

Organosilicon Polymers with Ion-Exchange and Complexing Properties

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Abstract

The present paper describes the methods to synthesize organosilicon monomers containing carbofunctional ionogenic and complex-forming groups, and polymers based on these monomers. The synthesized organosilicon polymers are studied as ion-exchange and complex-forming sorbents with respect to wide range of precious metals, lanthanides and other transition and non-transition elements. The features of sorption activity of the studied sorbents are discussed, as well as the areas and perspectives of their practical application.

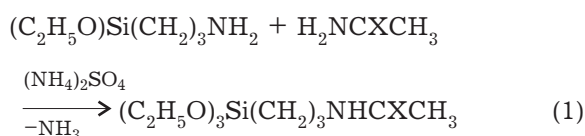
INTRODUCTION

Hydrated and high dispersed silicas are well known as efficient sorbents for inorganic and organic compounds [1]. Low selectivity of these sorption materials forced researchers to modify them. One of the methods to modify them is the immobilization of carbofunctional organic and organosilicon reagents on the surface of silica [2–4]. Modified silicas are successfully used in analysis for sorptive concentrating and isolation of some elements [3]. However, this way of synthesis of organosilicon ion-exchange and complex-forming sorbents named the surface assembly method is often multistage and labour-consuming. The simplest way to obtain organosilicon sorbents is hydrolytic polycondensation of organosilicon monomers of the general formula $YRSiX$ where Y is ionogenic or complex-forming group, R is hydrocarbon radical and X is halogen or alkoxy substituent [5, 6]. However, this approach to the synthesis of organosilicon ionites and complexites had not been used until we started our investigations in 1977.

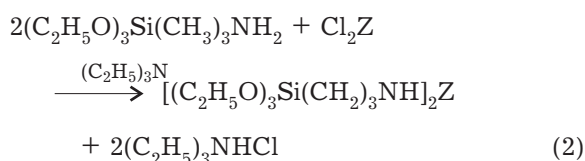
MONOMER SYNTHESIS

The progress in this direction of the chemistry of organosilicon ion-exchange and complex-forming sorbents was promoted by our development of simple and available methods to synthesize organosilicon monomers of the general structure $Y(CH_2)_nSiX_3$ or $Z[(CH_2)_nSiX_3]_2$, where $n = 1-3$; X = AlkO, Cl; Y = HS—, ClSO₂—, NH₂(CH₂)_mS— ($m = 2, 3$), CH₃C(O)NH—, CH₃C(S)NH—, CH₃C(O)NHC(S)NH—, HOOCCH₂S—; Z = —S—, —SCH₂CH₂S—, —NHC(O)NH—, —NHC(S)NH—, —NHC(O)NHC(O)NH—, NHC(O)C₆H₄C(O)NH—, —NHS(O₂)NH—, —NHSSNH—, —NHS(O)NH—, etc. The synthesis of these organosilicon monomers is based mainly on condensation and photochemical processes. For example, the condensation of 3-triethoxysilylpropylamine with acetamide, thioacetamide, acetylthiocarbamide (reaction (1)), S₂Cl₂, SOCl₂, SO₂Cl₂ (reaction (2)) and carbamide, biurete, thiocarbamide, phthalamide (reaction (3)) leads to organosilicon monomers with

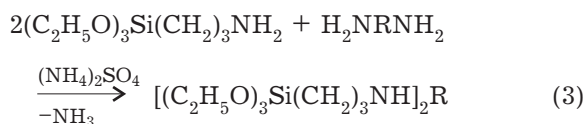
corresponding carbofunctional substituents [7–11]:



X = O, S.



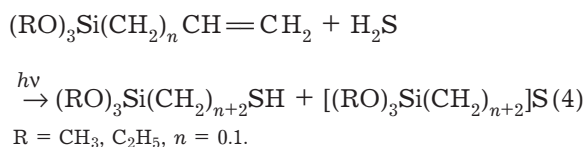
Z = –SS–, –SO–, –SO₂.



R = –C=O, –C(O)NHC(O)–, –C=S, –C(S)C(O)CH₃, –C(O)C₆H₄C(O)–.

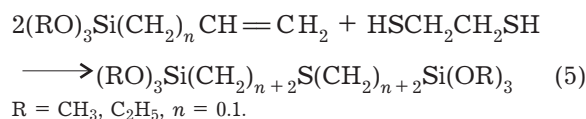
Photochemical thiylation of alkenyl(trialkoxysilanes by gaseous hydrogen sulphide [9, 12, 13], 1,2-ethanedithiol [14], 1,2-aminoethanethiol [15] and thioglycolic acid [16] leads to trialkoxysilylalkanethiols, bis-(trialkoxysilylalkyl)sulphides, S,S'-bis-(trialkoxysilylalkyl)-substituted ethylenedisulphide and S-(trialkoxysilylalkyl)-substituted 1,2-aminoethanethiol and thioglycolic acid.

Photochemical reaction of alkenyl(trialkoxysilanes with hydrogen sulphide is not selective and leads to the corresponding thiols and sulphides:

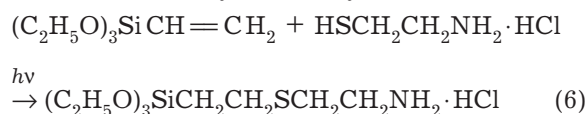


The possibility for yttrium (III) chloride to act as a metal catalyst for this reaction (which was discovered by us) allowed to increase its selectivity substantially towards the formation of monoadducts and thus to develop one of the simplest methods to synthesize mercaptoalkyl(trialkoxysilanes [17]. In the absence of YCl₃, the predominant product of this process is bis-(trialkoxysilylalkyl)sulphide. Direct photochemical addition of aminoethanethiol to alkenyl(trialkoxysilanes is impossible because

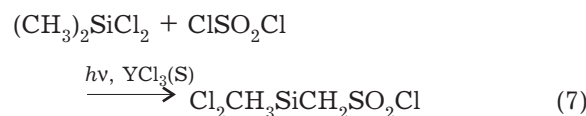
of its zwitterion structure, so we used aminoethanethiol hydrochloride [15]:



At the same time, homologous 2-diethylaminoethanethiol easily forms addition products with alkenyl(trialkoxysilanes:



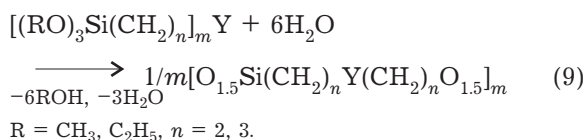
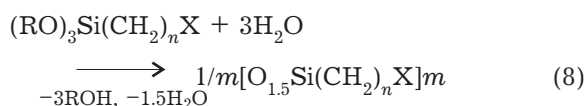
Photochemical sulphochlorination of dimethyldichlorosilane is the route to the synthesis of organosilicon monomer chlorosulphonylmethyl(dichloro)methylsilane [18]:



The reaction is catalyzed by yttrium (III) chloride which increases the yield of the target product of sulphochlorination. A similar effect is observed when the process is conducted in the presence of catalytic amounts of elemental sulphur.

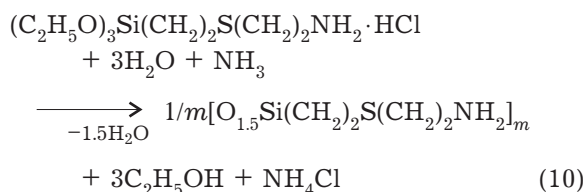
THE SYNTHESIS OF POLYMERS

Wide series of cross-linked polymers was obtained by hydrolytic polycondensation of the synthesized organosilicon monomers. These polymers are efficient ion-exchange and complex-forming sorbents. Hydrolytic polycondensation of organosilicon monomers was carried out in weakly alkaline or water-dioxane medium at pH 7–8 and a temperature of 20 or 60–70 °C [19]:



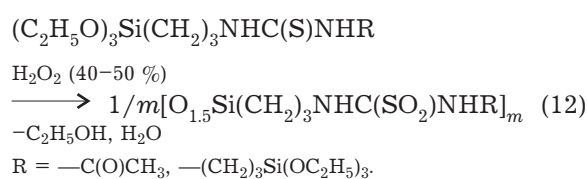
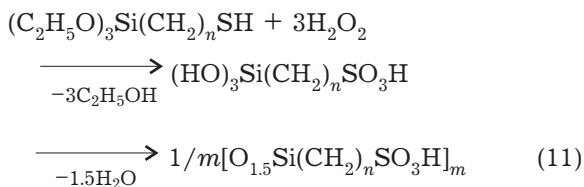
Hydrolytic polycondensation of trialkoxysilylalkylthioethylamine was carried out in 6 M

aqueous ammonia in order to achieve, along with polymerization, also dehydrochlorination of the initial monomer [9]:



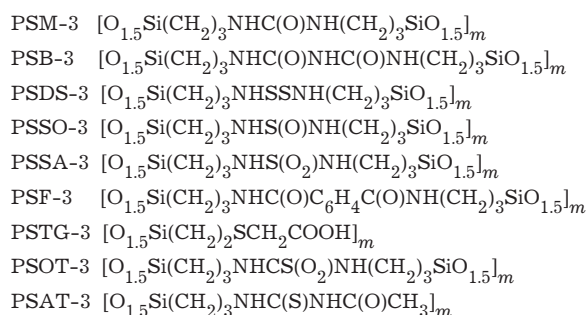
Hydrolytic polycondensation of organosilicon monomers with diaminodisulphide, diamino-sulphoxide and diaminosulphone carbonyl groups was carried out in similar conditions.

We developed the method of oxidative hydrolytic polycondensation of mercaptoalkyl(trialkoxysilyl)silanes [13], N-(3-trialkoxysilylalkyl)-N'-acetyl- and bis-N,N'-(3-trialkoxysilylpropyl)thiocarbamides. This method allowed to synthesize organosilicon sulphocationites (reaction (11)) and organosilicon polymer derivatives of sulphonocarbamide (reaction (12)):



All the organosilicon sorbents thus obtained are powder polymers exhibiting space-cross-linked structure (polyorganosiloxane):

Polymer	Structural unit
PMMS-1	$[\text{O}_{1.5}\text{SiCH}_2\text{SH}]_m$
PMES-2	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_2\text{SH}]_m$
PSSK-1	$[\text{O}_{1.5}\text{SiCH}_2\text{SO}_3\text{Na}]_m$
PSSK-2	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_2\text{SO}_3\text{Na}]_m$
PSSK-3	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}]_m$
PSTA-2	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{NH}_2]_m$
PSTA-3	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{NH}_2]_m$
PSAS-3	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{CH}_3]_m$
PTAS-3	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{CH}_3]_m$
PES-2	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{SiO}_{1.5}]_m$
PSTM-3	$[\text{O}_{1.5}\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NH}(\text{CH}_2)_3\text{SiO}_{1.5}]_m$



They are distinguished by their extreme chemical stability. They are not decomposed and do not lose their sorption activity in boiling concentrated hydrochloric acid, as well as in 10–18 M solutions of sulphuric acid at 100 °C. The sorbents are not decomposed also under the action of 5 M aqueous ammonia. Only concentrated alkaline solutions lead to the decomposition of the sorbents due to the rupture of Si—O bonds. Concentrated nitrous acid destroys mainly carbonyl group of sorbents.

Sorption activity of the synthesized organosilicon ionites and complexites was studied with respect to precious metals (gold, silver, platinum metals), lanthanides, some actinides (uranium (VI) and thorium (IV)), a series of toxic elements (cadmium, zinc, copper, mercury, tin, lead, selenium (IV), selenium (VI), tellurium (IV), as well as some halide anions (Cl^- , Br^-) and elemental bromine. The studies were carried out with both artificial and natural samples (fresh and mineral water, ores, minerals). Besides, we studied waste water and industrial wastes.

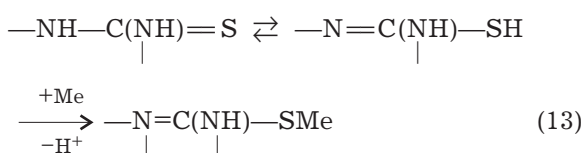
FEATURES OF SORPTION ACTIVITY OF THE SYNTHESIZED ORGANOSILICON SORBENTS

The presence of sulphur-containing carbonyl groups in the major part of synthesized sorbents has defined the choice of chalcophilic precious metals as one of the main objects to determine their sorption activity. The most efficient sorbents with respect to noble elements were PMMS-1, PMES-2, PSTM-3, PSDS-3, PTAS-3, PSTA-2 and PSAT-3.

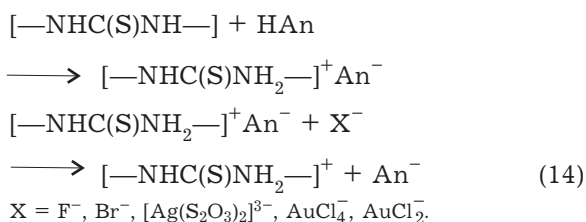
Like organic sorbents with mercapto groups, organosilicon sorbents PMMS-1 and PMES-2 exhibit high sorption activity with respect to silver [13, 20]. Sorption occurs through

ion-exchange mechanism. Higher activity of PMES-2 sorbent compared to PMMS-1 is likely to be explained by larger distance of mercapto groups from silsesquioxane matrix in this sorbent and their consequent better accessibility for silver ions. Among the sorbents listed above, the one most efficient with respect to silver is PSDS-3 [21]. Its static sorption capacity (SSC) to the metal is $396 \text{ mg} \cdot \text{g}^{-1}$, compared to SSC of PMES-2 to Ag^+ which is $140 \text{ mg} \cdot \text{g}^{-1}$ [13]. PSDS-3 is also distinguished by its higher rate of sorption equilibrium establishment (60 min, compared to 90 min for PMES-2 and 240 min for PSTM-3). The dependence of Ag(I) sorption degree on the acidity of the medium (maximum sorption being achieved at 0.5 M HNO_3) for PSDS-3 is the evidence of complex-forming character of sorption. Silver can be coordinated either with nitrogen atom or with the sulphur of diaminosulphide fragment of the PSDS-3 sorbent, or can be chelated with both of them, taking account of the fact that the coordination number of Ag(I) can be either 2 or 3 [21].

Organosilicon sorbents PSDS-3, PTAS-3 and PSTM-3 sorb silver efficiently also from thiosulphate solutions [19, 21] in which this metal is present in the form of complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$. The highest efficiency is exhibited by PSTM-3. For PSDS-3, the transition from nitrous solutions to thiosulphate ones causes a substantial decrease of the sorption ability of the polymer with respect to silver (SSC for Ag^+ is 396 and $108 \text{ mg} \cdot \text{g}^{-1}$ in nitrous and thiosulphate medium, respectively) while for PSTM-3 the sorption capacity increases when passing from nitrous to thiosulphate medium (SSC increases from 128 to $170 \text{ mg} \cdot \text{g}^{-1}$). This phenomenon is due to the features of the reactivity of thiocarbamide fragment of this sorbent. One of the features responsible for this phenomenon is the ability of thiocarbamides to react, under definite conditions, in the thiol form due to thione-thiol tautomerism:

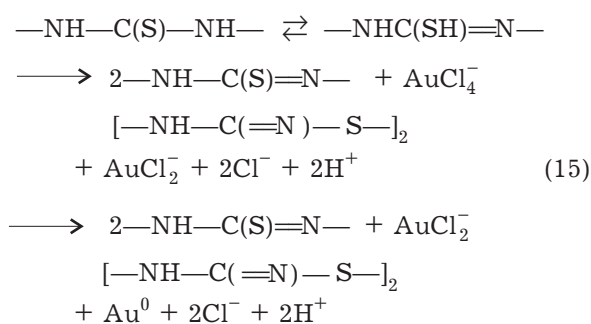


Besides, it is characteristic for thiocarbamides to form thiuronium salts with acids:



These properties of thiocarbamate fragment define the ability of PSTM-3 to function as ampholyte, *i.e.* to act as a cationite or anionite depending on the acidity.

Cation-exchange properties of PSTM-3 explain the sorption of $\text{Me}(\text{O})_n^{2+}$ where $\text{Me} = \text{Se}, \text{Te}, n = 1; \text{Me} = \text{U}, n = 2$, and possibly the sorption of silver ions, though in this case also complexing can occur [22]. Sorption of all the other precious metals is likely to proceed also through the formation of complex, though in the case of chloride complex of gold $[\text{AuCl}_4]^{3-}$ anion exchange is also possible. From the viewpoint of only anion exchange one can explain the increase of PSTM-3 sorption activity with respect to silver in thiosulphate solutions, as well as the sorption of fluoride and bromide anions by this sorbent. PSTM-3 sorbent exhibits one more specific property, namely, it can act as redoxite [22]. Redoxite action of PSTM-3 is well exhibited for the sorption of gold as an example. The increase in the acidity of medium observed during the sorption of Au(III), as well as the data of IR spectroscopy (the appearance of the band at 1620 cm^{-1} in IR spectrum of the sorbent saturated with gold, this band being characteristic of azomethyne group $\text{—C}=\text{N—}$) are the evidence that in this case the formation of complex is accompanied by the reduction of Au(III) to Au(I):



Even more clear redoxite action is exhibited by the sorbent PSAT-3 [23]. Its interaction with $H[AuCl_4]$ leads to the release of elemental gold; the total SSC of PSAT-3 being $694 \text{ mg} \cdot \text{g}^{-1}$, only about $200 \text{ mg} \cdot \text{g}^{-1}$ remain in the sorbent matrix which means that more than two thirds of Au(III) interacting with the sorbent is released as metal. PSAT-3 sorbent is also distinguished by the highest rate of sorption equilibrium establishment. Sorption equilibrium is established as soon as after 5–10 min of the sorbent contact with the sorbate.

Interesting data have been obtained on the sorption of rare earths by the synthesized sorbents. Similar to the case of organic sulphocationites, their organosilicon analog PSK-3 was found to be efficient with respect to all the lanthanides. However, unlike organic sulphocationites, the PSK-3 sorbent is capable of sorbing rare earths in acidic media within pH range of 1–4 [24]. The decrease in the degree of lanthanides sorption by the PSM-3 and PSB-3 sorbents with increasing the acidity of the medium is the evidence of ion-exchange sorption mechanism for these elements [7].

Unlike the PSSO-3 sorbent which is rather efficient with respect to the lanthanides of both cerium and yttrium groups, structurally similar PSAS-3 sorbs rather efficiently only the lanthanides of the end of the series [25]. This opens wide possibilities to use it to selectively extract and separate rare earths. For example, Tm(III) is selectively extracted by PSAS-3 on the background of 50-fold excess of La(III), 20-fold – of Ce(III), 5-fold – of Nd(III) and twofold excess of Sm(III). Finally, the tetrad effect (which is a poorly studied phenomenon in rare earths chemistry) is vividly exhibited in the sorption of lanthanides by

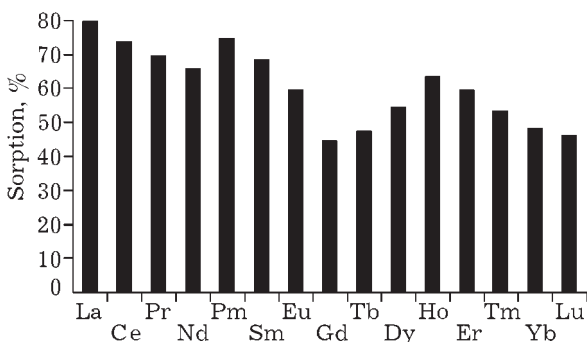


Fig. 1. Tetrad effect in the lanthanide series for sorption by the PSOT-3 polymer.

organosilicon sorbents PSMA-3, PSF-3 and PSOT-3 [26–28] (Fig. 1).

SOME ASPECTS OF PRACTICAL APPLICATION

The synthesized sorbents provide the possibilities to determine and isolate separate elements from artificial and natural samples. On the basis of the sorbents synthesized, the method of utilizing silver from the waste waters and materials of motion picture and photographic industry has been developed [21]. On the basis of organosilicon sorbents, the method was proposed that provides profound purification of industrial waste water of chlorine production and chemical metallurgy from mercury and other toxic components [29, 30]. Organosilicon sorbent PSTM-3 has been used as the grounds for the method providing silver determination in copper concentrates and gold in gold-bearing sands and polymetallic ores of Mongolia [31]. Also a sensitive chemical atom-emission method has been developed to determine microamounts of gold in lean ores and minerals [22, 32]. The use of PSTM-3 for sorption concentrating of gold in this method allowed to increase the gold sensitivity threshold from 10^{-7} to $10^{-8} \%$.

Organosilicon sorbents, in particular PSTM-3, are widely used at present in analytical procedures in the geochemical and geological academic establishments to provide sorption concentrating of separate elements in different natural samples. In particular, the PSTM-3 sorbent is used to determine mercury in the Pri-Baikalia water reservoirs. The use of the sorbent for concentrating solves one of important tasks of hydrochemical analysis, *i. e.* conservation of samples at sampling sites thus decreasing energy consumption for transportation and thermal treatment of samples according to the dry residue technique. The method has been developed on the basis of organosilicon sorbents to determine toxic tin and lead in mineral waters of East Siberia; a new approach has been worked out to the hydrochemical analysis of highly fresh water of Baikal [33].

CONCLUSION

Thus, organosilicon polymers with carbonyl functional ionogenic and complex-forming groups are a numerous class of sorption materials possessing high adsorption activity to a wide range of elements, chemical and thermal stability. Silsesquioxane matrix does not change specific reactivity of carbonyl functional substituents. The synthesized organosilicon polymers are used in the development of progressive methods to determine the contents of noble, toxic and other elements in the samples of natural and artificial origin, as well as in the studies of intragroup effects in the lanthanide series.

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