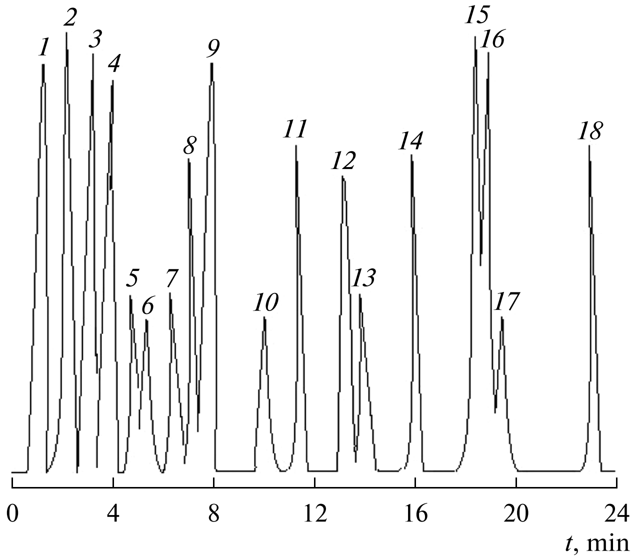

Fig. 2. Chromatogram of a mixture of aromatic hydrocarbons separated at a glass column (1.2 m ± 3 mm) packed with Silipor 200 modified with nickel malonate in the temperature rise from 150 to 250°C at a rate of 10 K/min: (*1*) benzene; (*2*) toluene; (*3*) ethylbenzene; (*4*) *o*-, *m*-, and *p*-xylenes; (*5*) decalin; (*6*) mesitylene; (*7*) pseudocumene; (*8*) *tert*-butylbenzene; (*9*) *p*-cymene; (*10*) naphthalene; (*11*) durene; (*12*) diphenyl; (*13*) acenaphthene; (*14*) fluorene; (*15*) phenanthrene; (*16*) anthracene; (*17*) stilbene; and (*18*) fluoranthene.

changes in the surface properties after modification. The chemical nature, structure, and geometric layout of the complex determine the individual nature of the interaction with a particular compound. For example, nickel acetylacetonate exhibits an increased tendency to retain aromatic hydrocarbons, which is probably due to the tetrahedral structure of the complex. In this case, π-complexation is expressed most clearly. The symmetry of the chromatographic peaks is improved, which also ensures the selective separation of the components of the test mixture.

In the transition from nickel acetylacetonate to nickel ethylacetoacetate and then to nickel malonate, the retention of arenes changes because of the different chemical nature of the ligands, namely, the effect of electron-donor oxygen atoms of the chelate ester groups. This causes a significant retention of PAHs at Silipor 200 with immobilized layers of nickel malonate. On all modified adsorbents, xylenes and ethylbenzene, *tert*-butylbenzene and *p*-cymene, and naphthalene and durene were successfully separated in an isothermal mode. Model mixtures of PAHs, including such high-boiling compounds as anthracene and fluoranthene, were separated selectively and more rapidly under temperature-programmed conditions (Fig. 2).

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