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Complex Formation Involving Hg^{2+} Ions on the Surface of the Polysiloxane Xerogels Functionalized by 3-Mercaptopropyl Groups

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Abstract—The influence of parameters of the porous structure and the surface layer composition of the xerogels containing 3-marcaptopropyl and alkyl groups on their sorption properties toward the Hg^{2+} ions and the stability constants of the formed complexes, which are calculated using the model of chemical reactions, is studied. An increase in the overall surface concentration of the functional groups is shown to induce a change in the composition of the formed complexes. At the concentration of the functional groups lower than 0.01 mmol/m^2 the $[HgS(CH_2)_3Si\equiv]^+$ complexes are formed, and above 0.01 mmol/m^2 the composition of the complexes depends on the mercury(II) content in the starting solution: at low contents the $[Hg\{S(CH_2)_3Si\equiv\}_2]$ complexes are formed, whereas at higher concentrations the composition of the complexes becomes simpler. Only the $[Hg\{S(CH_2)_3Si\equiv\}_2]$ complexes are formed on the nearly nonporous xerogel with the polymeric structure of the surface layer (the functional group concentration is 0.38 mmol/m^2). This, in turn, leads to the situation that the maximum static sorption capacity (590–620 (mg of Hg^{2+})/(g of sorbent)) is observed for the xerogels with a rather low content of the 3-mercaptopropyl groups (3.0–3.8 mmol/g). The stability of the formed complexes also depends on the surface concentration of the functional groups: the stability constant of the 1 : 1 Hg(II) complexes decreases with an increase in the concentration of thiol groups. The introduction of alkyl groups into the surface layer also decreases the stability of the complexes formed. The $[Hg\{S(CH_2)_3Si\equiv\}_2]$ complexes formed in the surface layer of the xerogels are characterized by similar stability constants.

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INTRODUCTION

Living organisms are seriously threatened by the abundance of heavy metals and their highly toxic compounds in the environment [1]. At present the World Health Organization classifies these substances as global pollutants. A considerable part of these pollutions falls on mercury and its compounds [2, 3]. Therefore, a wide range of sorbents containing, in particular, the donating sulfur atoms capable of interacting with mercury(II) creates prerequisites for the efficient solution of specific applied problems of environmental protection from such pollutants [4].

From this point of view, hybrid organic–inorganic sorption materials are of special interest: functionalized polysiloxane xerogels and mesoporous silicas, which are usually prepared using the sol–gel [5] or template method [6]. The application of the sol–gel method makes it possible to obtain in one stage the xerogels with the surface layer of necessary nature and a specified content of functional groups in it [7], which is an approach to the creation of selective sorbents for heavy metal extraction from aqueous solutions [8]. Such sorbents are characterized by high chemical and thermal stability and have the developed porous structure and often a high static sorption capacity (SSC) [9]. We earlier [10–12] showed that the variation of the nature of reacting alkoxysilanes and their ratio allows the easy preparation of polysiloxane xerogels functionalized by 3-mercaptopropyl ($\equiv Si(CH_2)_3SH$) groups or simultaneously 3-mercaptopropyl and alkyl (methyl or *n*-propyl) groups.

The purpose of this work is to study the influence of the surface layer composition and the porous structure parameters of these xerogels on the composition and stability of the mercury(II) complexes with the surface 3-mercaptopropyl groups.

EXPERIMENTAL

Polysiloxane xerogels containing thiol groups in the surface layer were prepared by the combined hydrolysis and polycondensation of tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) and 3-mercaptopropyltrimethoxysilane ($(CH_3O)_3Si(CH_2)_3SH$, MPTMS) in methanol (fluoride ion as a catalyst) [10]. Analogously to the use of ethanol as the solvent, the xerogels containing

Table 1. Content of 3-mercaptopropyl groups in the synthesized xerogels and the parameters of the xerogel porous structure

Sample*	Molar ratio of alkoxysilanes in starting solutio**	S_{sp}, m^2/g	$V_{\text{Ò}}$, cm^3/g	d_{eff}, nm	c_{SH}, mmol/g	c_{SH}, $mmol/m^2$
	TEOS : MPTMS					
1TM	4 : 1	631	0.36	2.3	2.9	0.005
2TM	2 : 1	356	0.22	2.5	4.1	0.012
3TM	1 : 1	13			5.0	0.38
	TEOS : MPTMS : MTES					
4TMM	4 : 1 : 3	394	0.23	3.4	1.7	0.004
5TMM	4 : 2 : 2	376	0.23	3.1	2.9	0.008
6TMM	4 : 3 : 1	44			4.4	0.1
7TMM	4 : 0.5 : 1.5	678	0.54	3.8	1.2	0.002
8TMM	4 : 1 : 1	564	0.36	3.8	2.1	0.004
9TMM	4 : 1.5 : 0.5	408	0.25	3.4	3.1	0.008
	TEOS : MPTMP : PTES					
10TMP	4 : 0.5 : 1.5	546	0.54	4.3	1.1	0.002
11TMP	4 : 1 : 1	379	0.27	3.8	2.0	0.006
12TMP	4 : 1.5 : 0.5	413	0.25	2.7	3.1	0.008

Notes: * The designation of the sample corresponds to the first letter of the alkoxysilane abbreviation.
** MTES is methyltriethoxysilane; PTES is *n*-propyltriethoxysilane.

3-mercaptopropyl ($\equiv Si(CH_2)_3SH$) and methyl ($\equiv SiCH_3$) or *n*-propyl ($\equiv Si(CH_2)_2CH_3$)) groups were prepared [11, 12]. The xerogels studied were nonhygroscopic white powders, and their main characteristics are listed in Table 1.

The sorption of mercury(II) from nitric acid solutions was studied in the static regime (a weighed sample of the sorbent was 0.1 g (±0.0005), the total volume of the solution was 20 cm^3, pH of the starting solution was ~2.0, $T = 20°C$). The xerogel fraction with the particle size <0.063 mm was used. In some cases, weighed samples of the xerogels containing alkyl groups were wet with a small amount of ethanol (0.2 cm^3). The ionic strength was maintained constant by the addition of a 0.1 M solution of $NaNO_3$. A solution of mercury(II) nitrate with a concentration of 0.05 mol/l was prepared by the dissolution of a weighed sample of $Hg(NO_3)_2 \cdot H_2O$ (analytical grade) in 0.01 M nitric acid. The mercury(II) content both in the starting solution and after sorption was determined by the inverse titration of a Trilon B excess with a 0.05 M solution of $MgSO_4$ [13]. In all experiments, the time of sorption of metal ions was 48 h to achieve the sorption equilibrium in the systems under study. The suspension was stirred several times during a working day. After the solution above the precipitate was completely clarified, an aliquot was taken and the Hg(II) content in it was determined. The amount adsorbed (in mmol/g) was estimated from the difference between the Hg(II) content in the solution before and after sorption.

The data obtained were used to plot the sorption isotherms of mercury(II) (Fig. 1). To determine the stability constants of the formed Hg(II) complexes, the experimental data were processed using the CLINP 2.1 program [14]. The experimental points in the isotherms for which the equilibrium concentration of mercury(II) did not exceed 10 mmol/l and the ionic strength of the solution was 0.10–0.11 mol/l were used in the calculation. At a specified stoichiometric composition of the reaction products, the stability constants $\log\beta_{11}$ and $\log\beta_{12}$ were calculated by the nonlinear least-squares method minimizing the residual dispersion

$$S_0 = \frac{1}{N-V}\sum_{k=1}^{N} W_k\left(A_k^{\text{выч}} - A_k^{\text{эксп}}\right)^2,$$

where A_k^{calcd} is the measured property calculated by the model, A_k^{exp} is the measured property obtained experimentally, N is the number of points in the composition–property dependence, V is the number of calculated parameters, k is the number of the experimental point, and $W_k = 1/[A_k s_r(A_k)]^2$ is the statistical weight of the kth measurement with the relative measurement error $s_r(A_k)$ (it was accepted in the calculations that $s_r(A_k) = 0.1$–0.25).

The model was recognized as adequate if the order of magnitude of the residual dispersion was 1.

The IR spectra of the xerogels were recorded on a Nicolet NEXUS FTIR spectrometer in a region of 400–

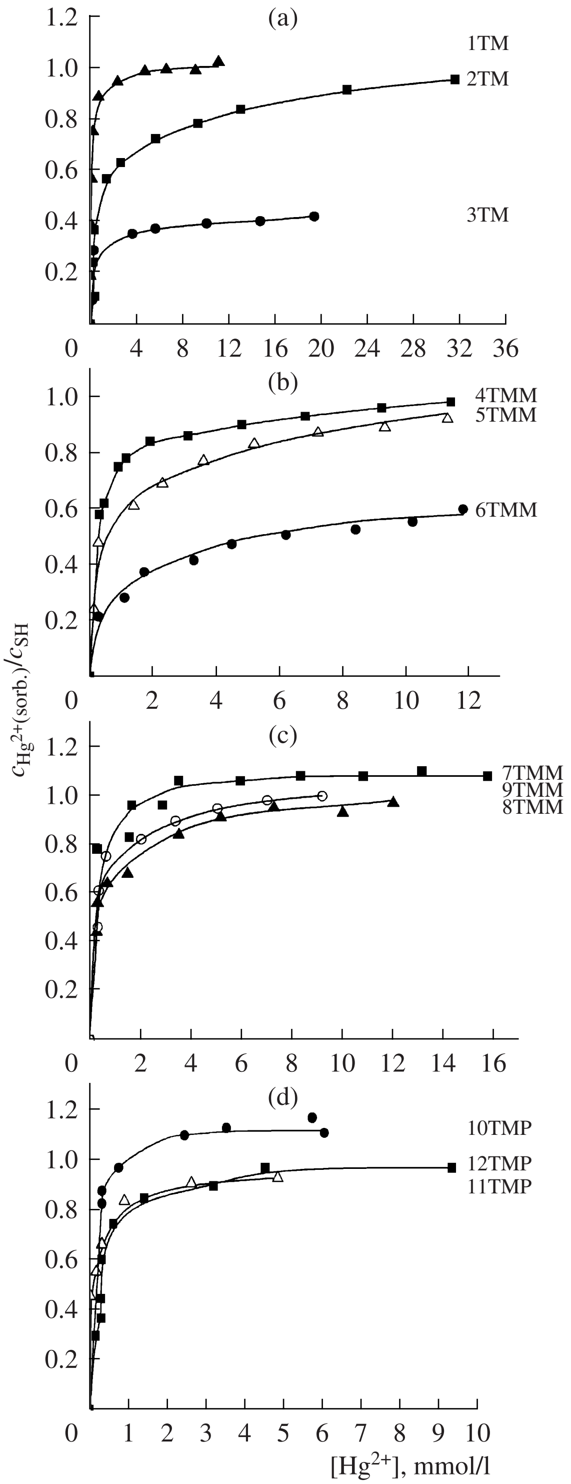

Fig. 1. Sorption isotherms of mercury(II) by the 3-mercaptopropyl-containingxerogels of the TM, TMM, and TMP series.

4000 cm^{-1} in the reflection mode with a resolution ability of 4 cm^{-1}. The samples were mixed with precalcined KBr (reagent grade) in a ratio of 1 : 30.

RESULTS AND DISCUSSION

The structural adsorption characteristics of the HS-containing xerogels [11, 12] considered in this work are given in Table 1. It is seen that an increase in the relative amount of MPTMS in the reacting systems decreases the specific surface and sorption pore volume (and often the size of these pores) in the final products. In some cases (at the molar ratio TEOS : MPTMS = 1 : 1 or close to this), xerogels with the weakly developed porous structure are formed (Table 1, samples 3TM and 6TMM). At the same time, the consecutive introduction of methyltriethoxysilane (MTES) or *n*-propyltriethoxysilane (PTES) instead of MPTMS, decreasing the relative amount of MPTMS, induces, as expected, an opposite effect. The content of 3-mercaptopropyl groups in the studied samples determined by the inverse titration [10–12] is also presented in Table 1. The data obtained by this method are close to the elemental analysis data, if the xerogel fraction with the particle size <0.063 mm is used in the titration. It was of practical interest to reveal whether the above-presented differences in the porous structure affect the complexation properties of the synthesized xerogels (in this case, toward the Hg^{2+} ions) or not. In addition, it was interesting to elucidate the dependence between the composition of the surface layer of the xerogels and the stability of the formed Hg(II) complexes.

The sorption isotherms of the Hg^{2+} ions by the studied xerogels are shown in Fig. 1. For example, in the case of the 1TM, 7TMM, and 10TMP samples with the highly developed porous structure and, as a consequence, having low surface concentrations of the HS groups (Table 1), the steep rise of the isotherms is observed in the region of low equilibrium Hg^{2+} concentrations. The isotherms reach a plateau at the molar metal to ligand ratio close to 1 : 1. Therefore, it can be assumed that the 1 : 1 mercury(II) complexes with 3-mercaptopropyl groups are formed in the surface layer of these xerogels. For the 3TM sorbent with the weakly developed porous structure but relatively high surface concentration of thiol groups (Table 1), the isotherm reaches a plateau at a metal to ligand ratio of 1 : 2.5 (Fig. 1a). The 1 : 2 complexes are formed, most likely, in this case.

The pH monitoring during the experiment showed that the pH of the suspension decreased successively from ~2 to ~1.5 with an increase in the equilibrium concentration of the metal ions in the sorption series. Therefore, mercury(II) interacts with the 3-mercaptopropyl group via the ion exchange mechanism and can be presented by equilibrium (1) for the first group of xerogels and by equilibrium (2) for the second group, taking into account that the sorption of the cations is

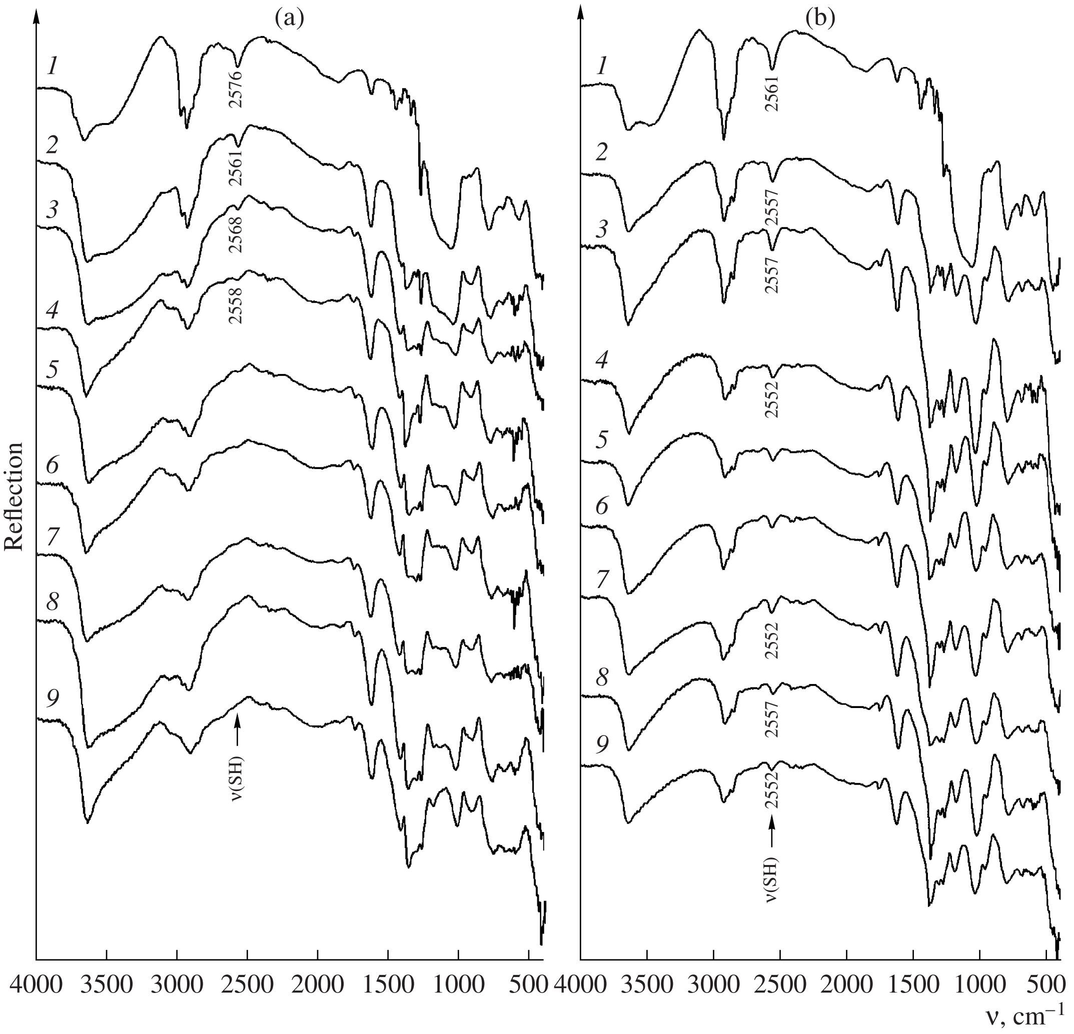

Fig. 2. IR spectra of the (a) 5TMM and (b) 6TMM xerogels (*1*) before and (*2–9*) after the sorption of mercury(II).

accompanied by the transition of an equivalent number of protons to the near-surface layer

$$\equiv Si(CH_2)_3SH + Hg^{2+} + NO_3^- \rightleftharpoons [HgS(CH_2)_3Si\equiv]^+NO_3^- + H^+, \quad (1)$$

$$2[\equiv Si(CH_2)_3SH] + Hg^{2+} \rightleftharpoons Hg[S(CH_2)_3Si\equiv]_2 + 2H^+. \quad (2)$$

Some porous xerogels with the intermediate surface concentration of the HS groups (~0.01 mmol/m^2), e.g., the 2TM and 5TMM samples in Table 1, are characterized by a steeper rise of the isotherms, and the sorption layer is saturated at considerably higher Hg^{2+} concentrations in the solution (Figs. 1a, 1b). Evidently, the formation of two types of complexes is possible for these sorbents. At a low concentration of the Hg^{2+} ions, i.e., in an excess of thiol groups, the 1 : 2 complexes are formed (according to equilibrium (2)). The further increase in the Hg^{2+} concentration in the solution simplifies the composition of the complexes; i.e., the 1 : 1 complexes are formed

$$Hg[S(CH_2)_3Si\equiv]_2 + Hg^{2+} + 2NO_3^- \rightleftharpoons 2[HgS(CH_2)_3Si\equiv]^+NO_3^-. \quad (3)$$

The study of the reflection IR spectra of the samples containing sorbed mercury(II) confirms this conclusion. For instance, the IR spectrum of the 5TMM xerogel contains an absorption band at ~2570 cm^{-1} assigned to ν(SH), whose intensity gradually decreases with an increase in the amount of sorbed mercury(II) (Fig. 2a). Moreover, this band disappears completely already to approximately the middle of the sorption series, although mercury(II) continues to sorb with the further increase in the Hg^{2+} equilibrium concentration (Fig. 1b).

The IR spectrum of the 6TMM xerogel, which differs from the 5TMM xerogel by the higher surface concentration of thiol groups (Table 1), also exhibits a decrease in the intensity of the ν(SH) stretching vibration with an increase in the amount of sorbed mercury(II) (Fig. 2b). However, this band does not completely disappear even in the IR spectra of the 6TMM xerogel sample attributed to the isotherm region that reached a plateau (Fig. 1b). Therefore, in this case, some portion of the thiol groups is inaccessible for the Hg^{2+} ions. It is most likely that the complexes formed in the initial period of sorption further block the access of the metal ions to some thiol groups. Probably, the 6TMM and 3TM samples differ from others by the structure of their functional layer. Indeed, the simple calculation for the sorbents with concentrations of the SH groups of 0.10 mmol/m^2 (6TMM) and 0.38 mmol/m^2 (3TM) shows that the distance between these groups is 1.3 and 0.7 Å, respectively, in the case of their random distribution on the sample surface, unlike other samples for which this distance is 3.7–9.1 Å according to the calculation. It is known [15] that the distance between two silicon atoms (Si–O–Si) on the silica surface is 3.2 Å (or somewhat shorter, if the SiOSi angle is smaller than 180°). Hence, the structure of the surface layer in the 3TM and 6TMM samples should be polymeric. A similar assumption was earlier advanced [16] when studying the xerogels with a high content of 3-mercaptopropyl groups.

We attempted to estimate the stability constants of the formed mercury(II) complexes with the 3-mercaptopropyl groups immobilized on the xerogel surface. It should be mentioned that complex formation on the surface has its specific features compared to that in solutions [14]. When describing equilibria, one should take into account the anomalously high local concentrations of reactants in the near-surface sorbent layer, a possibility of their nonuniform distribution over the sorbent surface, the energy nonuniformity of the latter, a possibility of lateral interactions of the functional groups, and others. In this case, several types of complexes and even compounds that have no analogs in solutions can be formed on the sorbent surface. Therefore, several models that take into account numerous chemical reactions on the support surface are known presently for the quantitative description of complex formation: the models of polydentate sites [17], immobilized polydentate sites [15, 18], random polydentate sites [15, 19], equivalent degree of sorption [20], and chemical reactions [14].

We used the model of chemical reactions to calculate the stability constants of the surface mercury(II) complexes with the thiol-containing xerogels. This model assumes that the stability of the immobilized complexes is determined only by their composition and is independent of the surface coverage. The model uses no a piori assumptions on the number and stoichiometric composition of the reaction products in the adsorption layer.

The complex formation of the metal ions with the ligands immobilized on the sorbent surface can be presented in the form

$$m\mathrm{M} + n\overline{\mathrm{L}} = \overline{\mathrm{M}_m\mathrm{L}_n}, \qquad (4)$$

where line above the formulas marks the components immobilized in the adsorption layer. Based on equilibrium (4), the concentration stability constant of the M_mL_n surface complex in the model of chemical reactions is written as

$$\beta_{mn} = \frac{[\overline{\mathrm{M}_m\mathrm{L}_n}]}{[\mathrm{M}]^m[\mathrm{L}]^n}. \qquad (5)$$

This equation is formally analogous to the equations for the stability constants of the complexes in solutions. In the model of chemical reactions, the concentration of immobilized reactants is expressed in mol/m^2 (“heterogeneous” approach) or mol/l (“homogeneous” approach). The both approaches are equivalent, if the ratio of the sorbent weight to the solution volume is the same for all experimental points. In this case, the dimensionality of the stability constants of the complexes immobilized on the silica surface coincides with the dimensionality of the constants of these complexes in solutions.

Using the model of chemical reactions [14], we calculated the constants

$$\beta_{11} = \frac{[\{\mathrm{HgS(CH_2)_3Si{\equiv}}\}^+]}{[\mathrm{{\equiv}Si(CH_2)_3S^-}][\mathrm{Hg^{2+}}]} \quad \text{and}$$

$$\beta_{12} = \frac{[\mathrm{Hg}\{\mathrm{S(CH_2)_3Si{\equiv}}\}_2]}{[\mathrm{{\equiv}Si(CH_2)_3S^-}]^2[\mathrm{Hg^{2+}}]}$$

for the $[HgS(CH_2)_3Si{\equiv}]^+$ and $Hg[S(CH_2)_3{\equiv}]_2$ complexes, respectively, formed on the surface of the considered thiol-containing xerogels. The data on the equilibria used in this case for calculations are given in Table 2. The pK_a values of ethylmercaptan were used in the calculation, because the ability of monobasic acids to dissociate remains unchanged upon their immobilization on the surface [14].

A comparable analysis of the obtained constants (Table 3) shows a tendency for a decrease in the stability of the 1 : 1 complexes with an increase in the surface concentration of 3-mercaptopropyl groups (particular series of the (4–6)TMM, (7–9)TMM, and (10–12)TMP samples) in the xerogels. The observed effect can be explained both by an enhancement of the mutual influence of the adjacent thiol groups on their complex formation with Hg^{2+} with an increase in the content of these groups in the surface layer and by an enhancement of the interaction between the sorbed ions. In other words, the sorption sites are not independent.

Such a series of xerogels as 1TM, 2TM, and 3TM is of special interest. These samples, unlike others, have a monofunctional surface layer (Table 1). As already

Table 2. Model of equilibria for the complex formation of Hg^{2+} ions with 3-mercaptopropyl groups on the xerogel surface

Stoichiometric coefficients at components			Equilibrium	$\log\beta_{1n}$
Hg^{2+}	–SH	H^+		
0	1	–1	–Sç – ç$^{+}$ = –S^{-}	–10.5*
1	1	–1	Hg^{2+} + –Sç – ç$^{+}$ = –SHg^{+}	(–10.5) + $\log\beta_{11}$
1	2	–2	Hg^{2+} + 2(–Sç) – 2ç$^{+}$ = $(-S)_2Hg$	2(–10.5) + $\log\beta_{12}$

* $\log K_a$ of ethylmercaptane at 21°C [21].

Table 3. Stability constants of the Hg(II) complexes formed on the surface of the SH-containing xerogels

Sample	Concentration of groups upon their random distribution, mmol/m^2		Overall concentration of functional groups, mmol/m^2	$\log\beta_{11}^{**}$	$\log\beta_{12}^{**}$
	c_{SH}	c^{*}_{alcyl}			
1TM	0.005	0	0.005	13.6 (0.3)	
2TM	0.012	0	0.012	12.6 (0.1)	23.1 (0.4)
3TM	0.380	0	0.380		23.8 (0.2)
7TMM	0.002	0.006	0.008	14.1 (0.1)	
8TMM	0.004	0.004	0.008	12.84 (0.06)	
9TMM	0.008	0.002	0.010	13.07 (0.05)	
10TMP	0.002	0.006	0.008	13.6 (0.1)	
11TMP	0.006	0.006	0.011	13.39 (0.04)	24.0 (0.3)
12TMP	0.008	0.002	0.010	13.2 (0.1)	23.5 (1.1)
4TMM	0.004	0.012	0.016	12.84 (0.04)	23.9 (0.2)
5TMM	0.008	0.008	0.016	12.59 (0.05)	23.1 (0.3)
6TMM	0.100	0.030	0.130	11.62 (0.02)	22.65 (0.03)

Notes: * Calculated from the MPTMS/MTES (or PTES) ratio in the starting solution.
** The root-mean-square deviations of $\log\beta$ are given in parentheses.

mentioned, the 1 : 1 Hg(II) complexes are formed at a low concentration of thiol groups (sample 1TM, 0.005 mmol/m^2). The absence of the 1 : 2 complexes can indicate that the thiol groups of this sample are too remote from each other and, in addition, are uniformly distributed in the surface layer. However, at low concentrations of functional groups the probability of formation of the 1 : 1 complexes increases in the case of their cluster (island) arrangement. In fact, when tetramers are formed on the xerogel surface (and are randomly arranged), the distance between the thiol groups of the adjacent clusters elongates compared to that between these groups in the case of their uniform distribution. The insertion of two thiolic sulfur atoms belonging to the same tetramer into the coordination sphere of mercury(II) is sterically hindered. It is clear that an increase in the surface functional group concentration results in the shortening of the distance between the adjacent clusters and an increase in the probability of formation of the 1 : 2 complexes (Table 3, xerogel 2TM). The possibility of formation of the $Hg[S(CH_2)_3Si\equiv]_2$ complexes increases in the case of the polymeric character of the surface layer, as it is observed for the 3TM sample (Table 3). The data in Table 3 show that the stability of the 1 : 1 complexes in the considered series of the xerogels decreases with an increase in the surface concentration of 3-mercaptopropyl groups. This agrees with the above conclusion.

The tendency for a decrease in the stability of the 1 : 1 complexes is also observed when the alkyl groups appear in the surface layer and the surface concentration of these groups increases. This conclusion follows from a comparison of $\log\beta_{11}$ of the $[HgS(CH_2)_3Si\equiv]^+$ complexes formed on the surface of such xerogels as 1TM and 8TMM, 9TMM and 5TMM, 12TMP and 5TMM (Table 3). Note that this comparison is correct, because the considered pairs of samples have the same (or rather close) concentrations of thiol groups. The influence of the concentration of alkyl groups on the stability constant of the $[HgS(CH_2)_3Si\equiv]^+$ complex can

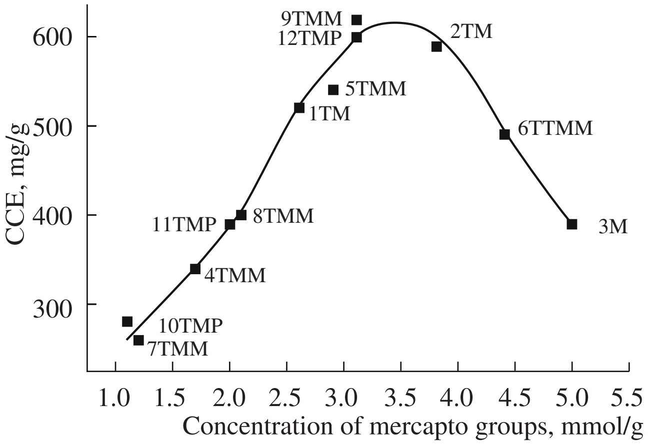

Fig. 3. Plots of the SSC value of the sorbents vs. content of 3-mercaptopropyl groups in the sorbents.

be understood if considering the cluster distribution of the hydrophobic and hydrophilic groups on the surface of the xerogel particles. An increase in the content of the hydrophobic groups induces a denser arrangement of the hydrophilic islands, thus decreasing the distances between the thiol groups and increasing the probability of formation of the $Hg[S(CH_2)_3Si\equiv]_2$ complexes. For this reason, a decrease in the stability constants of the $[HgS(CH_2)_3Si\equiv]^+$ complexes should be expected.

The stability of such single-charge complexes decreases in the xerogel series 11TMP ⟶ 12TMP ⟶ 9TMM ⟶ 2TM and 10TMP ⟶ 8TMM (Table 3). As already mentioned, this is due to the increase in the surface concentration of thiol groups in these series. Since the overall concentration of functional groups is the same for the samples of the same series, this implies that the surface concentration of alkyl groups decreases with an increase in the concentration of thiol groups. However, this does not contradict the above conclusion on the influence of the alkyl group concentration on the stability of the complexes, because in this case, in fact, a part of the thiol groups is simply replaced by the alkyl groups.

The stability constants for the $Hg[S(CH_2)_3Si\equiv]_2$ complexes are rather close (with allowance for the root-mean-square deviations) (Table 3) and are almost independent of the concentration of thiol groups.

Based on the data presented in Table 3, we can conclude that there are boundary overall concentrations of functional groups, which divide the considered xerogels into three groups. The equimolar complexes are formed, as a rule, below the first boundary concentration (~0.010 mmol/m^2), whereas the Hg(II) complexes with two surface ligands, namely, $Hg[S(CH_2)_3Si\equiv]_2$, are formed together with these complexes at higher concentrations of functional groups. The second boundary overall concentration of functional groups lies at ~0.13 mmol/m^2 (Table 3). Above this concentration, the xerogels contain the polymeric functional layer (sample 3TM) and form only the $Hg[S(CH_2)_3Si\equiv]_2$ complexes.

In conclusion, let us analyze the SSC value for all the sorbents studied. It seemed that a gradual increase in the content of 3-mercaptopropyl groups should lead to a systematic increase in the SSC values of the xerogels. However, as follows from the data in Fig. 3, this dependence has a maximum at a content of thiol groups of 3.0–3.8 mmol/g. The further increase in the content of 3-mercaptopropyl groups decreases the SSC value due to the formation of the complexes with the metal to ligand ratio equal to 1 : 2 on the sorbent surface. It should be mentioned that the maximum SSC value equal to 620 (mg of Hg(II))/(g of sorbent) (Table 3) is comparable to that for the best organic cation-exchange resins used for mercury(II) extraction [22].

Thus, the 3-mercaptopropyl-containing xerogels studied in this work can be used for the extraction of Hg(II) from aqueous solutions. The composition of the complexes formed on the surface of these thiol-containing sorbents and their stability depend on the surface concentration of functional groups (mmol/m^2). Since the surface concentration of functional groups depends on both the specific concentration of these groups (mmol/g) and the specific surface of the sorbent (m^2/g), the sorption properties of the mercapto-containing xerogels are substantially affected by the parameters of their porous structure. The composition of the xerogel surface layer, which is determined by the ratio of thiol and alkyl groups, also affects the composition and stability of the surface mercury(II) complexes.

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