Interaction of cadmium nitrate with the surface of functionalized organosilicas

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The adsorption of Cd^{II} cations on the surface of amorphous macroporous silicas chemically modified by β-cyclodextrin and its functional derivatives was studied. The adsorption of Cd^{II} cations was shown to follow the equation of the Freundlich isotherm for the heterogeneous surface. Analysis of the adsorption kinetic curves showed that two parallel processes occurred on the surface of β-cyclodextrin-containing silicas. A substantial increase in the adsorption of $Cd(NO_3)_2$ is a result of the formation of uncharged supramolecular structures on the surface of silica adsorbents. The composition of these structures depends on the polarizability of functional substituents of β-cyclodextrins.

Key words: organosilica, chemical modification, β-cyclodextrin, cadmium(II) nitrate, inclusion complex, adsorption isotherm, adsorption kinetic curve, supramolecular structure.

Chemical immobilization of macrocyclic organic compounds on the surface of oxide materials is accompanied by the formation of host—guest inclusion complexes with ions and molecules. As a result, active sites are formed, which are capable of sorbing and in this way extracting and concentrating trace amounts of toxic substances.[1—3] Among oxide materials, highly dispersed amorphous silicas are undoubtedly advantageous. These adsorbents are characterized by high chemical, hydrolytic, thermal, and radiation stability, and the structure and reactivity of their active sites on the surface are well studied.[4—6]

The purpose of the present work is to study the effect of the surface structure of β-cyclodextrin-containing silicas on the adsorption of Cd^{II} cations from weakly acidic dilute solutions.

Experimental

Chemical immobilization of β-cyclodextrin (β-CD) was carried out on the surface of highly dispersed amorphous macroporous silica (Silochrome C-120) by multistep chemical modification. The interaction of hydroxylated silica (adsorbent **1**) with γ-aminopropyltriethoxysilane gave aminopropylsilochrome (adsorbent **2**). Organosilicas chemically modified with β-CD were synthesized by reacting aminopropylsilochrome with mono(toluenesulfonyl)-β-CD (adsorbent **3**), the bromo-substituted derivative of heptakis(toluenesulfonyl)-β-CD with aminopropylsilochrome (adsorbent **4**), and the bromoacetyl groups of adsorbent **4** with thiosemicarbazide (adsorbent **5**).

The structural adsorption parameters, chemical composition, and structure of the surface layer of the silica adsorbents (Table 1) were determined from the low-temperature nitrogen adsorption isotherms, elemental and chemical analyses, potentiometric titration, and data of thermogravimetry, IR spectroscopy, and ^1H NMR spectroscopy.

The adsorption of cations Cd^{II} was studied at 22 °C under static conditions by the method of separate weighed samples from $2.5 \cdot 10^{-4}$—$4.0 \cdot 10^{-3}$ *M* aqueous solutions of $Cd(NO_3)_2$ with pH ~1 at different contact times with silicas and at different concentrations of the equilibrium solution. Suspensions containing 0.025 g of the silica adsorbent and 20 cm^3 of a $Cd(NO_3)_2$ solution were maintained at constant temperature for 4 h in a JULABO SW22 aqueous thermostat with continuous shaking. The content of Cd^{II} in the starting and equilibrium solutions was determined spectrophotometrically by the absorption band intensity at λ_{max} = 576 nm on a Perkin—Elmer Lambda 35 instrument using Xylene Orange as a reagent.

The relative content of different forms of Cd^{II} in aqueous solutions at pH 1—5, which depends on the concentration of free ions NO_3^-, was calculated by the Chemical Equilibria in Aquatic System program.

UV absorption spectra of $Cd(NO_3)_2$ solutions were obtained on a Specord M-40 spectrophotometer in the wavelength range from 240 to 400 nm in quartz cells (l = 1 cm).

Table 1. Chemical composition of the surface layer of the synthesized silica adsorbents

Adsorbent	Concentration of functional groups of adsorbent /mmol g^{-1}	Content of chemical elements (%)				
		H	C	N	S	Br
1	0.40	—	—	—	—	—
2	0.28	0.45	1.00	0.40	—	—
3	0.035	0.70	2.80	0.40	—	—
4	0.01	0.60	2.20	0.40	0.20	0.70
5	0.01	0.65	2.30	0.80	0.50	—

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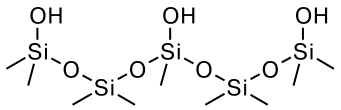

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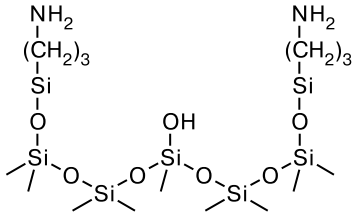

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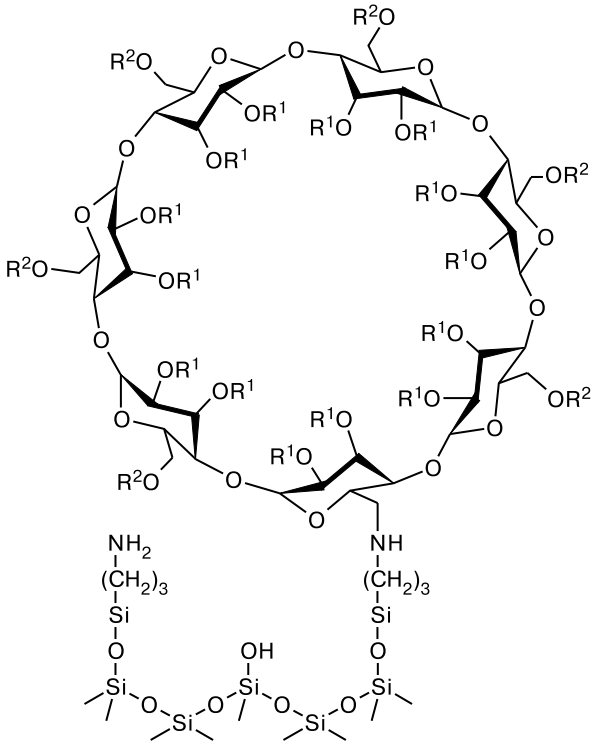

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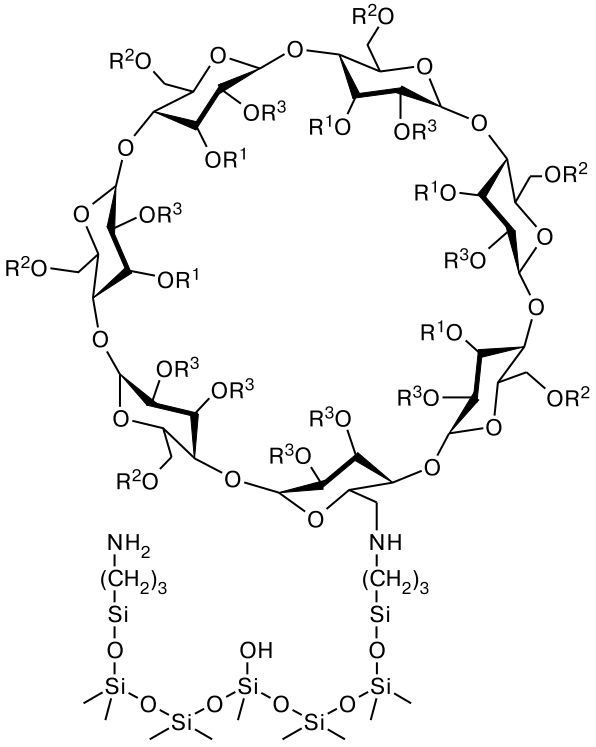

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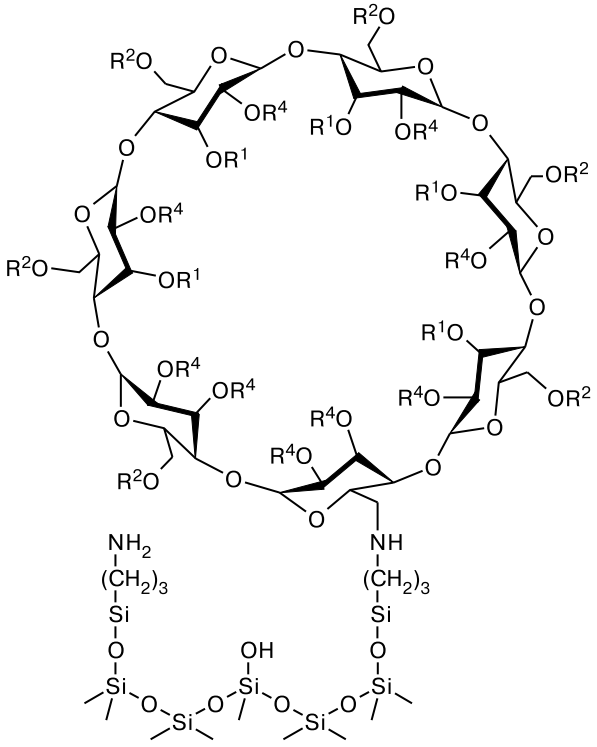

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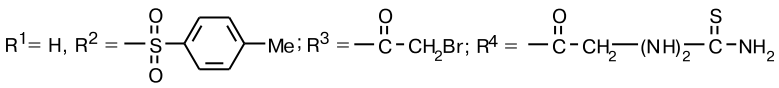

Infrared spectra were recorded on a Thermo Nicolet NEXUS one-beam FTIR spectrometer in the frequency range 4000—500 cm^{-1}; ~30-mg plates of adsorbents were pressed at 10^8 Pa.

Results and Discussion

The surface of the silica studied can adsorb Cd^{II} from aqueous solutions of $Cd(NO_3)_2$ with pH ~1, Cd^{II} as ions Cd^{2+} and $Cd(NO_3)^+$. The most part (80%) of cadmium is adsorbed as a divalent cation (Fig. 1). The adsorption equilibrium is achieved within 1 h, and organosilicas **3**—**5** adsorb the major amount of cadmium already within the first 15 min (Fig. 2). The adsorption isotherms of cations Cd^{II} for all functionalized silicas studied are shown in Fig. 3. Adsorption of cations Cd^{II} from solutions with the concentration <0.001 mol L^{-1} by adsorbents **1** and **2** is negligible. The maximum amount of Cd^{II} adsorbed from 0.001 *M* aqueous solutions 1.1, 4.6, and 5.2 times exceeds the content of chemically immobilized β-CD for adsorbents **3**, **4**, and **5**, respectively, and the distribution coefficients are two orders of magnitude higher than that of the starting silica (Table 2).

The IR spectrum of silica **1** remains almost unchanged after adsorption of cations Cd^{II} (Fig. 4, *a*, *f*). Adsorbent **2** exhibits a slight shift of the absorption bands of bending vibrations of the N—H bond of the primary amino groups (1571 and 1542 cm^{-1}) to the low-frequency region (1520 cm^{-1}), which indicates their participation in complex formation with cations Cd^{II} (see Fig. 4, *b*, *g*). The IR spectrum of adsorbent **3** (see Fig. 4, *c*) contains the absorption bands belonging to the aminopropyl groups[7] and the bands of stretching vibrations of the O—H bond of the secondary alcohol groups of β-CD (3375 and 3290 cm^{-1}). The intensity of the bands of stretching and bending vibrations of the C—H bonds (2950, 2880 cm^{-1} and 1460, 1390 cm^{-1}, respectively) is higher than that of silica **2**. After adsorption of cations Cd^{II} (see Fig. 4, *h*), the ab-

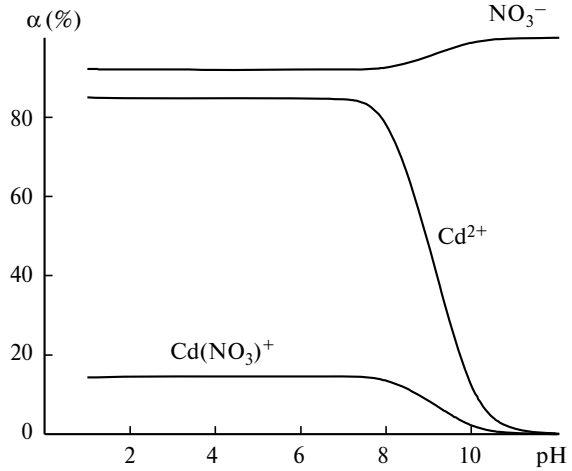

Fig. 1. Distribution of Cd^{II} forms in a 0.1 *M* solution of $Cd(NO_3)_2$ at different pH in the solution.

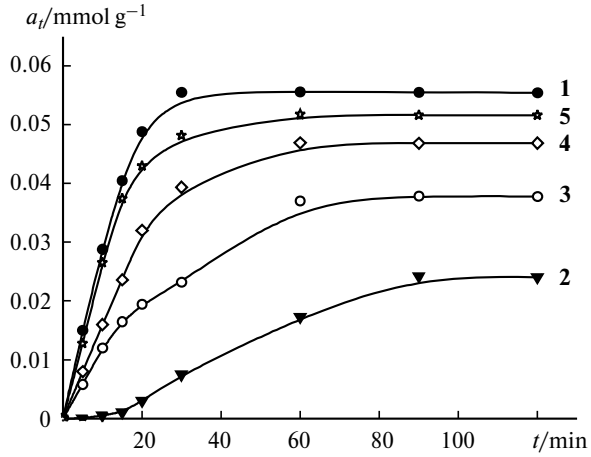

Fig. 2. Adsorption kinetics of cations Cd^{II} on silica adsorbents **1**—**5** (10^{-3} *M* aqueous solution of cadmium nitrate).

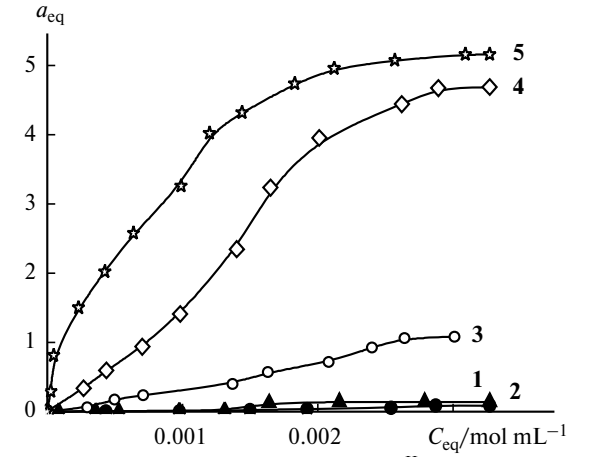

Fig. 3. Adsorption isotherms of cations Cd^{II} on silica adsorbents **1**—**5**; the values of a_{eq} are given in (mmole of Cd) (mmole of functional group)$^{-1}$.

Table 2. Structural adsorption parameters of the silica adsorbents

Adsorbent	Specific BET surface /m^2 g^{-1}	Specific adsorption* of cations Cd^{II} (%)	Distribution coefficient** /mL mg^{-1}
1	118	14	7
2	111	9	5
3	98	110	125
4	90	460	200
5	85	520	340

* The concentration of functional groups of the adsorbent was accepted to be 100%.

** The ratio of the concentration of adsorbed cadmium cations (mmol (mg of adsorbent)$^{-1}$) to its equilibrium concentration in solution (mmol mL^{-1}).

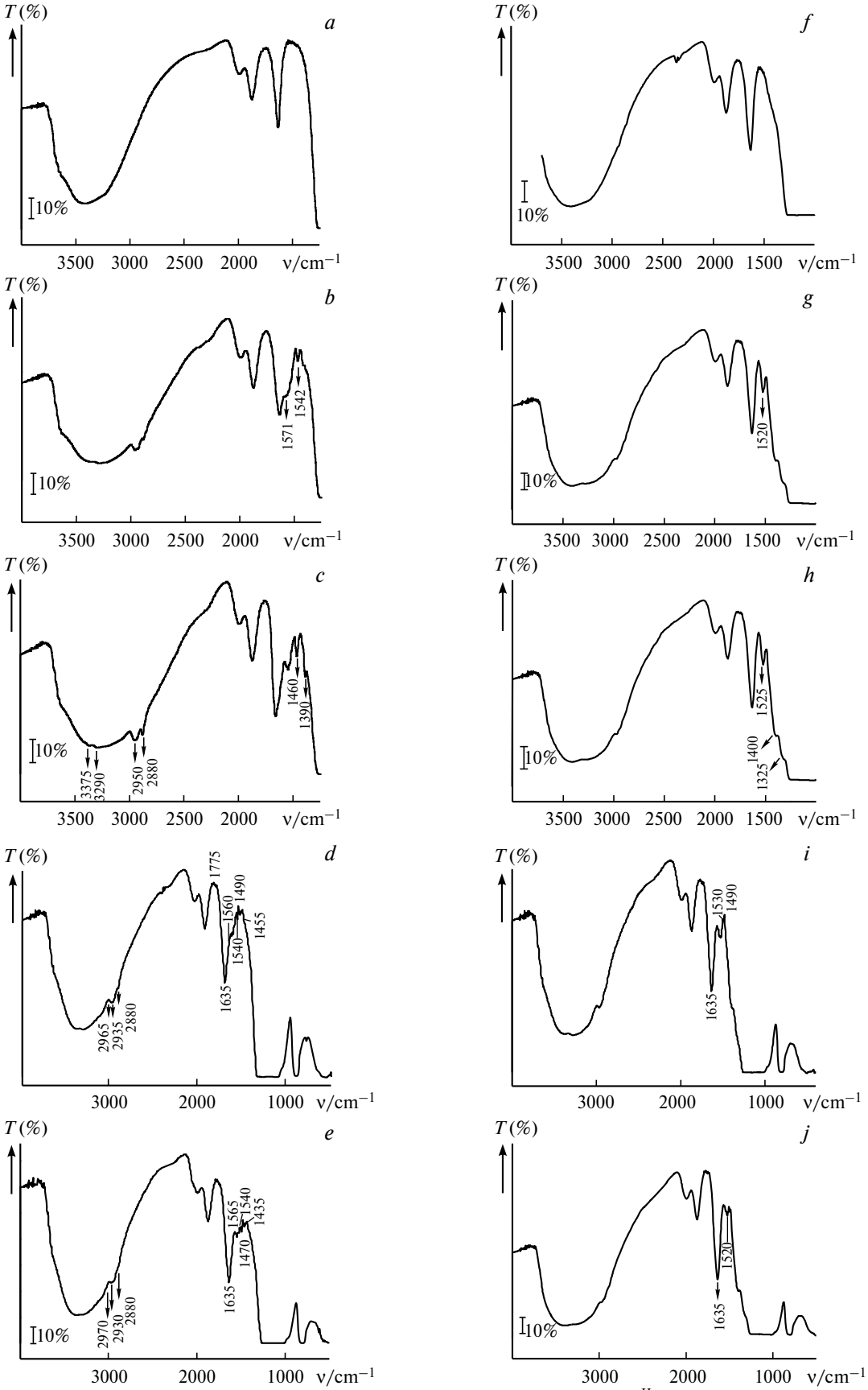

Fig. 4. IR spectra of adsorbents **1**—**5** before (*a*—*e*) and after (*f*—*j*) adsorption of cations Cd^{II}.

sorption bands of stretching vibrations of β-CD become less distinct and the absorption bands of bending vibrations of the N—H and C—H bonds shift to the low-frequency region (1525 and 1400, 1325 cm^{-1}). The IR spectrum of adsorbent **4** (see Fig. 4, *d*) contains absorption bands of bromoacetylated toluenesulfonyl-β-CD: bending vibrations of the O—H bonds in the COH groups (1635 cm^{-1}), stretching vibrations of the C=C bond (1490 cm^{-1}) of the benzene ring, and characteristic bands of stretching vibrations of the C=O (1755 cm^{-1}) and C—Br (680 cm^{-1}) bonds of the bromoacetyl group. The absorption band at 1455 cm^{-1} belongs to bending vibrations of the C—H bond, and the absorption bands at 1560 and 1540 cm^{-1} are attributed to bending vibrations of the N—H bonds of the amino groups. After adsorption of cations Cd^{II} (see Fig. 4, *i*), the absorption bands of stretching vibrations of the C—H bonds become less pronounced, the characteristic absorption bands of the C—Br and C=O bonds of the bromoacetyl groups are absent, whereas the absorption bands of bending vibrations of the N—H bonds shift to the low-frequency region (1530 cm^{-1}). The IR spectrum of adsorbent **5** (see Fig. 4, *e*) exhibits bands of C—H stretching vibrations (2970, 2935, and 2880 cm^{-1}) of the methylene groups and bending vibrations of the O—H bond (1635 cm^{-1}) of the COH groups. The absorption band at 1540 cm^{-1} belongs to bending vibrations of the N—H bond of the aminopropyl groups, and the absorption bands at 1470 and 1435 cm^{-1} are attributed to bending vibrations of the amino groups and stretching vibrations of the N—C—N and C=S bonds of thiosemicarbazide.[7] After adsorption of cations Cd^{II} (see Fig. 4, *j*), no absorption bands of N—C—N and C=S bonds are detected and the absorption band of bending vibrations of the aminopropyl groups shifts to the low-frequency region (1520 cm^{-1}). Thus, the side functional groups of the upper (broader) edge of molecules of β-CD and its two derivatives immobilized on the macroporous amorphous silica surface are involved in complex formation with Cd^{II} and the order of increasing adsorption affinity for the adsorbents is **3** < **4** < **5**.

The interaction of β-CD with $Cd(NO_3)_2$ in solution was studied to determine the characteristics of interaction of cations Cd^{II} with the internal cavity of molecules of β-CD or its functional derivatives during adsorption of $Cd(NO_3)_2$ by organosilicas **3**—**5**. The UV spectrum of a 0.001 *M* aqueous solution of $Cd(NO_3)_2$ exhibits a symmetric absorption band with λ_{max} = 301 nm and ε = = 710 L mol^{-1} cm^{-1} (Fig. 5), which belongs to the transition $n \rightarrow \pi^*$ of the N=O chromophore in the nitrate ion.[8] When specified amounts of β-CD are added to a solution of $Cd(NO_3)_2$, the absorption band of NO_3^- becomes nonsymmetrical (see Fig. 5) and its intensity increases sharply (ε = 4000 L mol^{-1} cm^{-1}). Since β-CD has no characteristic absorption bands in the UV spectral region, these spectral changes in the absorption band of the N=O chromophore indicate the interaction of NO_3^- with β-CD to form a host—guest inclusion complex[9] (Fig. 6).

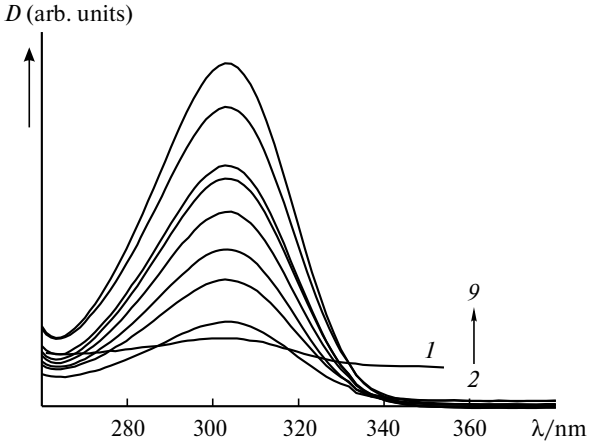

Fig. 5. UV absorption spectra of a $1 \cdot 10^{-3}$ *M* solution of $Cd(NO_3)_2$ (*1*) and binary solutions of $Cd(NO_3)_2$ and β-CD with the molar ratio [β-CD] : $[NO_3^-]$ = 20 : 1 (*2*), 12 : 1 (*3*), 7.5 : 1 (*4*), 5 : 1 (*5*), 1 : 0.3 (*6*), 1 : 0.5 (*7*), 1 : 0.8 (*8*), and 1.8 : 1 (*9*); pH = 1.08, 22 °C, exposure time 10 min.

The composition of the inclusion compound formed was determined by the method of isomolar series.[9] The experimental points lie on a straight line (Fig. 7) in the coordinates of the Benesi—Hildebrand equation for the 1 : 1 complex

$$C^0_{NO_3^-} \cdot l/D^\lambda = 1/\varepsilon^\lambda + 1/(K_s \varepsilon^\lambda C^0_{\beta\text{-CD}}),$$

where C^0 is the initial concentration of the reactant, mol L^{-1}; D^λ is the absorbance of the equilibrium solution, arb. units; ε^λ is the molar absorption coefficient of the equilibrium solution, L mol^{-1} cm^{-1}; K_s is the stability constant of the complex, L mol^{-1}; and *l* is the thickness of the absorbing layer of the analyzed solution, cm.

The volume of the internal cavity of a β-CD molecule[10] is $V_{\beta\text{-CD}} = 0.262$ nm^3, the volume of its upper part is $V_{0.5(\beta\text{-CD})} = 0.156$ nm^3, and the volume and diameter of the hydrated nitrate ion are $V_{NO_3^-} = 0.153$ nm^3 and $d_{NO_3^-} =$ = 0.67 nm, respectively. Therefore, the anion can penetrate into the internal cavity of β-CD only through the broader edge and NO_3^- can be accomodated only in the upper part of the torus of the β-CD molecule. The stability constant of the β-CD—NO_3^- complex is 1425±70 L mol^{-1}. A reason for the high strength of the β-CD—NO_3^- inclusion complex is that the volumes of the upper part of the internal cavity of β-CD and hydrated anions are almost equal.

It was found by chemical analysis that the products of interaction of β-CD (or its bromo- and sulfur-containing derivatives) with $Cd(NO_3)_2$ contain in addition to nitrate ions cadmium in the ratio $[NO_3^-]$: [Cd] = 2 : 1. Therefore, molecular adsorption of $Cd(NO_3)_2$ is observed for β-CD-containing silicas. The chemical composition of

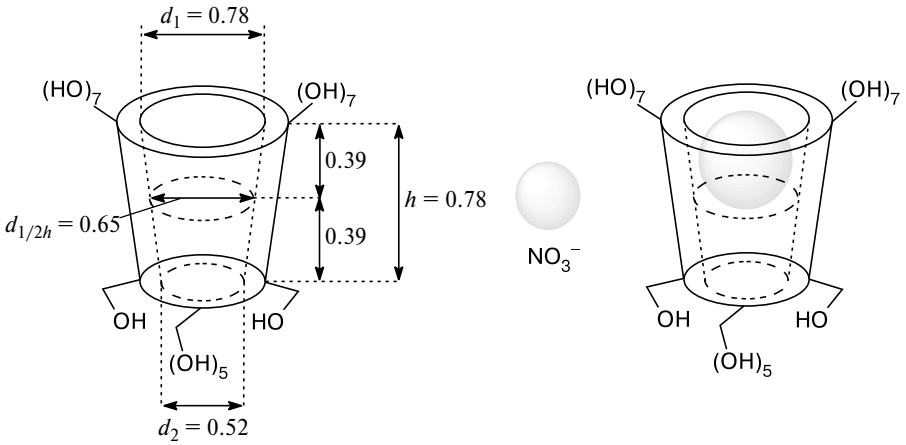

Fig. 6. Formation of the 1 : 1 β-CD—NO_3^- inclusion complex; distances (nm) are indicated.

the formed surface supramolecular compounds is listed in Table 3.

The adsorption isotherms of cations Cd^{II} for adsorbents **3**—**5** are plotted in the coordinates of the Freundlich and Langmuir equations.[11,12] The experimental data are well approximated in the coordinates of the linearized Freundlich equation describing adsorption on the heterogeneous surface (Fig. 8)

$$\log a_{eq} = \lg K_F + (1/n)\lg C_{eq},$$

where a_{eq} is the equilibrium amount adsorbed, mg g^{-1}; K_F is the Freundlich constant that characterizes the absorption capacity, mg g^{-1}; n is the Freundlich constant that characterizes the interaction of the adsorbed species; and C_{eq} is the equilibrium concentration of the adsorptive in solution, mg L^{-1}.

The calculated Freundlich constants are listed in Table 4. An increase in constants K_F and n (see Ref. 13) in the series of adsorbents **3** < **4** < **5** reflects an increasing contribution to adsorption from the side functional groups of immobilized β-CD. Thus, heterogeneity of the surface of adsorbents **3**—**5** can be due to the presence of two types of sites for adsorption of cations Cd^{II}, namely, the internal cavity of immobilized molecules of β-CD and side alcohol, bromoacetyl, or thiosemicarbazide groups. In this case, both Cd^{2+} and $Cd(NO_3)^+$ ions can be adsorbed.

To analyze the kinetic curves of Cd^{II} adsorption, the Lagergren equations[13] for processes of the pseudo-first order

$$\ln(a_{eq} - a_t) = \ln a_{eq} - k_1 t$$

(a_t and a_{eq} are the adsorption at the moment t and at equilibrium, respectively, mg g^{-1}; and k_1 is the adsorption rate constant, min^{-1}) and the pseudo-second order

$$t/a_t = 1/(k_2 a_{eq}^2) + t/a_{eq}$$

(k_2 is the adsorption rate constant, g mg^{-1} min^{-1}) were used.

For adsorbent **3**, the kinetic curve (Fig. 9) is approximated by a linear dependence in the coordinates of the

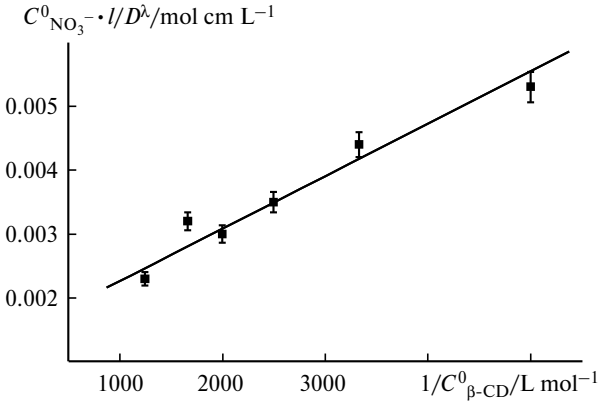

Fig. 7. Spectral characteristics of NO_3^- *vs* amount of β-CD in aqueous solutions in the coordinates of the Benesi—Hildebrand equation for the 1 : 1 inclusion compounds.

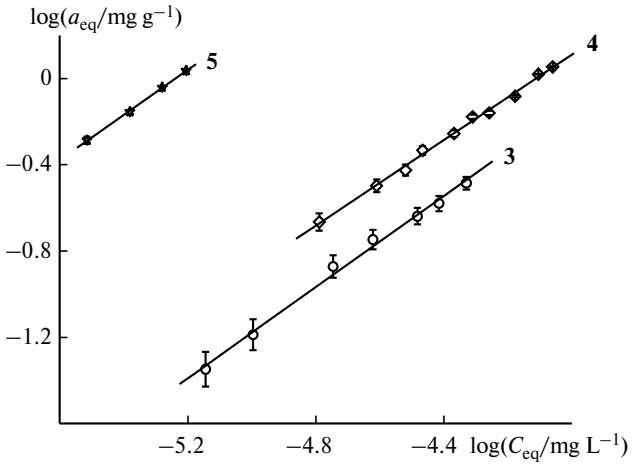

Fig. 8. Adsorption isotherms for cations Cd^{II} in the coordinates of the Freundlich equation on organosilicas **3**—**5**.

Table 3. Chemical composition of supramolecular structures formed on the surface of β-cyclodextrin-containing silicas due to the adsorption of cadmium nitrate (10^{-3} *M* $Cd(NO_3)_2$, 22 °C, 1 h)

Adsorbent	Functional groups of β-cyclodextrins		Chemical composition of supramolecular structures (elemental analysis)
	Form	Number	
3	Alcohol	21	$C_{42}H_{70}O_{34} \cdot Cd(NO_3)_2$
4	Bromoacetyl	9	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 4Cd(NO_3)_2$
5	Thiosemicarbazide	9	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 5Cd(NO_3)_2$

equation of the pseudo-second order (adsorption rate constant $k_2 = 0.312 \pm 0.019$ g mg^{-1} min^{-1}, correlation coefficient $R^2 = 0.99$), which can be due to the occurrence of two parallel reactions with sharply different rates on the adsorbent surface.[13] It is assumed that cadmium cations interact with the inner surface of chemically immobilized molecules of β-CD and with its side alcohol groups. This explanation seems quite reasonable, if we take into account that the amount of cations Cd^{II} adsorbed by adsorbent **3** insignificantly exceeds the content of chemically immobilized β-CD (see Tables 2 and 3). In adsorption of cations Cd^{II} the internal cavity of β-CD is involved and the activity of its alcohol groups in the adsorption process is low.

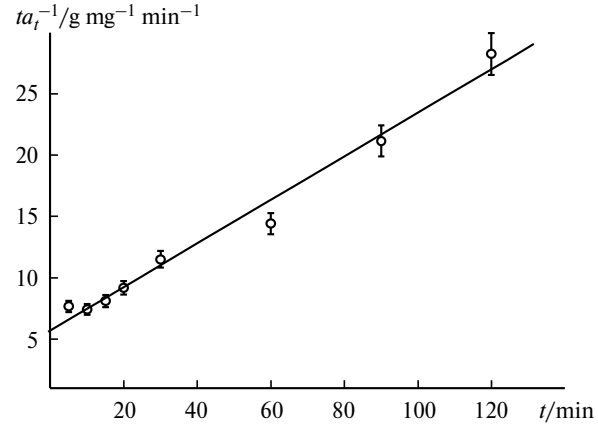

Fig. 9. Adsorption kinetics of cations Cd^{II} on adsorbent **3** in the coordinates of the Lagergren equation for the pseudo-second-order processes.

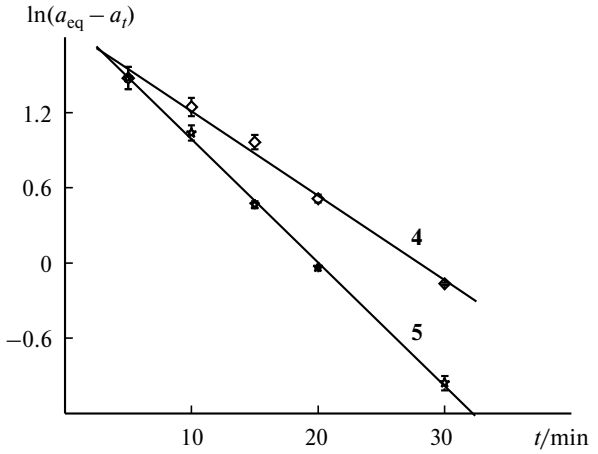

Fig. 10. Adsorption kinetics of cations Cd^{II} on adsorbents **4** and **5** in the coordinates of the Lagergren equation for the pseudo-first-order processes.

The kinetic curves for adsorbents **4** and **5** (Fig. 10) are consistent with the model of pseudo-first-order processes ($R^2 = 0.99$ and the adsorption rate constants $k_1 = 1.88 \pm 0.11$ and 1.97 ± 0.12 min^{-1}, respectively). A higher complexation ability of bromoacetyl and thiosemicarbazide substituents compared to alcohol groups[14] favors this model (see Table 3). The character of changing the IR spectra of adsorbents **1**—**5** before and after adsorption of cations Cd^{II} confirms this conclusion. Thus, cations Cd^{II} interact with the side functional groups of β-CD chemically immobilized on the silica surface and also with the internal cavity of β-CD (through NO_3^-) to form uncharged supramolecular structures on the surface of the silica adsorbents, The composition of these supramolecular structures depends on the polarizability of the functional substituents of β-CD.[14]

Thus, the interaction of $Cd(NO_3)_2$ with β-CD in solutions and on the surface of highly dispersed amorphous silicas chemically modified by β-CD and its bromo- and sulfur-containing functional derivatives was studied by IR and UV spectroscopies, elemental and chemical analyses, and adsorption measurements. Adsorption of cations Cd^{II} is described by the equation of the Freundlich isotherm for the heterogeneous surface. The adsorption kinetic curves analyzed in terms of the Lagergren model for reactions of

Table 4. Freundlich constants n and K_F for the adsorption of cadmium(II) cations on β-cyclodextrin-containing silicas at 22 °C

Adsorbent	n	K_F/mg g^{-1}	R^2
3	0.80	3.90±0.23	0.99
4	1.00	4.30±0.26	0.99
5	1.25	5.50±0.33	0.99

the pseudo-first and pseudo-second orders confirm that two parallel processes occur on the surface of β-CD-containing silicas. It was proved that the molecular adsorption of $Cd(NO_3)_2$ occurred with the formation on the surface of β-CD-containing silicas of supramolecular structures, whose chemical composition depends on the polarizability of their functional substituents.

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