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Physicochemical Properties of Sorbents Based on Silica Gel Modified by 1-Phenylazo-2-naphtholic Complexes of Transition Metals

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Abstract—Gas chromatography sorbents based on Silokhrom C80 and modified by 1-phenylazo-2-naphtholic complexes of 3d metals (Co(II), Ni(II), Cu(II)) are obtained. Their structural, chromatographic, and sorption characteristics are investigated. It is found that modifying them with 1-phenylazo-2-naphthols of transition metals has a considerable effect on the chromatographic polarity and selectivity of sorption materials. The prospects for the practical application of the obtained sorbents are demonstrated by experiments on the gas chromatographic separation of mixtures of different classes of organic compounds.

INTRODUCTION

Gas chromatography is now solving many important analytical problems regarding the separation of mixtures of anthropogenic and natural origin, which requires a wide set of sorption materials. The targeted creation of new chromatographic materials with enhanced properties and analytical characteristics therefore remains of great interest [1, 2].

Complex compounds of transition metals are used as modifiers of sorption materials, due to their ability to perform specific intermolecular interactions in sorbate–sorbent systems. These materials enable us to expand the set of analytical possibilities in the separation of multicomponent organic mixtures, and open up additional prospects for their use in the adsorption concentration of microimpurities [3, 4].

1-Phenylazo-2-naphthol (Sudan I, SI) forms thermally stable complexes with 3d metals in stoichiometric compositions of 2 : 1, which were thoroughly studied in [5–7]. Due to the presence of electron-donating atoms of nitrogen and oxygen, along with the π-systems and complexing ions of metals, these compounds are quite promising for application as modifying agents of sorption materials.

The aim of this work was to obtain sorbents based on Silokhrom C80 and adsorption-modified by 1-phenylazo-2-naphtholic complexes of cobalt(II), nickel(II), and copper(II). We also study their physi-cochemical and sorption properties, and the possibility of using them for the selective gas chromatographic separation of multicomponent mixtures of organic compounds.

EXPERIMENTAL

A number of chemical reactants (ZAO Vekton) were used to synthesize our chromatographic sorbent: copper chloride ($CuCl_2 \cdot 2H_2O$); nickel chloride ($NiCl_2 \cdot 6H_2O$); cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$); sodium hydroxide (NaOH), all of analytical grade; hydrochloric acid (HCl, special purity grade 20-4); sodium nitrite ($NaNO_2$, analytical grade); aniline ($C_6H_5NH_2$, pure grade); 2-naphthol ($C_{10}H_8O$, 99%, Aldrich); ethanol (C_2H_5OH, 96%, OOO SirtMed); deionized water (H_2O), Silokhrom S80 silica gel (fraction, 0.20−0.316 mm; OOO KhromLab).

The structure of 1-phenylazo-2-naphtholic complexes of Cu(II), Co(II), and Ni(II) was studied via Fourier transform infrared spectroscopy (FTIR) in the range of 400 to 4000 cm^{-1} using a Cary 600 Fourier transform infrared spectrometer (Agilent Technologies). For the synthesized chelates and unbound ligands, the Raman spectra were registered using a Senterra spectrometer (Bruker) with a radiation wavelength of 538 nm and a power of 2 mW.

The range of working temperatures of the resulting sorption materials was determined via thermal analysis using an STA 449C thermal analyzer (Netzsch). DSC

curves were obtained in the 25–900°C range of temperatures at a rate of 10°C/min in air.

The surfaces of chelate-containing sorbents were examined visually by scanning electron microscopy at an accelerating voltage of 15 kV using a Hitachi TM 3000 microscope equipped with a QUANTAX 70 microanalyzer.

Specific surface areas S_{sp} of the sorbents were measured with a TriStar 3020 analyzer (Micromeritics). The multi-point BET method was used to calculate S_{sp}.

The chromatographic parameters were studied at temperatures of 150, 170, 200°C using a MAESTRO 7820 gas chromatograph (Agilent Techologies) equipped with a flame ionization detector. The flow rate of carrier gas (helium) was 30 mL/min.

Our 1-phenylazo-2-naphthol was synthesized by two consecutive reactions of diazotization and azoassociation [8]. The resulting bright red precipitate was crystallized with ice deionized water and recrystallized from ethanol. The yield of product was 83.5%; $T_{melt} = 131°C$.

Copper (II), cobalt (II), and nickel (II) bis-1-phenylazo-2-naphthol were obtained [5–7] by slowly combining hot solutions of transition metal salts (CuCl$_2 \cdot$2H$_2$O, Co(CH$_3$COO)$_2 \cdot$4H$_2$O, or NiCl$_2 \cdot$6H$_2$O) (0.005 mol in 70 mL of water) and 0.01 mol 1-phenylazo-2-naphthol (in 200 mL of ethanol). The mixture was boiled with reflux condenser for 4 h. The precipitate was filtered and washed with hot ethanol. The yield was 83% Cu(Sudan I)$_2$, 61% Co(Sudan I)$_2$, and 90% Ni(Sudan I)$_2$.

Silokhrom S80 was used as a support to create chelate-containing materials. The synthesized complex compounds of transition metals were deposited from the chloroform onto surfaces of Silokhrom S80 in quantities of 4 wt % via the gradual evaporation of the solvent. Metallic packed columns 1 m long and with inner diameters of 3 mm (Agilent) were filled with the modified sorbents. Sorption steel tubes 89 × 5 mm in size (Markes International) were also used.

The applicability of chelate-containing chromatographic sorbents for sorption concentrating was evaluated through dynamic gas extraction of model solutions of volatile organic compounds of different classes: hexane, benzene, chloroform, acetone, and ethyl acetate. Nitrogen with a flow rate of 30 mL/min was passed through an aqueous solution with a given concentration of volatile organic compound (VOC). The flow of gas extractant from the space on the model solution was then fed through a cartridge filled with modified sorbent (0.2 g). To control the sorption process, samples of gas phase were taken upstream and downstream of the sorption cartridge, and the concentrations of VOC were determined by gas chromatography.

The retention curves of the test compounds were plotted on the basis of the resulting data. They reflected the dependences observed upon dynamic sorption: C/C_0 on V, where C and C_0 are the concentrations of the analyte in the gas phase downstream and upstream of the tube with sorbent, respectively; and V is the volume of the sample that passes through the sorption tube. The volume before passing through the filter (V_B) and the volume of retention (V_R) were determined from the retention curves for each tested substance. Value V_B was taken as the volume of the sample passed through the column corresponding to 95% extraction ($C = 0.05C_0$) of the test analyte. Value V_R corresponded to the volume of the sample passed through the column at which the concentration at the outlet of the sorption tube was equal to half of the initial concentration [9, 10].

RESULTS AND DISCUSSION

Absorption bands characteristic of several types of vibrations by ligand bonds (e.g., 740 cm^{-1}, ωCH; 970 cm^{-1}, δ CH; 1349–1394 cm^{-1}, ν_s CC + δ CH + ν_s CN; and 1442–1458 cm^{-1}, ν_s CO + δ CH + ν_s CN) are visible in the spectra of the synthesized complex compounds. Absorption lines of medium intensity in the area of 3450 cm^{-1} corresponding to the valence vibrations of O–H bonds are present only in FTIR spectra of 1-phenylazo-2-naphthol. The vibrations of M–O and M–N bonds in complex compounds are apparent in the Raman spectra in the regions of 230 cm^{-1} and 520/290 cm^{-1}, respectively. The results obtained through FTIR and Raman spectroscopy agree with the data in [6] and allow us to assess the complexation processes that occur during the synthesis of 1-phenylazo-2-naphthol complexes with transition metals.

According to data from thermal analysis, the temperatures of the onset of the decomposition of 1-phenylazo-2-naphthol complexes indicates the following order of changes in their thermal stability: Co(Sudan I)$_2$ < Cu(Sudan I)$_2$ < Ni(Sudan I)$_2$, and are 210, 250, and 260°C, respectively. This is the reason for the relatively high thermal stability of chelate-containing sorbents, and it allows us to use them in (among other things) separating mixtures of high-boiling organic compounds.

Scanning electron microscopy estimates of Silokhrom C80 surfaces showed that complex compounds were deposited fairly evenly on the sorbent in the form of needle-like crystals (for Cu(Sudan I)$_2$ and

Table 1. Kovacs indices of retention (I), Rorschneider constants (x, y, z, s, u), and the total polarity of sorbents, 150°C

Sorbent	Benzene		Ethanol		Butanone-2		Nitropropane		Pyridine		$\Sigma(x, y, z, s, u)$
	I	x	I	y	I	z	I	s	I	u	
Silokhrom S80	706	1.45	1005	7.09	1207	7.31	1111	7.53	1544	9.97	33.35
Silokhrom S80 + Co(Sudan I)$_2$	625	0.64	701	4.05	841	3.65	870	5.12	–	–	–
Silokhrom S80 + Ni(Sudan I)$_2$	683	1.22	875	5.79	1084	6.08	1010	6.52	1380	8.33	27.94
Silokhrom S80 + Cu(Sudan I)$_2$	639	0.78	745	4.49	946	4.70	910	5.52	1237	6.90	22.39

Table 2. Differential mole free energies of adsorption (ΔG) of test compounds, 150°C

Sorbent	$-\Delta G$, kJ/mol					
	benzene	ethanol	butanone-2	nitropropane	pyridine	$-CH_2-$
Silokhrom S80	4.38	9.72	13.32	11.61	19.30	1.77
Silokhrom S80 + Co(Sudan I)$_2$	5.14	6.87	10.16	10.63	–	2.29
Silokhrom S80 + Ni(Sudan I)$_2$	3.28	7.53	5.95	8.98	17.54	2.23
Silokhrom S80 + Cu(Sudan I)$_2$	4.24	6.48	10.55	9.84	16.57	2.09

Ni(Sudan I)$_2$) and flaky particles (for Co(Sudan I)$_2$), with some increase in the density of the coating in the areas with defects in the silica gel surface.

The results from calculating specific surface areas via the multi-point BET method indicate that the deposition of chelate-type complex compounds on a surface of Silokhrom C80 in the form of adsorption layers reduces their size and thus their porosity, due to the complexes being retained by the edges of large pores. For unmodified Silokhrom, S_{sp} is 84 m^2/g, and d_{pore} is 42.2 nm; after the deposition of 1-phenylazo-2-naphtholates of metals, S_{sp} lies in the range of 61–76 m^2/g, and d_{pore} is 36.4–33.7 nm.

The parameters of the retention of test compounds of different classes (alkanes, alkenes, aromatic hydrocarbons, alcohols, ketones) were determined for the obtained sorption materials. It was established that aromatic hydrocarbons take longer to elute on sorbents containing copper and cobalt as complexing agents, in comparison to unmodified Silokhrom S80. A considerable reduction in the time of retention is observed for Silokhrom S80 + Co(Sudan I)$_2$ and Silokhrom S80 + Cu(Sudan I)$_2$ with respect to oxygen-containing test substances. The changes not as great for sorbents containing complexes with nickel.

The polarity of our synthesized sorbents was estimated using Kováts' retention indices, Rorschneider's constants, and the thermodynamic parameters of the sorption of the test substances. The chemical nature and structure of a complex predetermines the character of changes in its parameters. The coefficients of polarity toward electron-donating, oxygen-containing, and nitrogen-containing compounds were reduced as a result of modification. The tendency toward a reduction in polarity coefficients was less pronounced for aromatic compounds (Table 1). According to the total polarity coefficients, Silokhrom S80 modified by the 1-phenylazo-2-naphthol complex of copper(II) was the most polar compound.

The differential free mole energy of adsorption (Table 2) characterizes the capability of the obtained sorbents with respect to different types of interaction with the molecules of sorbates. Modifying Silokhrom S80 by Co(II), Ni(II), Cu(II) 1-phenylazo-2-naphthol complexes lowered the polarity of the studied sorbents toward electron-donating compounds (e.g., alcohols, ketones, and nitro-compounds), due to the reduced ability to form hydrogen bonds and the weakening of donor−acceptor interaction with the test substances. The values of ΔG were minimal for our aromatic compounds, due to their weaker ability to form the π-complexes in comparison to other types of intermolecular interaction. The molar energy of the adsorption of methylene chains increased relative to the unmodified silica gel, as was reflected in the prolonged elution time of n-alkanes. The absolute values of ΔG_{CH_2} indicate that the con-
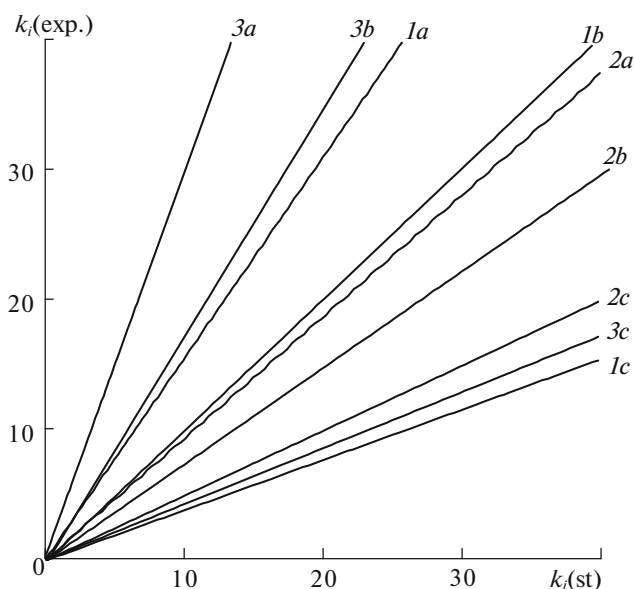
Fig. 1. Dependences of capacity coefficients of (*a*) alkanes, (*b*) arenes, and (*c*) alcohols on Silokhrom S80 modified by (*1*) Cu(Sudan I)$_2$, (*2*) Ni(Sudan I)$_2$, and (*3*) Co(Sudan I)$_2$.

tribution from dispersion interaction to the total energy of adsorption was negligible.

To estimate the selectivity of the chromatographic materials, we plotted the dependences of the capacities of the columns ($k_{i(\exp)}$) with chelate-containing sorbents on the same value for the column with unmodified Silokhrom S80 ($k_{i(\mathrm{st})}$) used as a standard (Fig. 1). Using the 1-phenylazo-2-naphthol complexes with transition metals to modify Silokhrom S80 allowed us to expand the possibilities of gas chromatography, due to changes in the capacity coefficients, which had relatively high values relative to *n*-alkanes and aromatic hydrocarbons for modified sorbents. For alcohols, k_i is characterized by low values as a result of Silokhrom S80 being modified by chelate-complexes; this enables us to increase the speed with which polar compounds are analyzed. The highest selectivity of

separation of homologs of one class of organic compounds or another was reached on the columns with the maximum slopes of the linear dependences of the columns' coefficients of capacity. According to the presented graphic dependences, the highest selectivity of separation inside the homological series of alkanes and arenes was observed on sorbents that contained cobalt(II) 1-phenylazo-2-naphtholate.

The output curves of retention of testing compound of different classes were plotted to study the sorption properties of chelate-containing sorbents when working in the regime of dynamic sorption concentration. The initial Silokhrom S80 and synthesized chelate-containing sorbents were depleted by the micropores responsible for the sorption of nonpolar, weakly polar, and medium-polarity compounds. The output curves of the retention of hexane and benzene therefore have forms different from the *s*-shape, with a sharp increase in the C/C_0 values at low volumes of the passed sample. The curves reach saturation relatively quickly. The maximum parameters of retention V_B and V_R (Table 3) are characteristic of the polar substances acetone and ethyl acetate, which is explained by the affinity of synthesized sorption materials for electron-donating oxygen-containing compounds, and by the predominance in the texture of Silokhrom of meso-pores with maximum sorption potential, which are responsible for the sorption of polar compounds. It is worth noting that the sorbents modified by 1-phenylazo-2-naphtholates were characterized by higher values of V_B and V_R than Silokhrom S80 for all of the tested VOCs.

The obtained chromatographic materials were tested for separating mixtures of organic compounds of different classes. Compared to silica gel, Silokhrom S80 modified by Co(Sudan I)$_2$ complex had low polarity toward carbonyl compounds, allowing the faster and more selective separation of aldehydes and ketones (Fig. 2).

Silica gel with deposited Ni(Sudan I)$_2$ allows the elution of mixtures of aromatic and high-boiling polyaromatic hydrocarbons in the regime of temperature programming, due to its high thermal stability and

Table 3. Volumes before passing through the filter (V_B, mL) and retention volumes (V_R, mL) upon the concentration of test VOCs for different sorbents

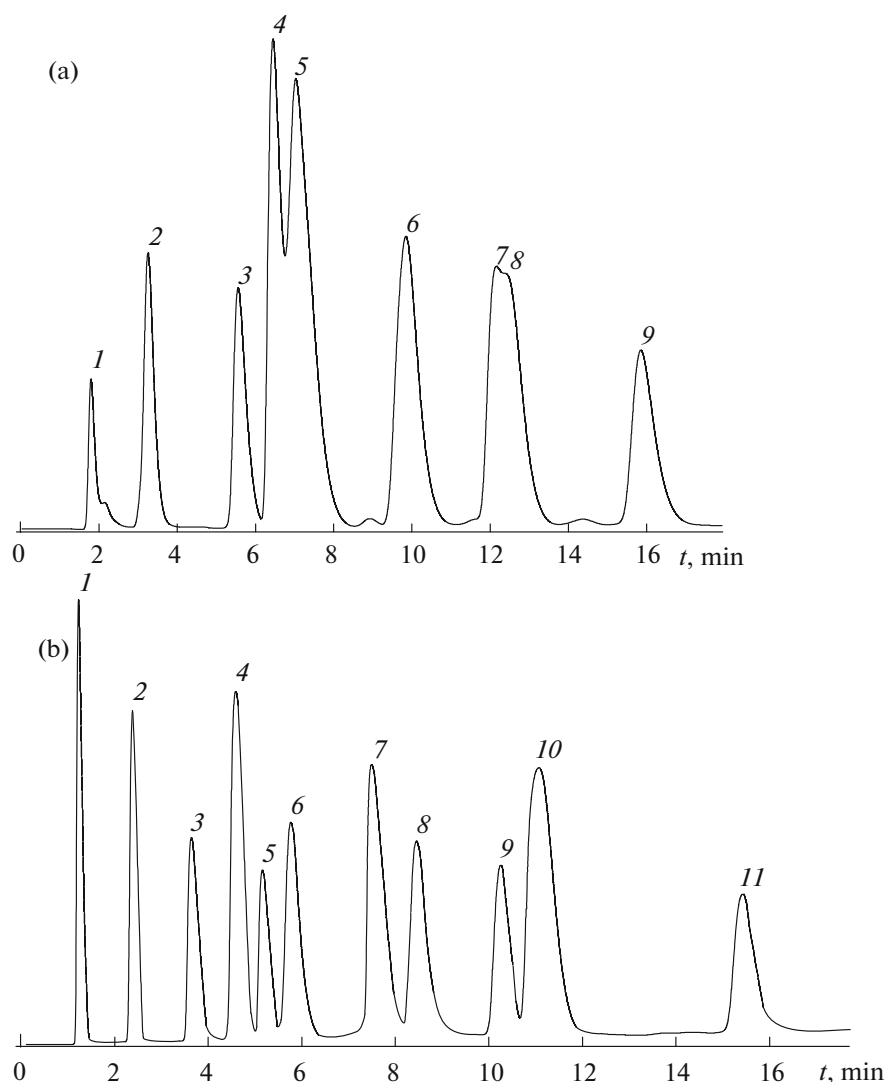| Sorbent	Hexane		Benzene		Chloroform		Acetone		Ethyl acetate	
	V_B	V_R	V_B	V_R	V_B	V_R	V_B	V_R	V_B	V_R
Silokhrom S80	4.7	36.5	2.1	18.5	1.9	10.4	153.6	377.3	43.3	670
Silokhrom S80 + Co(Sudan I)$_2$	9.4	49.5	11.1	52.3	2.6	36.5	203.6	320.9	386.7	787.8
Silokhrom S80 + Ni(Sudan I)$_2$	18.8	62.5	17.5	122.2	3.3	58.4	272.7	479.1	448.9	673.3
Silokhrom S80 + Cu(Sudan I)$_2$	6.3	35.1	11.1	44.4	1.4	10.6	200.0	448.2	466.7	766.7

Fig. 2. Chromatograms of the separation of mixtures of aldehydes and ketones on (a) Silokhrom S80 and (b) Silokhrom S80 + Co(Sudan I)$_2$. Regime of temperature programming: 150°C (2 min) and 200°C at a rate of 4°C/min; (*1*) 2-methylpropanal, (*2*) 3-methylbutanal, (*3*) 3-methylbutanone-2, (*4*) 3,3-dimethylbutanone-2, (*5*) hexanal, (*6*) 2,4-dimethylpentanone-3, (*7*) benzaldehyde, (*8*) 4-methylhexanone-2, (*9*) octanal, (*10*) 2,6-dimethylheptanone-4, (*11*) nonanone-2.

fairly high polarity toward aromatic hydrocarbons. It enables us to separate such components as π-xylene and decaline, acenaphthene and biphenyl, and phenanthrene and anthracene, which is impossible on Silokhrom S80. In separating mixtures of light saturated and unsaturated hydrocarbons of C$_1$–C$_4$ composition, using adsorbents modified with 1-phenylazo-2-naphthol complexes with metals lengthens the duration of analysis in comparison to unmodified Silokhrom, and enables us to achieve high selectivity.

CONCLUSIONS

New sorption materials based on Silokhrom C80, surface-modified by 1-phenylazo-2-naphthol com-

plexes of cobalt(II), nickel(II), and copper(II), were synthesized. Their structural-sorption and chromatographic properties were studied using a combination of physicochemical means. The prospects for their effective application in gas chromatography for separating complex mixtures of carbonyl compounds, saturated and unsaturated light hydrocarbons, and aromatic and polyaromatic hydrocarbons, along with the gas-extraction concentration of VOCs from bodies of water, was shown.

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