ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2008, Vol. 82, No. 8, pp. 1357–1362. © Pleiades Publishing, Ltd., 2008.
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# The Adsorption of Mercury(II) on the Surface of Silica Modified with β-Cyclodextrin

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Received April 17, 2007

**Abstract**—Multistage chemical modification of the surface of silica with β-cyclodextrin was performed. IR spectroscopy and quantitative analysis of surface compounds were used to prove the structure of modified silica. The adsorption of Hg(II) from dilute solutions was studied. The adsorption affinity of silica for mercury ions increased because of the formation of supramolecular structures with chemically immobilized β-cyclodextrin.

**DOI:** 10.1134/S0036024408080190

## INTRODUCTION

The increased interest of researchers in cyclodextrins (cyclic oligosaccharides) stems from their unique ability to form inclusion host–guest complexes with many organic compounds [1, 2] and the possibility of using them in various areas of science and technology, including the preparation of selective adsorbents, active catalysts, and sensitive sensor elements [3–5]; the chromatographic separation and purification of organic compounds with similar structures and compositions [6]; the extraction and concentration of traces of toxic compounds [7]; and the preparation and detoxication of medicines of prolonged action [8, 9]. Studies of the adsorption selectivity of cyclodextrins with respect to heavy metal ions are of obvious interest. The results can be used in chemical analysis, removal from the environment, and utilization of these ions [10–12]. Insoluble cyclodextrins and cyclodextrins immobilized on various carriers, including inorganic carriers, are most suitable in practice [1, 2, 13].

In this work, we studied the influence of the chemical immobilization of β-cyclodextrin (β-CD) on the adsorption properties of amorphous macroporous silica with respect to Hg(II) ions.

## EXPERIMENTAL

Macroporous amorphous silica, silochrom S-120 with a specific surface area of 118 $m^2$/g, mean pore diameter 40 nm, and silanol group concentration 0.4 mmol/g, was used as the initial silica adsorbent. β-Cyclodextrin (Fluka, major component content no less than 99%, water content 12.7%) was evacuated before use at 105°C for 7 h. 4-Tolylsulfonyl chloride (*p*-tosyl chloride, TsCl, Merck) was used without additional purification.

The infrared spectra were recorded on a Thermo Nicolet NEXUS single-beam IR Fourier transform spectrophotometer over the frequency range 4000–500 $cm^{-1}$. The samples were prepared by pressing adsorbents into pellets of weight ~30 mg at a pressure of $10^8$ Pa. The nuclear magnetic resonance $^1$H NMR spectra were recorded at 25°C on a Varian-VXR-300 (300 MHz) spectrometer in dimethylsulfoxide-$d_6$ (DMSO-$d_6$) with tetramethylsilane as an internal reference. Elemental analyses were made on an Elemental Analyzer EA 1110 instrument.

The concentration of silanol groups in the adsorbents was determined from the chemisorption of dimethylchlorosilane, and the concentration of aminopropyl groups, by pH titration and thermogravimetry. Thermogravimetry was also used to find the content of immobilized β-cyclodextrin [14]. The adsorption of mercury(II) ions was performed from solutions with pH ~ 1 and mercury nitrate concentrations $2.5 \times 10^{-4}$–$4.0 \times 10^{-3}$ M depending on the contact time with silica and equilibrium solution concentration. Adsorption was studied under static conditions by the method of separate samples at 22°C. The content of Hg(II) in the initial and equilibrium solutions was determined by atom absorption spectrometry on a Pye Unicam SP-9 instrument and by back trilonometric titration [15].

## RESULTS AND DISCUSSION

β-Cyclodextrin was chemically immobilized by the multistage modification of the surface of silica, including the preparation of β-cyclodextrin modified by tosyl groups, silica surface modification with aminopropyl groups, and chemical fixation of tosyl-β-cyclodextrin on the surface of aminopropylsilica.

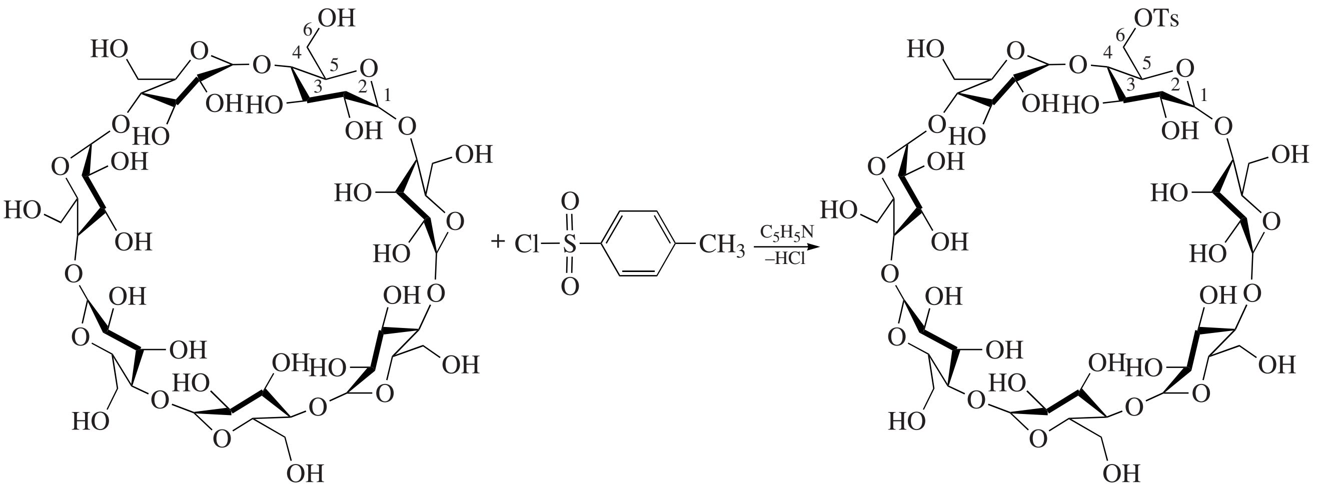
Tosyl-β-cyclodextrin was prepared as described in [16]. The interaction of β-cyclodextrin with 4-tolylsulfonyl chloride results in the electrophilic substitution of tosyl groups for alcohol group protons (first, primary protons in position 6) [2, 16]. The IR spectrum of β-cyclodextrin (Fig. 1) brought in contact with a solution of 4-tolylsulfonyl chloride contained not only β-CD bands but also absorption bands of the tolylsulfonyl group at 1598 cm$^{-1}$ (benzene ring C=C bond stretching vibrations), 1366 cm$^{-1}$ (asymmetric S=O bond stretching vibrations of the $R_1$–O–$SO_2$–$R_2$ group), and 815 cm$^{-1}$ (out-of-plane bending vibrations of aromatic C–H bonds).

The appearance of proton signals (Fig. 2) in the $^1$H NMR spectrum of modified β-cyclodextrin with chemical shifts δ (ppm) of 2.433 (s, the methyl radical of the tosyl group), 7.452 (d, benzene ring 3 and 5 protons), and 7.747 (d, benzene ring 2 and 6 protons) [17] was indicative of tosyl group grafting.

The elemental analysis data on modified β-CD,

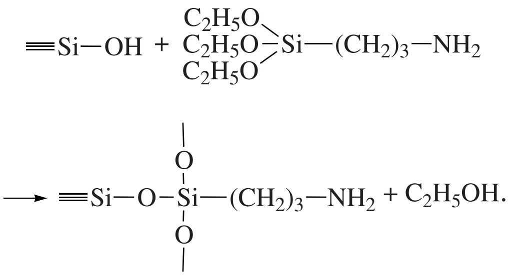
| Element | C | H | S |
|---|---|---|---|
| Found, % | 45.65 | 5.97 | 2.41 |
| Calculated, % | 45.62 | 6.01 | 2.48 |

are evidence of the participation of only one primary alcohol group in the reaction with 4-tolylsulfonyl chloride,



The yield of synthesized mono-(6-O-tolylsulfonyl)-β-cyclodextrin (Ts-β-CD) was 35%.

The modification of the surface of silica with aminopropyl groups was performed following the procedure described in [18],



$$\equiv Si{-}OH + (C_2H_5O)_3Si{-}(CH_2)_3{-}NH_2 \longrightarrow \equiv Si{-}O{-}\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}{-}(CH_2)_3{-}NH_2 + C_2H_5OH.$$

The interaction of aminopropylsilica (table) with mono-(6-O-tolylsulfonyl)-β-cyclodextrin was performed under the conditions optimum for electrophilic substitution of β-cyclodextrin groups for aminopropyl group protons on the surface of silica [14]. The IR spectrum of aminopropylsilica (Fig. 3a, spectrum *3*) modified with a solution of Ts-β-CD in pyridine at 60°C contained absorption bands of O–H bond stretching vibrations of secondary alcohol groups (3373 and 3289 cm$^{-1}$), β-cyclodextrin C–H bond stretching vibrations (2948 and 2877 cm$^{-1}$),

Chemical composition of the surface layer of silica adsorbents and their structure-sorption parameters

| Adsorbent | $R_i$, mmol/g | | | $s_{sp}$, m$^2$/g | [Hg] : [$R_i$] |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | | |
| 1 | 0.40 | – | – | 118 | 0.25 |
| 2 | 0.12 | 0.28 | – | 111 | 0.28 |
| 3 | 0.12 | 0.24 | 0.035 | 98 | 3.80 |

Note: $R_i$ is the adsorbent functional group ($R_1$, silanol; $R_2$, aminopropyl; and $R_3$, β-cyclodextrin) and $s_{sp}$ is the specific surface area.

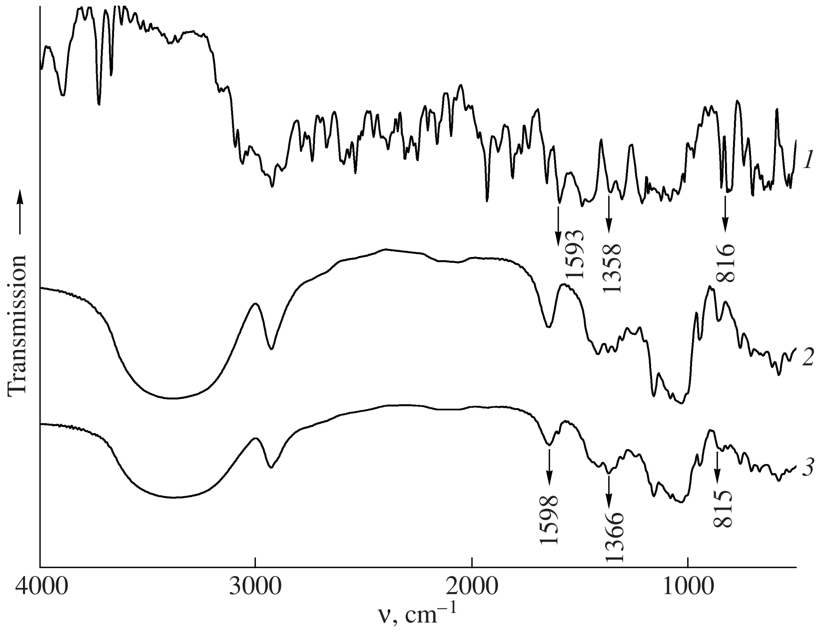
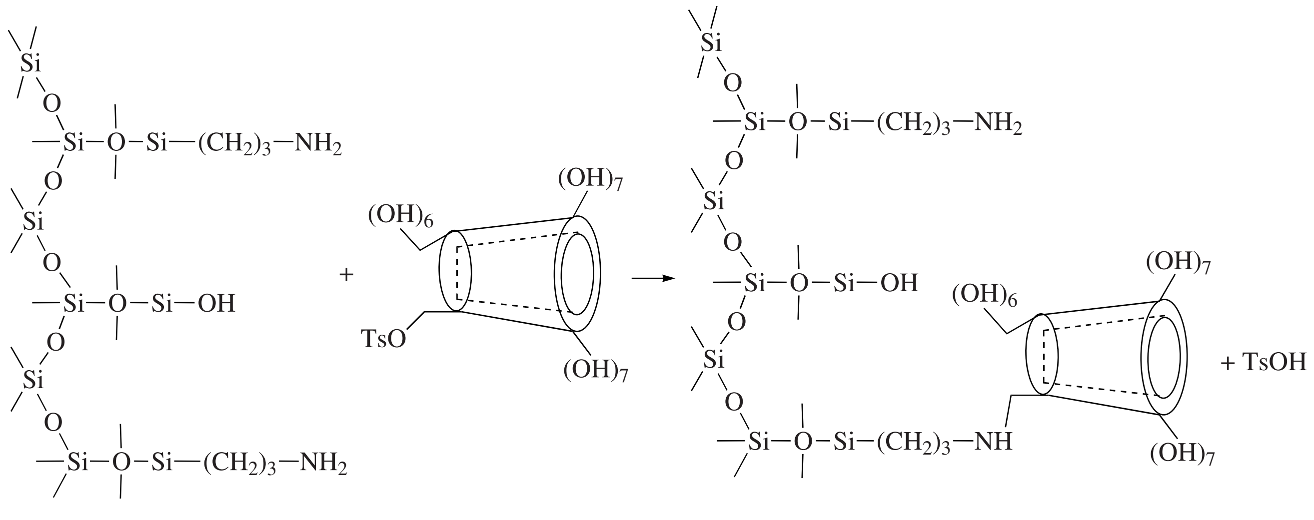
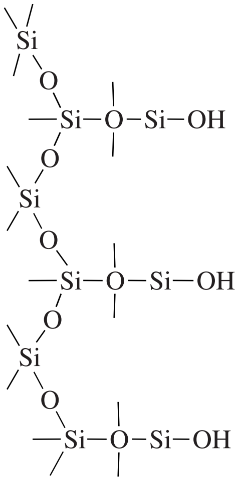


**Fig. 1.** IR spectra of (*1*) 4-tolylsulfonyl chloride, (*2*) β-cyclodextrin before interaction with *p*-tosyl chloride, and (*3*) β-cyclodextrin after interaction.

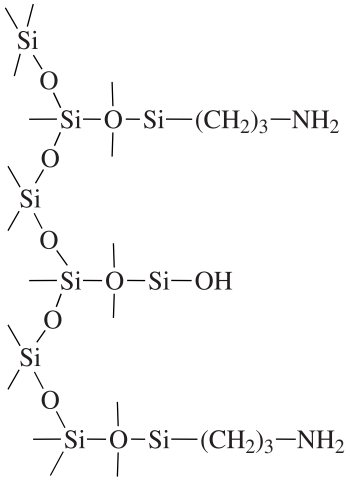
and N–H and C–H bond bending vibrations (1590, 1542 and 1458, 1388 cm$^{-1}$, respectively). The presence of bending vibrations of primary and secondary amino groups in the IR spectrum is evidence of the partial participation of primary aminopropyl groups in the chemical grafting of Ts-β-CD. The absence of absorption bands of C=C benzene ring bonds and S=O asymmetric stretching vibrations of $R_1$–O–$SO_2$–$R_2$ groups in the IR spectrum of modified silica proves that the electrophilic substitution of the tosyl group Ts-β-CD occurs on the surface of aminopropylsilica,



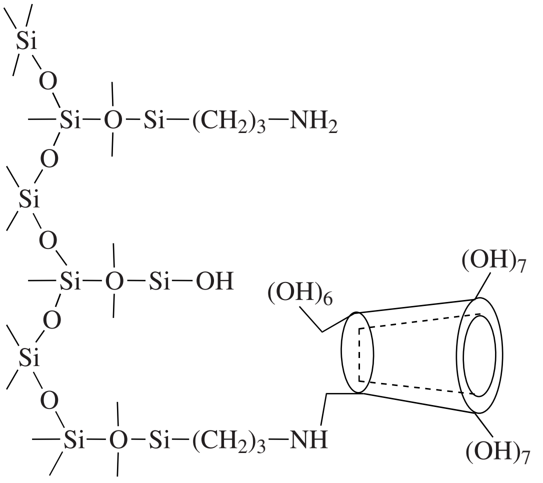
The amount of grafted β-cyclodextrin was 0.035 mmol/g silica. Since the contact area of the β-CD molecule is 2.41 nm$^2$, immobilized β-cyclodextrin occupies ~50% of the surface of modified silica. The structure of the surface of the silica adsorbents studied is shown in the scheme,



(adsorbent 1)



(adsorbent 2)



(adsorbent 3)

and their structure-sorption parameters and the chemical composition of the surface layer are presented in the table.

Adsorption equilibrium is established in 1 h for adsorbents 1 and 3 brought in contact with solutions of mercury nitrate and in 2.5 h for adsorbent 2 (Fig. 4). This is evidence of the absence of diffusion limitations also after the modification of the surface of macroporous silica. Hydroxylated silica (adsorbent 1) virtually does not absorb mercury ions from ~$10^{-4}$ M solutions of $Hg(NO_3)_2$ (Fig. 5). At a Hg(II) concentration higher by an order of magnitude, only 25% of silanol groups on the surface of adsorbent 1 participate in adsorption.

Similar results were obtained for aminopropylsilica (adsorbent 2), whereas the modification of the surface of silica with β-cyclodextrin substantially increased the affinity of the sorbent for Hg(II), and the static capacity was already attained in dilute solutions. The distribution coefficient for adsorbent 3 is 625. These results are in agreement with the data obtained using IR spectroscopy. The IR spectrum of hydroxylated silica does not change substantially after the adsorption of mercury(II) (Fig. 3b, spectrum *1*). After the adsorption of mercury on aminopropylsilica (Fig. 3b, spectrum *2*), the IR bands corresponding to bending N–H bond vibrations in primary amino groups (1571 and 1542 $cm^{-1}$) slightly shift to lower frequencies (1526 $cm^{-1}$), likely because of complex formation on the surface of the adsorbent [19].

The IR spectrum of adsorbent 3 (Fig. 3a, spectrum *3*) contains not only absorption bands of aminopropyl groups but also O–H bond stretching vibration frequencies of secondary alcohol groups of β-cyclodextrin (3373 and 3289 $cm^{-1}$), and the intensity of stretching and bending C–H bond vibrations (2948, 2877 and 1458, 1388 $cm^{-1}$) increases compared with aminopropylsilica. After the adsorption of mercury

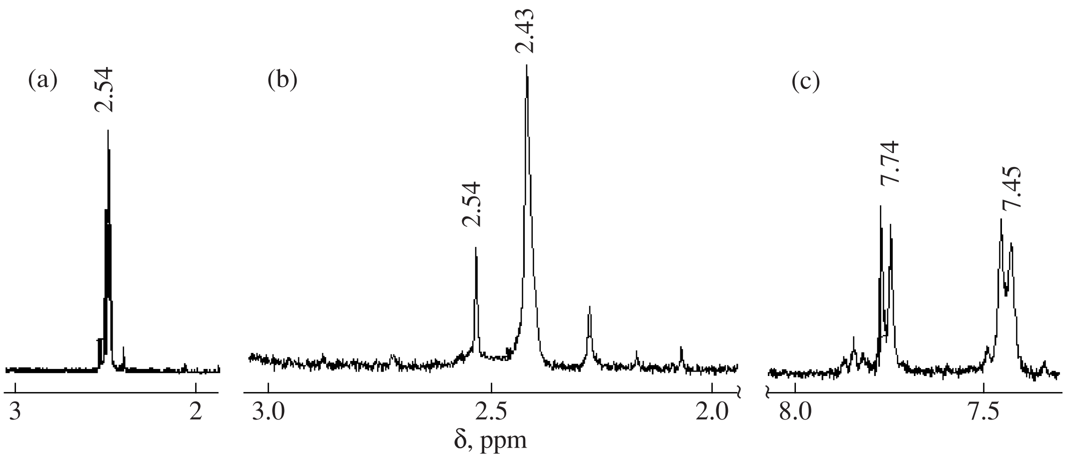


**Fig. 2.** NMR spectra of β-cyclodextrin (a) before and (b, c) after its interaction with *p*-tosyl chloride.

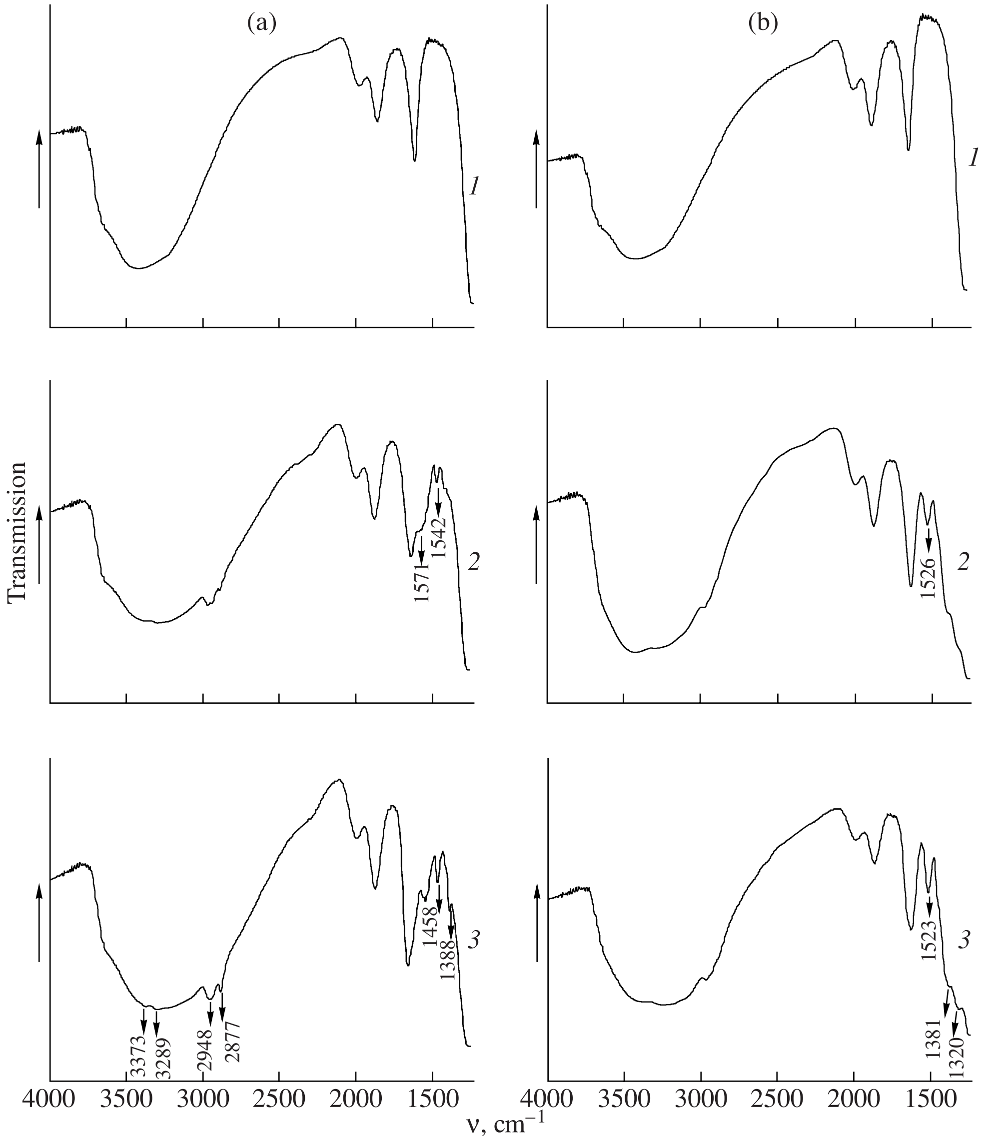


**Fig. 3.** IR spectra of adsorbents 1–3 (a) before and (b) after adsorption of mercury(II).

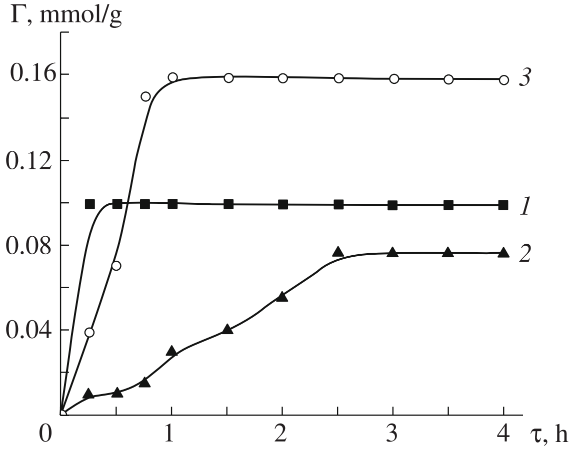


**Fig. 4.** Adsorption of mercury(II) ions on silica adsorbents 1–3 depending on contact time with a 0.01 M aqueous solution of mercury nitrate.

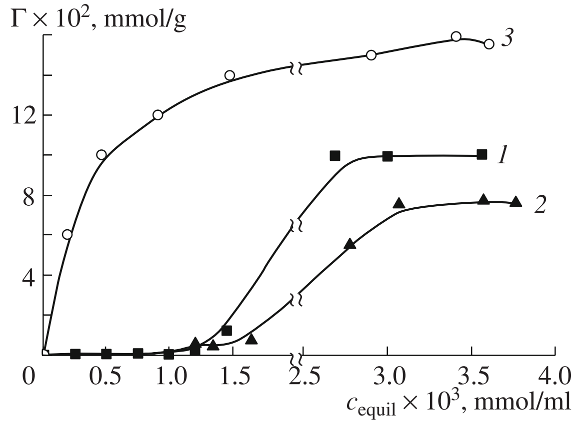


**Fig. 5.** Isotherms of the adsorption of mercury(II) ions on silica adsorbents 1–3 from aqueous solutions of mercury nitrate of concentration $c_{\mathrm{equil}}$.

(Fig. 3b, spectrum *3*), the absorption bands of β-cyclodextrin stretching vibrations become less pronounced, and the absorption bands of N–H and C–H bond bending vibrations shift to lower frequencies (1523, 1381, and 1320 $cm^{-1}$). It follows that the centers of mercury(II) adsorption in adsorbent 3 are chemically anchored β-cyclodextrin molecules and primary aminopropyl groups unreacted with mono-(6-O-tolylsulfonyl)-β-cyclodextrin (table). Since the total concentration of active centers of adsorbents 1–3 is constant (table), and only the chemical composition of their surface changes, an increase in the adsorption of Hg(II) is related to the immobilization of β-cyclodextrin. The [Hg] : [functional group] ratio is smaller than one for adsorbents 1 and 2 and an order of magnitude higher for adsorbent 3 (table). This leads us to suggest that supramolecular structures (inclusion complexes between β-cyclodextrin and Hg(II) ions) are formed on the surface of silica modified with β-cyclodextrin.

## ACKNOWLEDGMENTS

This work was financially supported by the European Commission (grant ICA2-CT-10052) and the Complex Program for Basic Research of the National Academy of Sciences of Ukraine “Nanostructured Systems, Nanomaterials, and Nanotechnologies” (project no. 0103U006289).

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