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PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

Adsorption Properties of a Silicagel Surface with Grafted Transition Metal Acetylacetonate Complexes

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Abstract—The adsorption properties of a Silipore 200 surface and chemically modified sorption materials containing nickel, cobalt, and copper acetylacetonates are studied via gas chromatography. *n*-Alkanes (C_6–C_9) and adsorbates, the molecules of which have different electron-donating and electron-acceptor properties, are used as test compounds. From experimental data on the retention of adsorbates; their differential molar adsorption heats $\overline{q}_{\mathrm{dif},1}$; changes in standard differential molar entropy $\Delta\overline{S}^{S}_{1,C}$; and, for polar adsorbates, contributions $\Delta\overline{q}_{\mathrm{dif},1(\mathrm{specific})}$ to the energy of dispersive and specific interactions, are calculated. The effect the metal ion in the structure of acetylacetonate has on the characteristics of thermodynamic retention is shown.

Keywords: adsorbents, chelates, gas chromatography, acetylacetonates, thermodynamic adsorption characteristics

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INTRODUCTION

A new class of surface-modified materials based on porous oxide carriers (silica with chemically grafted layers of metal chelates) has now become widespread in the analytical practice of gas chromatography. Such adsorbents with mechanical strength, chemical and thermal stability, no swelling in most solvents, and having the ability to control the chromatographic properties and the nature of adsorbate–adsorbent interactions by changing the structure and composition of the modifier, are used for the sorption concentration of volatile organic compounds and the analytical separation of different classes of organic substances [1–5]. The problem of synthesizing and investigating the properties of chelate-containing materials is thus of great interest.

In synthesizing adsorbents, it is very important to select a chelate complex that has sorption-exchange characteristics on the one hand, and selectivity and thermal stability on the other. The transition metal ion primarily determines the formation of the chelate ensemble and selectivity through donor–acceptor interactions, while the organic ligand determines the strong kinetic characteristics and high thermal stability of the material [6].

Varying the nature and mutual arrangement of metal ions and ligands offers wide possibilities of controling acid-base centers on a surface, thermal stability, chromatographic properties, the rate of establishing sorption equilibrium, desorption parameters, and the elution of substances. Depending on the level of saturation, the coordination sphere of the metal ion allows us to affect the structure of the conjugate ligands on the carrier surface and to create multifunctional materials with different physicochemical and sorption characteristics. The combination of several retention mechanisms and the selectivity of complexation reactions give advantages over the nonspecific adsorbents and synthetic polymers used for the concentration and separation of mixtures of different organic compounds [7–9].

The aim of this work was to study the thermodynamic characteristics of the adsorption of organic compounds of different types on silica gel Silipore 200 with chemically grafted chelates of nickel, cobalt, and copper acetylacetonates.

EXPERIMENTAL

Chemically modified adsorbents were prepared on the basis of silica gel Silipore 200 (0.16–0.20 mm), a product of the polycondensation of silicic acids, via sequential assembly through the silica chlorination stage using thionyl chloride at room temperature. To conduct the surface chemical modification, sodium acetylacetonate was grafted on the SiO_2 surface. At the stage of addition, it was dissolved in dimethylformamide and applied to the surface of chlorinated silica

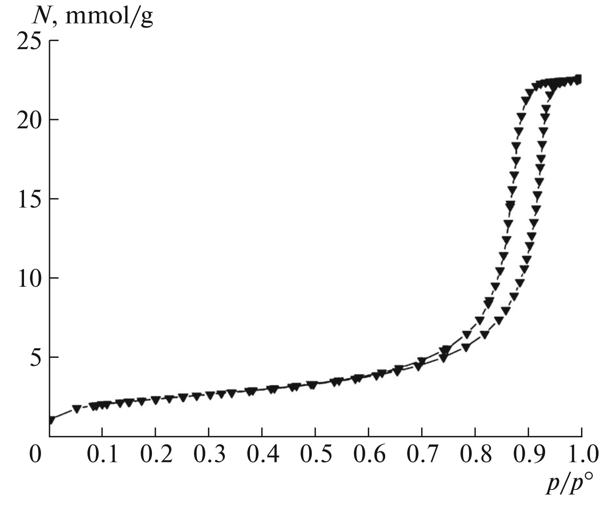

Fig. 1. Isotherm of static low-temperature nitrogen adsorption at 77 K on Silipore 200: N is the amount of adsorbed nitrogen (mmol) per 1 g of adsorbent.

gel through gradual evaporation of the solvent. At the final stage, the modified Silipore 200 was treated with an ethanolic solution of copper, nickel, and cobalt chlorides [10].

IR and Raman spectroscopy were used to confirm the structure of the chelates and their adhesion on the SiO_2 surface. The spectra were recorded on a Nicolet 6700 Fourier spectrometer in the 4000–400 cm^{-1} region and a Nicolet NXR 9650 Raman spectrometer in the 4000–200 cm^{-1} region.

The specific surface area parameters and porosity of the adsorbents were estimated with a TriStar II automatic gas adsorption analyzer using the volumetric variant of the sorption approach. The specific surface area was calculated via BET in the automatic mode after evacuation at 200°C for 2 h, using the low-temperature sorption isotherm of nitrogen vapors.

The thermal stability of the adsorbents was determined from the results of thermogravimetric analysis on a Netzsch STA 449 C instrument in the temperature range of 25–1000°C.

To study the distribution of acetylacetonates on the Silipore 200 surface, elemental analysis was performed on an automated Euro EA-3000 HCNS-element analyzer using the Callidus 5.1 software package. The amount of the grafted compound, the surface concentration of the grafted groups, and the thickness of a grafted layer were determined from the carbon content in the samples and changes in the specific surface area of the adsorbents before and after chemical modification [5].

The adsorption of different test compounds (saturated and aromatic hydrocarbons, ketones, alcohols, and nitro compounds) on the obtained sorbents was studied by gas chromatography. Our studies were performed on a Chrom 5 gas chromatograph equipped with a flame ionization detector in the isothermal mode. Glass columns 1.2 m long with inside diameters of 3 mm were used. The consumption of the carrier gas (helium) was 30 cm^3/min.

The main values determined from the experiment were the specific retention volumes per unit surface of the adsorbent $V_{g,1}$, which for the small volumes of the introduced samples were Henry adsorption constants $K_{1,C}$ (cm^3/m^2) [11]. The thermodynamic characteristics of adsorption $\bar{q}_{\text{dif},1}$ and $\Delta\bar{S}_{1,C}^{S^0}$ were calculated from the linear dependence [12]

$$\ln K_{1,\mathrm{C}} = \frac{\bar{q}_{\text{dif},1}}{RT} + \frac{\Delta\bar{S}_{1,C}^{S^0}}{R} + 1,$$

where $\bar{q}_{\text{dif},1} = -\bar{U}$ is the differential molar heat of adsorption, and $\Delta\bar{S}_{1,C}^{S^0} = \bar{S}_1^{S^0} - \tilde{S}_{g,C}^0$ is the change in the standard differential molar entropy.

The error in determining $V_{g,1}$, $\bar{q}_{\text{dif},1}$, and $\Delta\bar{S}_{1,C}^{S^0}$ did not exceed 10% for all of the tested compounds.

RESULTS AND DISCUSSION

Adsorption processes involving chromatographic adsorbents depend not only on the chemical nature of the material, but also on the textural properties of a surface. The porous structure of the investigated materials based on Silipore 200 was studied using experimental data obtained for static low-temperature nitrogen adsorption. The corresponding isotherm shown in Fig. 1 differs in that it has a hysteresis loop in the region of relative pressure $p/p° = 0.6–1.0$ whose branches are vertical and parallel to one another, which characterizes porous adsorbents. According to the IUPAC classification, the observed hysteresis loop is of type H1, which describes ensembles of rigidly connected globules that are uniformly packed and of equal size [13].

The pore distribution curve (Fig. 2) constructed by analyzing the desorption branch of the sorption–desorption isotherm shows that Silipore 200 is characterized by mesoporosity with a narrow pore distribution in the range of 5–20 nm. At the maximum volume of 0.2 cm^3/(g nm), the pore diameter is 17 nm.

Chemical modification of the initial silica with metal chelates alters the geometry of the surface, as can be seen from the results of studying the specific surface areas and porosities presented in Table 1 for the considered adsorbents.

The application of complex compounds reduces the specific surface area from 200 to 171 m^2/g with the volume and average pore size changing only slightly. According to calculations of the Henry adsorption constants (K_G) and BET constant (C_{BET}) characterizing the force of adsorbate–adsorbent interaction, the

BET model describes the adsorption of nitrogen on the investigated adsorbents, as can be seen from the rather high numerical values of K_G and C_{BET}, and from the correlation coefficients R close to unity (R = 0.999) for the investigated chelate-containing adsorbents.

According to thermogravimetric analysis, nickel acetylacetonates on surfaces of silica gels are stable up to 300°C, while cobalt and copper acetylacetonates are stable up to 290°C.

According to the results from elemental analysis, the amount of the grafted layer of acetylacetonates was 0.50 mmol/g; the surface density of the grafted chelates was 1.60 groups per nm^2 (2.66 μmol/m^2), and the volume and thickness of the grafted layer were 1.77 × 10^{-3} cm^3/g and 0.089 nm, respectively.

To prove the adhesion of the complexes on the Silipore 200 surface, IR subtraction spectra were obtained in which the basic functional groups of the modifier coincided with the vibrations of sodium acetylacetonate (Fig. 3).

The absorption band at 1618 cm^{-1} in the spectrum of acetylacetone was due to symmetric ν(C=O) stretching vibrations. The stretching vibrations of the ν(C=C–C–O) conjugate bond system appear as a band at 1583 cm^{-1}. The set of absorption bands at 1490 and 1515 cm^{-1} characterizes the system of stretching ν(C=O) and bending δ(C–H) vibrations. The sum ν(C–C=C–O) + δ(OH) + δ(C–H) + ν(C–CH_3) is apparent as bands at 1397 and 1420 cm^{-1}. In the IR spectrum of the acetylacetonate, an absorption band is observed in the region of 1260 cm^{-1} that is associated with asymmetric ν_{as} (C–O) stretching vibrations. The band at 1175 cm^{-1} corresponds to δ(C–H) bending vibrations. The bands at 1010 and 1020 cm^{-1} describe the bending vibrations of methyl groups. In the region of 980 cm^{-1}, ν(C–CH_3) stretching vibrations are observed [14, 15].

Figure 4 shows the Raman spectra of acetylacetone and chelates based on it, grafted to the Silipore 200 surface. The adsorption band at 1467 cm^{-1} corresponds to δ(CH_3), while the band at 1405 cm^{-1} characterizes ν(C–C=C–O) + δ(OH) + δ(C–H) + ν(C–CH_3). The absorption in the region of 1082 and 1009 cm^{-1} corresponds to ν(C–C) and ρ(CH_3). The adsorption bands in the region of 884, 826, and 813 cm^{-1} correspond to ν(C–CH_3) + ν(C–O) and ρ(H_2O), respectively. In the Raman spectra of acetylacetone and metal chelates, a three-humped peak is observed in the 273–274 cm^{-1} region; its oscillation corresponds to the vibrations of the chelate ring. The formation of metal–oxygen bonds is confirmed by the presence of bands in the Raman spectrum in the region of 484–490 cm^{-1} [16, 17].

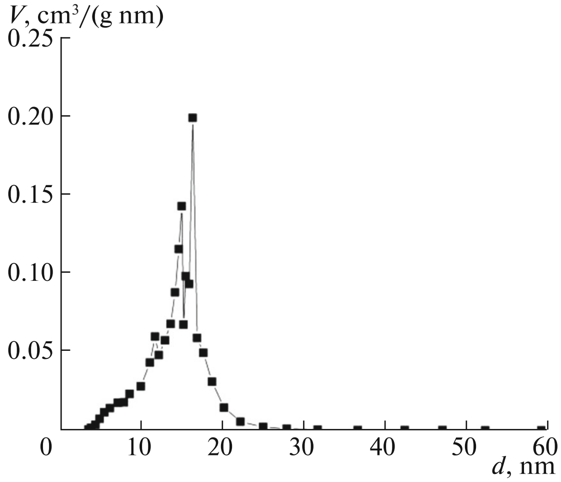

Fig. 2. Pore size distribution differential curve for Silipore 200.

When studying the thermodynamics of adsorption of organic substances on the investigated materials via gas chromatography at fairly high column temperatures and low volumes of samples, the adsorption isotherm obeys the Henry law with the $K_{1,C}$ adsorption equilibrium constant [18]. To estimate the thermodynamic parameters of adsorption, compounds capable of performing different types of intermolecular interactions were chosen as test compounds: alkanes for dispersion interactions, butanone-2 and nitropropane for proton-acceptor and orientation interactions, benzene for π–π interactions, and ethanol for orientation interactions and hydrogen bonds. Adsorbents based on Silipore 200 and classified by A.V. Kiselev as type II adsorbents with positive charges localized on their surfaces and electron-acceptor centers that are atoms of the metal of chelate rings, interact specifi-

Table 1. Textural characteristics of the investigated adsorbents

Adsorbent	$S_{specific}$, m^2/g	V, cm^3/g	d_{av}, nm	C_{BET}	K_G
Silipore 200	200	0.91	17	130	28
Silipore 200 + nickel acetylacetonate	173	0.71	16	123	24
Silipore 200 + cobalt acetylacetonate	171	0.70	15	121	23
Silipore 200 + copper acetylacetonate	171	0.70	15	121	23

V is the total pore volume; d_{av} is the average size of samples. For $S_{specific}$, the relative error is Δ ± 10%.

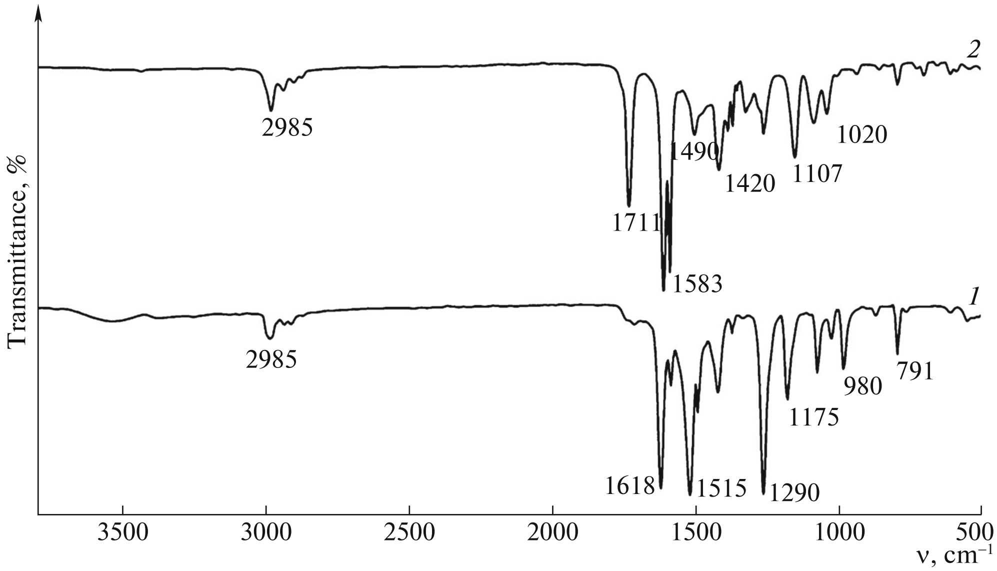

Fig. 3. (*1*) IR spectrum of sodium acetylacetonate and (*2*) IR subtraction spectra of Si-L–Si-Cl on Silipore 200.

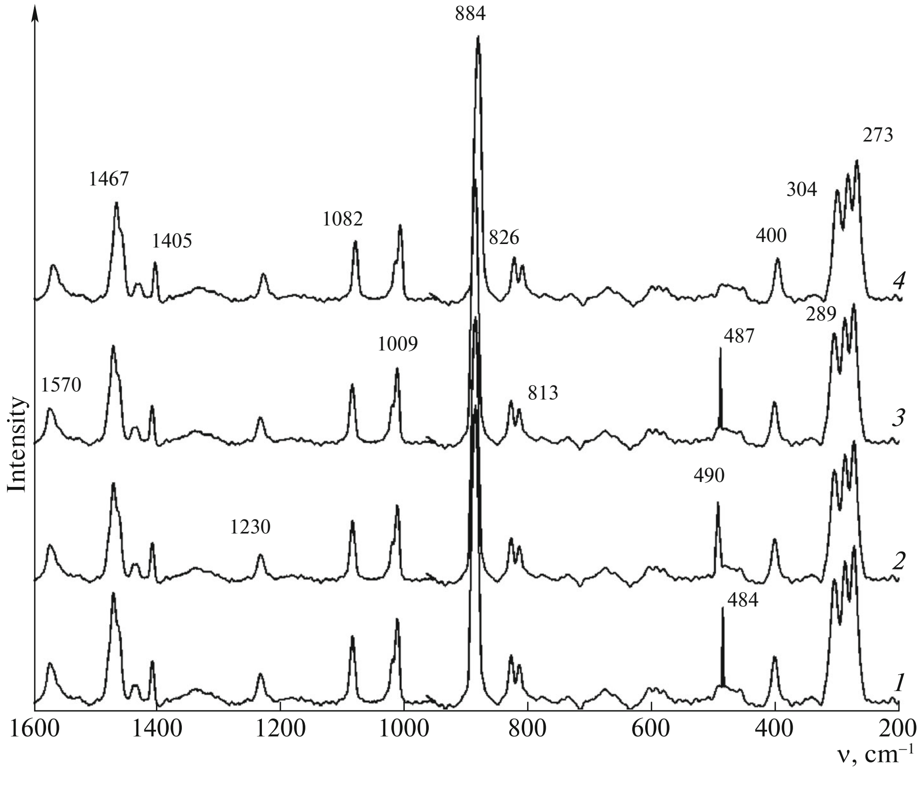

Fig. 4. Raman spectra of acetylacetonates of (*1*) nickel, (*2*) cobalt, (*3*) copper, and (*4*) acetylacetone grafted onto a Silipore 200 surface.

cally with electron-donating molecules of adsorbates according to the scheme shown in Fig. 5.

Using the retention times of sorbates, differential molar changes in the internal energy of adsorption $-\Delta\bar{U}$ equal to the differential heat of adsorption at a constant volume are calculated at different temperatures. The contribution from the specific energy of interaction $\Delta\bar{q}_{\mathrm{dif,1(specific)}}$ to the total energy of adsorption was also determined for specifically sorbed substances. It was estimated from the difference between $\bar{q}_{\mathrm{dif,1}}$ of the sorbate and the nonspecifically sorbing normal alkane with the same value of polarizability α [18]:

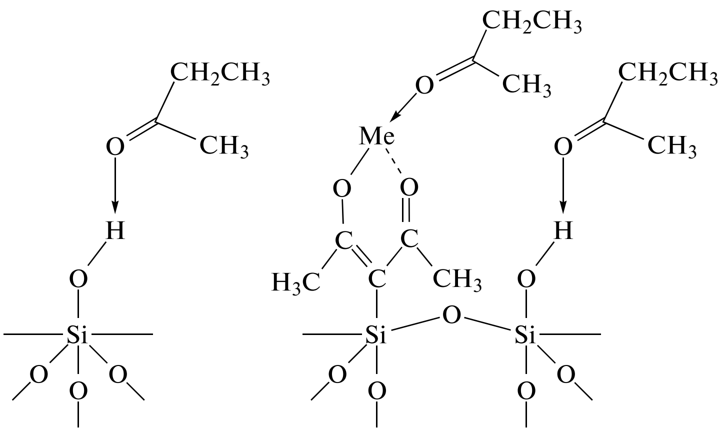
(a) (b)

Fig. 5. Possible adsorption centers of butanone-2 on surfaces of (a) the initial Silipore 200 and (b) Silipore 200 modified by metal acetylacetonates.

$$\Delta\bar{q}_{\text{dif},1\text{specific}} = \bar{q}_{\text{dif},1(\text{sorbate})} - \bar{q}_{\text{dif},1(n\text{-alkane})}.$$

Table 2 shows data on the Henry adsorption constants at 150°C for adsorbents based on Silipore 200 with chemically grafted metal acetylacetonates.

According to our results, the values of $K_{1,\mathrm{C}}$ of n-alkanes (C_6–C_9) adsorbed due to the dispersion interactions differed considerably for the initial and modified silica, while the Henry adsorption constant ($K_{1,\mathrm{C(modified)}}/K_{1,\mathrm{C(initial)}}$) grew by 1.5–1.7 times. This could indicate both an increase in the nonspecific activity of the sorption centers and an increase in their concentration. Alongside dispersion interactions with a surface of hydroxylated Silipore 200, aromatic hydrocarbons are capable of interacting with the π-electrons of an aromatic nucleus and with OH groups. Benzene is therefore sorbed on hydrophilic silica much more strongly than n-alkanes with the same number of carbon atoms in a molecule (Table 2). Removal of a part of the hydroxyl cover of silica via chemical modification doe not reduce the retention of benzene, indicating specific interaction with the modifier; meanwhile, SiO_2 with grafted layers of cobalt and copper acetylacetonates is characterized by $K_{1,\mathrm{C(modified)}}/K_{1,\mathrm{C(initial)}} = 1.23$–$1.41$. For ethanol, butanone-2, and nitropropane adsorbed on a surface of chemically modified silica due to donor–acceptor and electrostatic interactions and the formation of hydrogen bonds, the Henry constants increase in the series nickel acetylacetonate < cobalt acetylacetonate < copper acetylacetonate. At the same time, the values of $K_{1,\mathrm{C(modified)}}/K_{1,\mathrm{C(initial)}}$ grow by 1.02–1.39 times.

Figure 6 shows the logarithm of the Henry adsorption constants as a function of inverse temperature on the initial and chemically modified Silipore 200 for benzene and butanone-2.

It should be noted that for all adsorbents there is a linear relationship between $\ln K_{1,\mathrm{C}}$ of sorbates and $1000/T$ and the monotonous reduction in the values of $K_{1,\mathrm{C}}$ as the temperature rises. Upon moving from the initial to the modified adsorbents in the case of

Table 2. Henry adsorption constants ($K_{1,\mathrm{C}}$) of test compounds and values of $K_{1,\mathrm{C(modified)}}/K_{1,\mathrm{C(I)}}$ on the initial Silipore 200 (**I**) and Silipore 200 modified with nickel (**II**), cobalt (**III**), and copper (**IV**) acetylacetonates at 150°C

Compound	$K_{1,\mathrm{C}}$ (cm^3/m^2)				$K_{1,\mathrm{C(modified)}}/K_{1,\mathrm{C(I)}}$		
	I	**II**	**III**	**IV**	**II**	**III**	**IV**
n-Hexane	0.040	0.051	0.062	0.068	1.52	1.55	1.7
n-Heptane	0.043	0.062	0.065	0.071	1.44	1.51	1.65
n-Octane	0.046	0.065	0.068	0.073	1.41	1.48	1.59
n-Nonane	0.051	0.068	0.070	0.076	1.33	1.37	1.49
Benzene	0.056	0.057	0.069	0.079	1.02	1.23	1.41
Ethanol	0.328	0.381	0.415	0.456	1.17	1.27	1.39
Butanone-2	0.379	0.410	0.479	0.480	1.08	1.26	1.27
Nitropropane	0.430	0.432	0.480	0.549	1.02	1.12	1.28

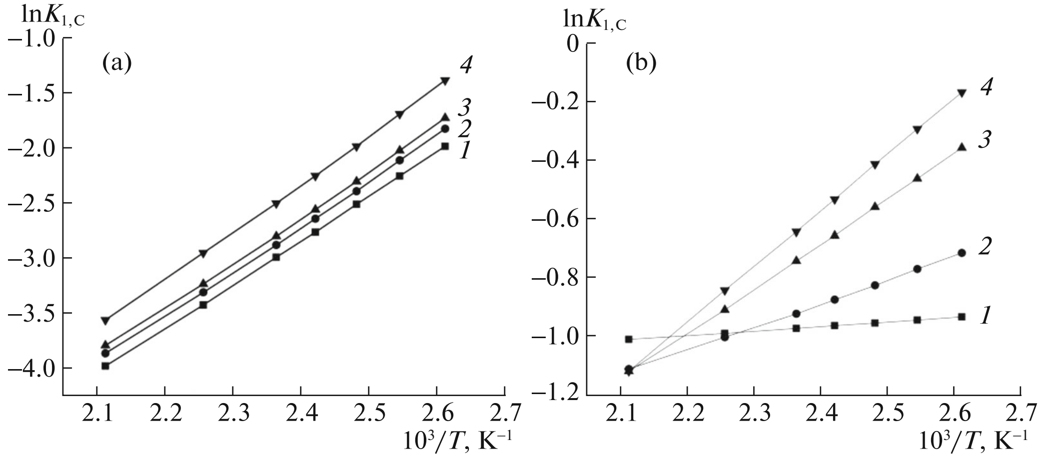

Fig. 6. Logarithm of the Henry adsorption constants of (a) benzene and (b) butanone-2 as functions of reverse temperature on (*1*) the initial Silipore 200 and Silipore 200 chemically modified by acetylacetonates of (*2*) nickel, (*3*) cobalt, and (*4*) copper.

adsorption of benzene (Fig. 5a) and hexane, there is no change in the slope of the direct dependence of $\ln K_{1,\mathrm{C}}$ as a function of $1000/T$. The modification of adsorbents with nickel, cobalt, and copper chelates (Fig. 5b) in the case of adsorption of polar organic compounds (exemplified by butanone-2) alters the slope of the direct dependence of $\ln K_{1,\mathrm{C}}$ as a function of $1000/T$, which is explained by the change in the force and concentration of active centers of the surface capable of manifesting orientational and donor-acceptor interactions [19]. Silica gels with layers of copper acetylacetonates are in this case characterized by the highest values of $K_{1,\mathrm{C}}$. Similar dependences are observed for ethanol and nitropropane.

The reasons for the changes in $K_{1,\mathrm{C}}$ when applying complex compounds are associated with the action of the energy and entropy factors. The values of $\bar{q}_{\mathrm{dif},1}$ and $\Delta\bar{S}_{1,C}^{S^0}$ are listed in Table 3.

The chemical modification of the surface of Silipore 200 with metal acetylacetonates raises the adsorption heats of organic substances from 22 to 48 kJ/mol. Comparing the values of the change in the entropy of one compound upon moving from the initial compound to the adsorbent with a layer of metal acetylacetonates, we may conclude that the mobility of adsorbate molecules changes in the adsorbed state.

The increase in $\Delta\bar{S}_{1,C}^{S^0}$ upon moving from SiO_2 to chelate-containing materials indicates a reduction in the mobility of molecules on the surfaces of modified adsorbents. At the same time, an increase in the values of $\bar{q}_{\mathrm{dif},1}$ and $\left|\Delta\bar{S}_{1,C}^{S^0}\right|$ is observed in the order Ni(II) < Co(II) < Cu(II) for SiO_2 with layers of acetylacetonates upon varying the metal ion. This effect is apparently due to the electronic structure and properties of the metal ions forming the chelate and the formation of coordinatively unsaturated complexes of metal β-diketonates on SiO_2 surfaces of different stoichiometry, mainly with an Me : L ratio of 1 : 2 for nickel and cobalt ions with square planar coordination. Intermolecular interactions of planar chelates in this case occur due to electrostatic forces at close distance.

Table 3. Thermodynamic characteristics of adsorption on the initial Silipore 200 (**I**) and Silipore 200 modified with nickel (**II**), cobalt (**III**), and copper (**IV**) acetylacetonates

Compound	$\bar{q}_{\mathrm{dif},1}$				$-\Delta S_{1,C}^{S^0}$			
	I	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**
n-Hexane	34.6	36.7	39.1	44.1	117.1	123.7	127.7	134.5
n-Heptane	34.9	37.2	39.6	44.5	119.2	124.5	128.4	135.6
n-Octane	35.6	37.5	40.3	45.6	119.8	126.3	129.3	137.1
n-Nonane	37.1	37.8	40.8	45.9	120.4	127.8	130.1	138.2
Benzene	34.7	36.9	39.1	43.2	114.9	118.4	126.6	131.5
Ethanol	21.9	26.8	28.2	29.8	82.2	83.8	85.7	87.8
Butanone-2	22.3	27.6	32.8	35.7	89.4	84.7	88.9	90.8
Nitropropane	33.6	41.9	42.7	47.7	93.6	103.5	105.6	108.9

Table 4. Values of specific energy of interaction $\Delta\bar{q}_{\text{dif},1\ (\text{specific})}$ for the initial Silipore 200 (**I**) and Silipore 200 modified by nickel (**II**), cobalt (**III**), and copper (**IV**) acetylacetonates and their contribution (%) to the total energy of adsorption

Adsorbate	**I**		**II**		**III**		**IV**	
	$\Delta\bar{q}_{\text{dif},1\ (\text{specific})}$	%	$\Delta\bar{q}_{\text{dif},1\ (\text{specific})}$	%	$\Delta\bar{q}_{\text{dif},1\ (\text{specific})}$	%	$\Delta\bar{q}_{\text{dif},1\ (\text{specific})}$	%
Benzene	7.4	21	9.1	25	10.1	26	13.2	31
Ethanol	16.1	73	22.3	83	24.8	88	27.1	91
Butanone-2	17.2	77	22.9	84	29.6	90	32.9	92
Nitropropane	26.8	79	34.6	82	37.5	88	42.8	90

Complexes of copper acetylacetonates with the d^9 configuration of the ion and a 17-electron shell characterized by square planar and tetragonal-distorted octahedral coordination, change in the ground state according to the Jahn–Teller effect [19] to form chelates of the predominant composition of Me : L = 1 : 1, as is confirmed by the data from gas chromatography and studying the acid–base centers of surfaces of the investigated adsorbents [20].

To estimate the contribution of inductive, dipole–dipole, and specific intermolecular interactions to the total energy of adsorption, the values of $\Delta\bar{q}_{\text{dif},1(\text{specific})}$ were calculated by comparing the experimental data to the heat of adsorption of a hypothetical *n*-alkane with the same polarizability as the molecules of the investigated adsorbate. The values of $\Delta\bar{q}_{\text{dif},1(\text{specific})}$ obtained for the investigated chelate-containing adsorbents (Table 4) indicate that the contribution from specific interactions to the total energy of adsorption on the surface of the initial SiO_2 was 20% for benzene. On the sample with chemically grafted copper acetylacetonate, it was up to 31%.

The highest values of $\Delta\bar{q}_{\text{dif},1(\text{specific})}$ on Silipore 200 modified with metal acetylacetonates were observed for nitropropane and butanone-2 (the value of $\Delta\bar{q}_{\text{dif},1(\text{specific})}$ reached 77–90%, indicating the emergence of strong donor–acceptor interactions) and for ethanol (91%, indicating the formation of hydrogen bonds).

CONCLUSIONS

The parameters of specific surface area, porosity, and concentration of grafted groups were determined for chelate-containing adsorbents based on Silipore 200. The thermal stability of the chelates was estimated according to data from thermal analysis; the maximum permissible temperature of the synthesized materials was 290°C.

It was found that the composition of the acetylacetonate complex affects the adsorption properties of the surfaces of chelate-containing chromatographic materials. Upon varying the metal ion in the Ni(II) < Co(II) < Cu(II) series, increases in the Henry constants and the heat and entropy of adsorption were observed with respect to all sorbates, due to the stoichiometry of the formed chelates. Chemical modification of Silipore 200 with metal acetylacetonates increased the contribution from specific interactions to the heat of adsorption, with the highest values of $\Delta\bar{q}_{\text{dif},1(\text{specific})}$ being characteristic of organic compounds that tend to form hydrogen bonds and participate in donor–acceptor complexation.

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