Reaction ability of heterochain complex-forming organopolymeric and organosilicon S-, N-containing sorbents toward noble metals

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Dedicated to Academician of RAS M. G. Voronkov on the occasion of his 80th birthday

(received 12 Jul 01; accepted 01 May 02; published on the web 09 May 02)

Abstract

Organopolymeric and organosilicon heterochain complex-forming sorbents containing aliphatic thioether or (and) weakly basic amino groups or the complex selective analytical groups are highly effective sorbents for selective recovery and concentration of noble metals. They are characterized by high values of distribution coefficients and sorption capacity for noble metals owing to high concentration of functional groups in the polymeric chain (Table 1, 2). The mechanism of sorption of some noble metals from hydrochloric (Pd (II), Pt (IV), Rh (III), Au(III)) and nitric (Pd (II), Ag (I)) solutions by heterochain sorbents of net, linear and cyclic structure is discussed. It was shown, that mechanism of the interaction of metals ions with functional groups of sorbents and the type of generated sorption complexes are defined by the nature of electron-donor atoms and the metal, by the structure of the functional groups and their state depending on the acidity of solution, by equilibrium of complexation and hydrolysis of complex metal forms in solution as well by the composition of solution. Selectivity and the rows of sorption affinity of S-; S,O- and S,N-containing sorbents are in agreement with the concept of hard and soft acids and bases.

Keywords: Organopolymeric sorbents, organosilicon sorbents, noble metals, heterochain, complex

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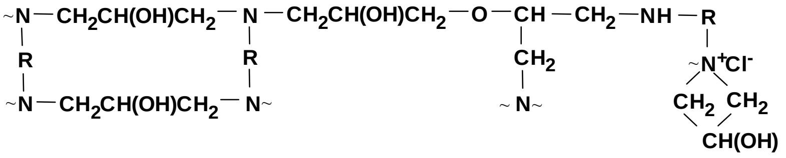
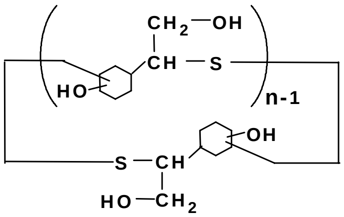
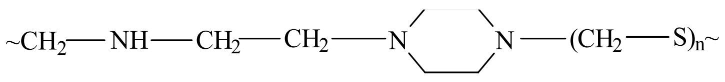
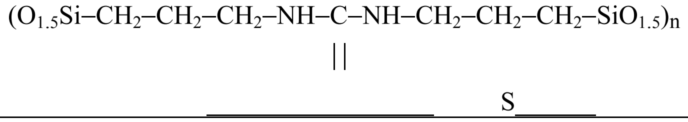
Introduction

The sorption by complex-forming sorbents (CS) is a perspective hydrometallurgical method of concentration and separation of noble metals in industrial and analytical practice.[1–4] Among CS's studied at the present time weakly basic anion-exchangers, CS's with thioether and also S,N-containing functional groups are the most selective toward noble metals. Considerable increase in efficiency of the recovery of noble metals may be achieved by the application of heterochain complex-forming sorbents (HS). Such sorbents are distinguished by higher sorption capacity and distribution coefficients for noble metals owing to a high concentration of functional groups in the sorbent mass[2–4] (Table 1,2). They provide an extensive class of organopolymeric compounds, which differ by the nature of electron-donor heteroatoms and their mutual arrangement as well by the general structure of the polymer, which may be linear, branched, net or cyclic. The structure of complexing groups of HS can vary - from a simple aliphatic group with the single heteroatom up to complex chelating groups[2,4] (Table 1). At Irkutsk Institute of Organic Chemistry since 1977 academician M. G. Voronkov's school has developed simple and convenient methods for the synthesis of a new type of complexing HS – polyorganylsilsesquioxanes, containing complex-forming functional groups. Such S-; S,N-containing organosilicon sorbents as $[O_{1.5}Si(CH_2)_2S(CH_2)_2SiO_{1.5}]_n$, $[O_{1.5}Si(CH_2)_2S(CH_2)_2S(CH_2)_2SiO_{1.5}]_n$, $[O_{1.5}Si(CH_2)_3NHC(S)NH(CH_2)_3SiO_{1.5}]_n$, $[O_{1.5}Si(CH_2)_3NHSSNH(CH_2)_3SiO_{1.5}]_n$ are highly selective towards Au (III), Ag (I), Pd (II), Pt

Table 1. Structure of complex-forming heterochain sorbent

Sorbent	Elementary unit of polymer
An	 $R=(CH_2CH_2)_2NH$
PHMTC	 n=7–8
PMS	$(–CH_2–S–)_n$ M=1230±60[a]
HS-SN	 n=4–6
PSTU-3	 $(O_{1.5}Si–CH_2–CH_2–CH_2–NH–\underset{\underset{S}{\Vert}}{C}–NH–CH_2–CH_2–CH_2–SiO_{1.5})_n$

[a] average molecular mass

(IV) in acidic solutions and are capable of separating effectively the noble metals from $10–10^5$-fold excess of accompanying transition metals with high distribution coefficients (K_d ~$10^3–10^4$ cm^3/g) for noble metals.[5] These organosilicon HS's belong to the class of volume-modified silicas[6] and differ favourably from organopolymeric HS's by the absence of swelling in aqueous solutions, by higher thermal stability (the initial temperature of polymer destruction is > 200 ^{O}C[5] (Table 2)), by higher chemical stability in HCl, H_2SO_4, HNO_3 solutions, and by good mechanical properties. These characteristics favor their application in aggressive media.[5] The concentration of functional groups in organosilicon HS's (3.5–4 mmol/g) is below that in organopolymeric ones (Table 2), but much higher than in the surface-modified silicas with graft complexing groups (0.2–0.9 mmol/g). This leads to higher values of sorption capacity of organosilicon HS's for noble metals (1.5–3.7 mmol/g) in comparison to the surface-modified silicas (0.1–0.5 mmol/g) and at the identical selectivity considerably extends their usefulness.[3,5,6]

Table 2. Some physicochemical characteristics of heterochain sorbents

Sorbent	$d·10^3$ cm	ρ_b g/cm^3	ρ_{tr} g/cm^3	T ^{O}C	E_N mg-atom/g	E_S mg-atom/g	E^M mmol/g	H_2O %
An(OH$^-$)	31.5–40.0	0.49	1.61	138	6.33	–	Pd(II) 3.3 Pt(IV) 3.3	5.5
PHMTC	2.5	0.30	1.83	182	–	5.37	Ag(I) 5.3[a]	2.2
PMS	10.0–20.0	0.40	1.30	125	–	21.66	Ag(I) 22.0[a] Pd(II) 10.0[a]	0.0
HS-SN	5.6	0.50	1.40	160	7.92	14.62	Ag(I) 30.7[a] Pd(II) 12.5 Cu(II) 8.0[b]	<0.5
PSTU-3		0.13	0.92	270		3.78[c]	Au(III) 2.3 Ag(I) 1.6[a] Pd(II) 1.5 Pt(IV) 0.6	

d –particle size; ρ_b – bulk density; ρ_{tr} - true density; T – initial temperature of polymer distraction (TG analysis); E_N, E_S – content of the N and S atoms in the polymer respectively (elemental analysis); E^M – maximum sorption capacity for the metal in HCl solutions, [a] in HNO_3 solutions, [b] both in the nitric and in the hydrochloric acid solutions; [c] content of the thiourea functional groups, mmol/g (elemental analysis)

To define the field of practical application of CS's, and to develop the sorption method for selective concentration of valuable metals besides the physicochemical and sorption characteristics of the sorbent, it is necessary to study the mechanism of interaction of the functional groups of the sorbent with ions of noble metals, with very sorption conditions (temperature, acidity and composition of the solution, phase contact time, etc.). The present review summarizes results of the study of the mechanism of sorption of the row of noble metals from hydrochloric and nitric acid solutions by organopolymeric N-; S,O-; S-; S,N-containing HS's, synthesized and investigated at the Institute of Organic Chemistry (Ufa Scientific Center, Russian Academy of Sciences), as well as organosilicon HS - poly-[*N, N '-bis*-(3-silsesquioxanylpropyl)thiocarbamide] (PSTU-3)[5,7,8] synthesized and investigated at Irkutsk Institute of Organic Chemistry (Table 1,2).

Sorption characteristics of HS's have been investigated by batch methods. The limiting stage of sorption kinetics has been determined by the method of sorption from restricted volume of solution. The values of static sorption capacity and concentrations of functional groups are presented concerning the mass of air-dry sorbent. The composition and the type of sorption complexes have been identified by elemental analysis and IR Spectroscopy (200–4000 cm^{-1}, nujol) of the sorption products in relation to phase contact time, solution acidity and degree of saturation of the sorbent phase by metal ion. All equilibrium sorption isotherms for noble metals (except for Rh (III)) have convex or approximately rectangular form under the optimal conditions of sorption (Table 3), that testifies to a high sorption affinity and selectivity of HS's toward these metals.

Table 3. Equilibrium isotherms for the sorption of the noble metals by heterochain organopolymers and the rows of the sorption affinity toward transition metals

Sorbent	Metal	C_{HA} M	C_e M	Type and parameters of isotherm at 20 ^{O}C
An(Cl$^-$)	Pd(II)	HCl		
		0.1	≤0.035	Langmuir E_m=2.98 b=6949.7
		3.0	≤0.035	Langmuir E_m=3.00 b=156.1
	Pt(IV)	HCl		
		0.1	≤0.035	rectangular form
		3.0	≤0.035	rectangular form
	Rh(III)	HCl		
		0.15	0.002–0.004	Langmuir E_m=4.25 b=81.6
		3.0	0.002–0.003	Langmuir E_m=2.08 b=281.6
				Pt(IV)≥Pd(II)»Rh(III)
PHMTC	Ag(I)	HNO_3	≤0.045 (20 ^{O}C)	Freundlich K=8.29 m=5.44
		1.5	≤0.017 (41 ^{O}C)	Freundlich K=6.58 m=4.96
PMS	Pd(II)	HNO_3		
		0.1^a	≤0.008	Langmuir E_m=3.50 b=163.0
		1.0^b	≤0.008	Langmuir E_m=3.19 b=1062.0
				Ag(I)>Pd(II)>Pt(IV)
HS-S,N	Ag(I)	HNO_3		rectangular form
		0.1	≤0.8	E_e=30.7±0.5
				Au(III), Ag(I)>Pt(IV)> Pd(II)>Cu(I),Cu(II)>Pb(II)
PSTU-3				**Au(III)>Ag(I)>Pd(II)>Hg(II)>Pt(IV)»Rh(III)>Ru(III)>Ir(IV)≥Os(IV)**

Langmuir equation $E_e = E_m bC_e/(1+bC_e)$;
Freundlich equation $E_e = KC_e^{1/m}$;
C_e – equilibrium concentration of the metal in solution;
E_e- equilibrium sorption capacity of the metal, mmol/g;
[a] hydrolyzed nitric solutions of Pd(II);
[b] freshly-prepared nitric solutions of Pd(II)

Sorption of Pd(II), Pt(IV), Rh(III) from hydrochloric acid solutions by net anionite An [9–11]

Polyfunctional weakly basic (pK_a=5.0±0.2) net anionite An was synthesized by the polycondensation of epichlorohydrin (ECH) with diethylenetriamine (DETA) in the medium of benzol–isopropanol (v/v=1:1) using the method[12] at the molar ratio ECH:DETA:NaOH=5:1:5. According to the data of the functional analysis of anionite An it contains, mmol/g: secondary – 0.15, tertiary – 5.76, quaternary – 1.20 amino groups, as well as OH-groups – 4.11. Saturation capacity of An for sorption of HCl is 6.73 meq/g. Thermal stability of An and its chemical stability in solutions of inorganic acids and NaOH, swelling in the aqueous solutions and selectivity toward platinum metals in hydrochloric acid solutions do not yield the relevant characteristics of a commercial analog EDE-10P. Higher specific surface area of An (10 m^2/g) in comparison with EDE-10P (1–5 m^2/g), and also the porous structure of its surface (meso- and micropores) in comparison with the gel structure of EDE-10P leads to higher rates of platinum metals sorption by anionite An (Table 4).

Table 4. Kinetic characteristics of the sorption of noble metals by heterochain organopolymer sorbents at 20 ^{O}C, g:v=1:250 (g:mL), speed of stirring 600–1000 revolutions/min

		Sorption conditions		Kinetic characteristics				
Sorbent	Metal	C_O M	C_{HA} M	$\tau_{0.5}$ min	τ_e h	D cm^2/s	Bi	E_{ac} kJ/mol
An(OH⁻)	H_2PdCl_4	0.021	HCl 0.1	1	3	$2.3\cdot10^{-7}$	3.2	37.4
An(OH⁻)	H_2PtCl_6	0.021	HCl 2.0	1	0.5	$3.2\cdot10^{-7}$	2.8	44.8
EDE-10P(OH⁻)	H_2PtCl_6	0.021	HCl 2.0	33	7	$9.2\cdot10^{-9}$	»10	
An(OH⁻)	H_2PtCl_6	0.021	HCl 0.1	1	3–4	$3.0\cdot10^{-7}$	4.4	45.2
An(OH⁻)	K_2PtCl_6	0.020	pH 5	25	72	$5.0\cdot10^{-8}$	»10	
An(Cl⁻)	H_3RhCl_6	0.005	HCl 3.0	2	3	$8.6\cdot10^{-8}$	»10	
EDE-10P(Cl⁻)	H_3RhCl_6	0.005	HCl 3.0	15	8	$1.5\cdot10^{-8}$	»10	
PHMTC	$AgNO_3$	0.010	HNO_3 1.5	23	4	$3.7\cdot10^{-11}$	»10	27.5
PMS[a]	$Pd(H_2O)_4(NO_3)_2$	0.010	HNO_3 1.0		480	$2.6\cdot10^{-10}$	»10	18.3
HS-SN	$AgNO_3$	0.208	HNO_3 0.1	10	≥288	$5.1\cdot10^{-10}$	»10	42.2

[a] freshly-prepared nitric solution of Pd(II), g:v=1:200 (g:mL); C_O, C_{HA} – initial concentration of metal and acid respectively; $\tau_{0.5}$ – time of achievement of the half of the equilibrium sorption

capacity; τ_e – time of achievement of sorption equilibrium; D – coefficient of intraparticle diffusion; Bi – diffusion criterion, $0.1<Bi<10$ for the limiting stage of both external and intraparticle diffusion and $Bi \gg 10$ ($Bi \to \infty$) for the limiting stage of intraparticle diffusion[29]; E_{ac} – energy of activation of intraparticle diffusion.

Anionite An can be used for selective concentration of micro-amounts of Pd(II), Pt(IV), Rh(III) over a wide range of HCl concentration independent of a saline background, and so for quantitative recovery of these metals from moderately acidic solutions (0.1−3 M HCl) with a low saline background at ambient temperature. Desorption of Pd(II) and Pt(IV) with thiourea solutions is possible (Table 5).The types of sorption complexes of platinum metals in the An phase and the sorption mechanism have been determined with respect to the composition of the solution at room temperature (Table 6). In acidic solution (> 0.1 M HCl) secondary and tertiary amino groups of the sorbent are completely protonated, and platinum metals sorption proceeds according to the ion-exchange mechanism with the formation of ionic associates (Equation 1):

$$p(R)NH^+Cl^- + [MCl_q]^{p-} \leftrightarrows \{(R)NH\}_p[MCl_q] + pCl^- \qquad (1)$$

where R is symbol of polymer matrix of the sorbent; q=4 for Pd(II), q=6 for Pt(IV), Rh(III). Thus, sorption affinity of An(Cl^-) toward Rh(III) and the composition of Rh(III) ionic associates in sorbent phase are defined by the equilibrium of complexation of Rh(III) in the solution. From the solution 0.005 M Rh(III) and 3 M HCl, where dominating species are $[RhCl_6]^{3-}$ and $[RhCl_5H_2O]^{2-}$ (ε=405 at 514 nm), $[RhCl_6]^{3-}$ is removed. From hydrolyzed 0.15 M HCl solution, where the prevalent forms are $[RhCl_{6-X}(H_2O)_X]^{(3-X)-}$ (x=1−3; ε=401 at 481 nm), the less charged Rh (III) aquachlorocomplex anions are sorbed.

Sorption affinity of An(Cl^-) toward them is less than that for $[RhCl_6]^{3-}$. This fact is confirmed by smaller value of Langmuir constant b for equilibrium isotherm in 0.15 M HCl solution (Table 3) and by the decrease of sorption capacity for Rh (III) with the decrease of solution acidity below 0.3 M HCl.[9,11] From 0.1 M HCl solutions, where amino groups are protonated incompletely, Pd (II) and Pt (IV) are sorbed both by the mechanism (Equation 1), and by the mechanism of inner-sphere replacement of ligands (Equation 2):

$$p(R)N + [MCl_q]^{p-} \leftrightarrows [MCl_{q-p}\{(R)N\}_p] + pCl^- \qquad (2)$$

Thus aquachlorocomplexes $[PdCl_{4-X}(H_2O)_X]^{(2-X)-}$ (x=1; 2), existing in the solution at chloride ion concentration less than 1 g-ion/L, also interact with deprotonated amino groups on the mechanism of inner-sphere replacement of ligands (Equation 3):[1]

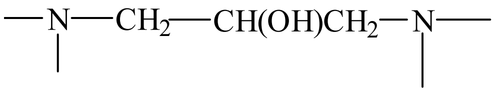
$$2(R)N + [PdCl_{4-X}(H_2O)_X]^{(2-X)-} \leftrightarrows [PdCl_2\{(R)N\}_2] + xH_2O + (2-x)Cl^- \qquad (3)$$

Table 5. Optimal conditions for the sorption recovery of noble metals and selectivity of heterochain sorbents at 20 ^{O}C

Sorbent	Metal	Optimal conditions of recovery	Selectivity	Desorption
An(Cl$^-$)	Pd(II)	0.1–3 M HCl;	pH≤1	5% Tio[a] in H_2O or
	Pt(IV)	Pd,Pt 10^{-3}–10^{-2} M	Cu(II), Co(II), Ni(II),	in 0.1 M HCl
	Rh(III)		Cd(II), Zn(II)	
		0.1–11 M HCl;		97–100% Pt(IV)
		Pd, Pt, Rh ≤10^{-3} M		
PHMTC	Ag(I)	≤5 M HNO_3;	pH<4	1 M NH_4CNS;
		Ag≤0.01 M	Cu(II), Co(II)	1 M KCNS;
				0.9 M Tio in
			>0.5 M HNO_3 Pb(II)	0.05 M H_2SO_4
				49–90% Ag(I)
PMS	Pd(II)	≤5 M HNO_3;	Cu(II), Ni(II), Pb(II),	
		Pd<0.01 M	Fe(III)	
HS-SN	Ag(I)	≤5 M HNO_3;	Co(II), Ni(II), Zn(II);	
		Ag 10^{-4}–1 M	pH<1 Pb(II)	
			>1 M HNO_3 Cu(II)	
	Pd(II)	1–8 M HCl;	Ni(II), Co(II), Zn(II),	
		Pd<0.01–0.1 M	Fe(III)	
	Cu(II)	<0.5 M HNO_3;	the same	
		1–3 M HCl;	the same	
		Cu≤0.1 M		
PSTU-3	Au(III)	3–6 M HCl	pH<1	2.4–4.5 M KCNS
	Pt(IV)	3–6 M HCl	Cu(II), Ni(II), Co(II),	or NH_4CNS
	Pd(II)	3–6 M HCl	Zn(II), Pb(II), Fe(III)	Au(III)
	Ag(I)	0.5–3 M HNO_3	the same	

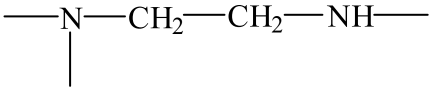
[a] thiourea

From solutions, close to neutral (K_2PdCl_4, 1 M KCl and K_2PtCl_6), Pd(II) and Pt(IV) are removed by deprotonated amino groups (mechanism Equation 2). In 0.1 M HCl solution Pd (II) forms sorption complex with *cis*-configuration according to Peyrone rule.[13] In 1 M KCl solution both *cis*- and chelate sorption complexes of Pd(II) are formed (Table 6). Probably, in weakly acidic solution Pd(II) forms *cis*-complex with two nitrogen donor atoms of the next chains owing to small concentration of free amino groups, while in neutral solution the formation of chelate complexes with the fragments of a polymeric network **1** or **2** is possible too. The change of the mechanism of the sorption of Pd(II) and Pt(IV) from anion-exchange to complex-forming with the decrease of solution acidity below 0.1 M HCl leads to the rise of diffusion resistance of sorbent phase because of the formation of anchored non-ionizing sorption complexes of the replacement type with free amino groups. This is confirmed by the decrease of sorption rate and by the change of limiting stage of sorption kinetics from both external and intraparticle diffusion to just intraparticle diffusion (Pt(IV), Table 4).



$\mathrm{-N(-)-CH_2-CH(OH)CH_2-N(-)-}$

or



$\mathrm{-N(-)-CH_2-CH_2-NH-}$

1

2

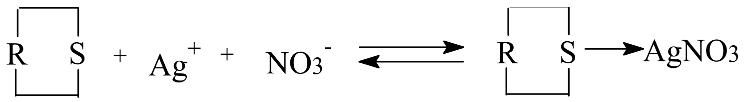
Table 6. The types of platinum metals sorption complexes generated in the phase of anionite An at 20 ^{O}C at different solution compositions

Solution	Type of sorption complex	ν(M^a–Cl) cm^{-1}	ν(M–N) cm^{-1}	Other frequencies cm^{-1}	M:N:Cl
H_2PtCl_6					
2.0 M HCl	$(R^b NH)_2[PtCl_6]$	326 s			1:2.3:5.9
0.1 M HCl	*trans*-$[Pt(RN)_2Cl_4]$ $(RNH)_2[PtCl_6]$	333 s 326 s	523 w		1:2.5:6.1
K_2PtCl_6					
H_2O, pH≤5	*trans*-$[Pt(RN)_2Cl_4]$	330 s	522 w		1:2.5:4.3
H_2PdCl_4					
3.0 M HCl	$(RNH)_2[PdCl_4]$	327 m			1:2.0:4.2
0.1 M HCl	*cis*-$[Pd(RN)_2Cl_2]$ $(RNH)_2[PdCl_4]$	330 s; 323 s			1:2.1:3.1
K_2PdCl_4					
1.0 M KCl	*cis*-$[Pd(RN)_2Cl_2]$	331 m, 322 m			1:2.5:1.8
	chelate $[Pd(RN)_2Cl_2]$	341 m, 306 m, 278 w		Skeletal 297	
H_3RhCl_6					
3.0 M HCl	$(RNH)_3[RhCl_6]$	312 m			
0.15 M HCl	$(RNH)_{3-X}[RhCl_{6-X}(H_2O)_X]$ x=1; 2	314 m		ν(Rh–O) 350 w δ(H_2O) 595–610	

[a] metal atom; [b] sorbent matrix

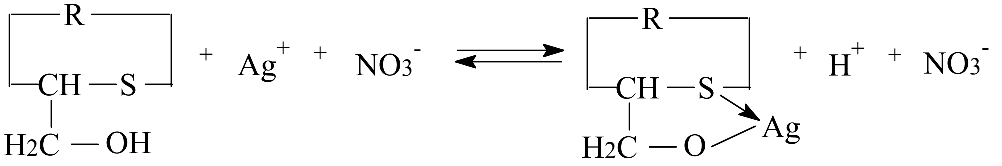
Sorption of Ag(I) from nitric acid solutions by polyhydroxymacrothiocyclane[14]

Polyhydroxymacrothiocyclane (PHMTC) has been prepared by alkaline hydrolysis of Cl-containing macrothiocyclane – cyclooligomeric adduct of 4-vinyl-1-cyclohexene and sulfur dichloride.[15] PHMTC is a macrothiocyclane a type of crown-ether, containing hydroxyl groups as substituents (Table1). Under the complexing sorbents classification based on the Pearson concept of hard and soft acids and bases (HSAB),[16] S-containing PHMTC is a soft electron donor polyligand. The reciprocal arrangement of sulfur donor atom and aliphatic alcohol group in the elementary unit of the macrocycle favours the formation of a strong five-membered S,O-chelate ring with a soft transition metal ion. According to HSAB S-containing complexing sorbents are more soft Lewis bases, than weakly basic anionites, and differ from the above by having major affinity and selectivity toward soft ions of noble metals. Common faults of the sorbents with aliphatic thioether groups are slow kinetics and nonreversible sorption of noble metals ions.[2] PHMTC is effective for quantitative recovery of Ag(I) at ambient temperature in a wide region of HNO_3 concentrations from solutions with moderate saline background (Table 5). The selectivity of PHMTC is similar to that of sorbents with aliphatic monothioether groups and is in agreement with HSAB.[2] PHMTC differs from sorbents with styrene-divinylbenzene matrix and graft aliphatic thioether groups by a six fold higher rate of Ag(I) sorption and by the possibility of quantitative desorption of Ag(I) with complexing agents solutions (Table 5). The value of maximum sorption capacity of PHMTC for Ag(I) in 1.5 M HNO_3 is less, than that of polymethylenemonosulphide (PMS) and is defined by the concentration of S donor atoms (Table 2). This magnitude indicates the formation of a sorbent complex of composition Ag:S=1:1. On the basis of the data of IRS and elemental analysis of the equilibrium sorption complexes, generated at various solution acidity, and also on the basis of the dependence of K_d from equilibrium concentration of hydrogen ions $[H^+]$ at constant ionic strength (1.5 M, $NaNO_3$) we have assumed two probable mechanisms of interaction of Ag(I) with sorbent functional groups. In the region of $[H^+] \geq 0.75$ g-ion/L, where K_d is independent of $[H^+]$, the silver(I) interacts with S donor atom according to the mechanism of addition similarly to the interaction of Ag(I) with PMS (Equation 4):[2]



$$R\;S + Ag^+ + NO_3^- \rightleftarrows R\;S \rightarrow AgNO_3 \qquad (4)$$

This mechanism is confirmed by the absence of changes in IR spectra of sorption complexes in the region of stretching vibrations of the aliphatic alcohol group ν(C–O) 1060–1090 cm^{-1}, by the appearance of absorption bands of nitrate-ion bound with Ag (I), at 720; 808; 1340–1350 cm^{-1}, as well by the decrease of sorption ability of PHMTC toward Ag(I) with temperature increase (Table 3). The decrease of extraction and sorption constants with temperature increase is characteristic of the interaction of Ag(I) with aliphatic thioether reagents.[2,17] In neutral and weakly acidic solutions ($[H^+] < 0.75$ g-ion/L) both the mechanism (Equation 4) and chelating mechanism (Equation 5) are realized.


(5)

The mechanism (Equation 4) in this region is supported by the presence of the bound nitrate-ions in the sorption complexes (IR, elemental analysis). The chelating mechanism is confirmed by the linear dependence of $\lg K_d = f(-\lg [H^+])$, by the shift of ν(C–O) of aliphatic alcohol groups to low-frequency area on 40–50 cm^{-1} in IR spectra of sorption complexes, by the decrease of the content of nitrate-ion in the sorbent phase with the decrease of acidity of the solution, as well as by considerable increase in acidity of the equilibrium solution (from pH_0 4.29 up to pH_e 2.92) in comparison with a blank run (from pH_0 4.86 up to pH_e 4.04).

Sorption of Pd(II) from nitric acid solutions by polymethylenemonothioether[18]

The sorption and complex-forming properties of the known highly selective and effective polymethylenemonothioether (polymethylenemonosulphide, PMS) toward platinum metals in hydrochloric acid solutions have been investigated, described and utilized for development of a series of hybrid methods of the analysis.[2–4] In connection with the need for recovery of Pd(II) from nitric solutions generated by the nuclear fuel cycle and processing of the wastage of electron technique, we have investigated an opportunity of the selective recovery and the mechanism of the sorption of Pd(II) by PMS from nitric solutions with consideration of the equilibrium of hydrolysis and complexation of Pd(II) in a solution. Because of high capability of nitric acid solutions of Pd(II) to hydrolyze, the sorption of Pd(II) has been investigated from solutions of two types in concentration ranges 0.004–0.07 M Pd(II) and 0.04–5 M HNO_3: freshly-prepared or fresh solutions not-containing the hydrolyzed polymeric and hydroxo forms of Pd(II) ($\varepsilon=100-140$ at $\lambda=386-412$ nm), and solutions hydrolyzed at a long-lived storage and containing polymeric and hydroxo species of Pd(II) (the change of ε from 781 to 198 and λ from 382 to 406 nm upon the increase of the solution acidity from 0.1 up to 5 M HNO_3). PMS is perspective for selective separation of Pd(II) from 50-fold excess of the ions of non-noble metals from solutions with a high saline background in a wide region of HNO_3 concentrations (Table 5) at ambient temperature both in static and dynamic conditions of the sorption. Its disadvantages are nonreversibility and slow kinetics of the sorption of Pd(II) (Table 4). The slow kinetics is characterized for extraction and sorption of platinum metals by thioether reagents on the mechanism of the inner-sphere replacement of ligands.[2] The sorption ability of PMS on Pd(II) in fresh solutions is higher, than that in hydrolyzed ones (Table 3) owing to the absence of non-sorbing polymeric hydrolyzed species of Pd(II). In the fresh solutions the sorption capacity is constant in the field of the chemical stability of PMS toward the oxidizing activity of HNO_3 (<4 M) and in a wide range of nitrate-ion concentrations (≤4 M $NaNO_3$). The sorption ability of PMS in hydrolyzed solutions is determined by hydrolytic equilibrium of Pd(II) in a solution and increases with the decrease of concentration of the polymeric forms of Pd(II) (ε) in the solution with increasing HNO_3 concentration in the range >2 M. The close values of Langmuir constants E_m for the equilibrium isotherms (Table 3) show, probably, identical stoichiometric relationships Pd:S in the sorption complexes generated in both fresh and hydrolyzed solutions. The magnitude of the maximum sorption capacity of PMS for Pd(II), obtained in a fresh 1.5 M HNO_3 solution, corresponds to $0.5E_S$ (Table 2) or to the molar relation Pd:S=1:2 in the sorption complex. Elemental and IRS analysis of this saturation product showed, that the ratio of elements in it is Pd:S:N=1:2.11:0.35 and the content of monodentate co-ordinated nitrate-ion (C_{2V}; 970 cm^{-1}, ν_S=1272 cm^{-1}, ν_{as}=1480 cm^{-1}) does not provide complete saturation of the internal coordination sphere of Pd(II) up to the coordination number 4, as is characteristic for extraction processes.[2] To establish the mechanism of the sorption of Pd(II) at ambient temperature, the products of the sorption have been explored with regard to the nature and acidity of the solution, contact time, content of Pd(II) and nitrate-ion in equilibrium products of the sorption. Irrespective of these factors, including the nature of the solution, the formation of sorption complexes of the type *trans*-PdS_2A_2 (ν(Pd–S) =306 cm^{-1}, S - donor atom of thioether group, A - anion) and the presence of the hydrolyzed species of Pd(II) in the sorbent phase (ν(Pd–OH) =583 cm^{-1}, δ(O–H) =1096–1112 cm^{-1} – the frequency of bending vibrations of OH-group coordinated with Pd(II), ν(O–H) =3368–3376 cm^{-1} - the frequency of stretching vibrations of the coordinated OH-group or water, $\delta(H_2O)$ =1660–1670 cm^{-1}) have been established. The presence of the hydrolyzed species in the products of Pd(II) sorption allowed us to assume the coordination–hydrolytic mechanism of interaction of Pd(II) with thioether groups of PMS. In view of equilibrium of the complexation in freshly-prepared solutions (Equation 6):

$$[Pd(H_2O)_4]^{2+} + nNO_3^- \leftrightarrows [Pd(H_2O)_{4-n}(NO_3)_n]^{(2-n)+} + (2-n)NO_3^- \qquad (6)$$

where n=0–2, the mechanism of the sorption of Pd(II) from fresh solutions may be described as follows (Scheme 1):

$$[Pd(H_2O)_{4-n}(NO_3)_n]^{(2-n)+} + (2-n)NO_3^- + 2(\sim CH_2SCH_2\sim) \xrightarrow{-2H_2O}$$

$$\longrightarrow [Pd(H_2O)_{2-n}(NO_3)_n(\sim CH_2SCH_2\sim)_2](NO_3)_{2-n} \xrightarrow{-(2-n)HNO_3}$$

$$\longrightarrow [Pd(OH)_{2-n}(NO_3)_n(\sim CH_2SCH_2\sim)_2]$$

Scheme 1

To describe the interaction of mononuclear hydrolyzed species of Pd(II) with PMS in strongly hydrolyzed nitric solutions of Pd (II) (< 0.5 M HNO_3) the following mechanism has been suggested, and is consistent with the absence of nitrate-ions in the sorption products (Scheme 2):

$$[Pd(H_2O)_{4-n}(OH)_n]^{(2-n)+} + (2-n)NO_3^- + 2(\sim CH_2SCH_2\sim) \xrightarrow{-2H_2O}$$

$$\longrightarrow [Pd(H_2O)_{2-n}(OH)_n(\sim CH_2SCH_2\sim)_2](NO_3)_{2-n} \xrightarrow{-(2-n)HNO_3}$$

$$\longrightarrow [Pd(OH)_2(\sim CH_2SCH_2\sim)_2]$$

Scheme 2

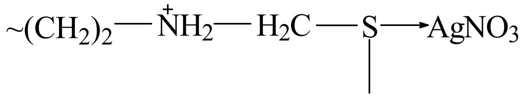
While the solvent extraction of Pd(II) by dialkylsulphides results in the formation of an extraction complex $[Pd(NO_3)_2S_2]$, the sorption of Pd(II) by polymeric thioether from nitric acid solutions results in the formation of the sorption complexes, whose composition of internal sphere is determined by the equilibria of complexation and hydrolysis in the solution. The coordination of thioether groups of the sorbent to Pd(II) leads to the increase of acidic properties of the coordinated molecules of water, what results in the formation of mixed-ligand – hydroxy-thioether complexes in the sorbent phase.The sorption affinity of soft polyligand PMS toward some noble metals in nitric solutions (Table 3) is in agreement with the decrease of the softness of these ions of metals and is similar to the sorption affinity for hydrochloric acid solutions.

Sorption of Ag(I) from nitric acid and Pd(II) from hydrochloric acid solutions by S,N-containing sorbent HS-S,N[19,20]

The sorbents with graft aliphatic bidentate S,N-containing functional groups are significantly more effective than complexing sorbents with monodentate thioether or amino groups. The introduction of a sulfur atom into an aliphatic amino group leads to changes in the donor properties of sorption centers and expands the range for concentrating metals. It is supposed, that such S,N-containing sorbents must combine high selectivity toward noble metals in acidic solutions (attributed to the thioether groups) with a rapid sorption of platinum metals at ambient temperature (attributed to amino groups). S,N-containing functional groups can act as ambidentate S- or N-donors or as chelating ligands, when their stereochemistry is favourable for the formation of five- or six membered chelate rings with coordinated ions of transition metals (for example $-S-(CH)_n-N=$ at n=2;3). S,N-containing HS's combine high selectivity of functional groups with the high capacity of heterochain polymer toward noble metals.[2] The data on sorption characteristics and the mechanism of the sorption of the ions of noble metals for such HS's are incomplete.

A weakly basic linear S,N-containing heterochain polymer HS-S,N (Table 1) has been prepared by the polycondensation of aminoethylpiperazine with formaldehyde (1:3) and H_2S in dimethylformamide under a current of H_2S, with agitation over 3 h at 20 ^{0}C. The sorbent is chemically stable in solutions ≤ 11.6 M HCl, ≤ 5 M HNO_3, ≤ 2 M NaOH. Its thermal (Table 2) and chemical stability is higher, than that of PMS. HS-S,N is characterized by the high sorption affinity towards noble metals and Cu(II) and high values of the sorption capacities at ambient temperature (Table 2). The sorption affinity of HS-S,N toward transition metals (Table 3) is in good agreement with the order of the decrease of softness of transition metals cations (the softness was estimated by the magnitude of Klopman's orbital electronegativity[21]) and reflects an affinity of soft donor atoms of sulfur toward soft ions of metals. This correlates with the increase of solubility of inorganic sulphides of transition metals similarly to the affinity for the sorbents with thiol groups and PMS.[2] The sorption of noble metals and Cu(II) is nonreversible and is accompanied by a destruction of HS-S, N. According to the data from elemental analysis general legitimacy of the sorption of studied metals is the decrease of the relative content of nitrogen in the polymer with the increase of the metal content in the sorption products. When large quantities of metals are sorbed, the final products of the sorption interaction are Ag_2S, the polymercaptides of Pd(II) and Cu(I, II); and Au(III) is reduced to metal. Among the disadvantages of HS-S,N, such as nonreversibility of the sorption and degradation of sorbent during the sorption, the partial solubility of sorbent (up to 1.3 g/L) in ≥0.5 M HCl solutions is less. The solubility decreases significantly in solutions with a high saline background. HS-S,N is characterized by higher reducing properties in comparison with PMS. The partial reduction of Ag(I) and full reduction of Au(III) up to metals in the sorbent phase under the sorption at ambient temperature have been revealed. By means of EPR the reduction of Cu(II) up to Cu(I) in the products of sorption, obtained from hydrochloric and nitric solutions without heating, have been established. The selectivity of HS-S,N toward Ag(I) in nitric and Pd(II) in hydrochloric solutions at presence of Cu(II) considerably yields to that of PMS and anionite An (Table 5). 50−700-fold excess of ferrous and non-ferrous metals does not prevent the effective recovery of Ag(I), Pd(II) and Pt(IV). The sorbent is perspective for selective concentration of Ag(I) from solutions with a high saline background in a wide interval of HNO_3 concentrations. From the solutions with low concentration of $AgNO_3$ (≤ 0.01 M) silver(I) may be selectively separated from Cu (II) in the field of ≥1M HNO_3. The large quantities of Ag(I) (≥1 M) may be effectively separated from comparable concentrations of Cu(II) irrespective of the acidity of the solution. The sorption capacity of HS-S,N for Cu(II) has considerable value at the optimal conditions of the sorption (Table 2,5). Therefore, the sorbent is effective for selective separation of Cu(II) from transition non-noble metals (Table 5).

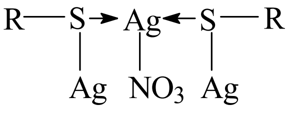
Investigation of the mechanism of sorption of Ag(I) at ambient temperature has shown, that it is multistage and complex. The first stage of this process in ≥0.1 M HNO_3 solution is the formation of an addition type complex **3** with thioether groups of the sorbent ($\nu(Ag{-}O) = 248$, $\delta(NO_2) = 812$ and $\nu(N{-}O) = 1036{-}1040\ cm^{-1}$) by a reaction similar to (Equation 4). The decrease of electron density on the sulfur atom co-ordinated with Ag(I), as well as close location of the protonated amino group characterized by negative inductive effect, apparently, weaken the bond



$$\sim(CH_2)_2{-}\overset{+}{N}H_2{-}H_2C{-}\underset{|}{S}\rightarrow AgNO_3$$

3

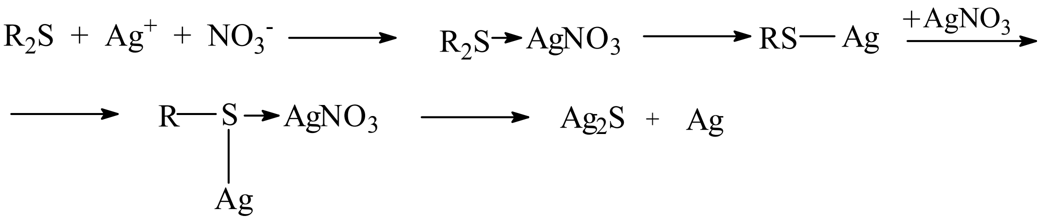
C−S and promote the destruction of sorbent, probably by *S*-dealkylation[22] or hydrolytic decomposition of the co-ordinated ligand similar to the hydrolysis of isothioamides or isothioacetamides with aliphatic substituents co-ordinated through an S atom to Pd(II) or Pt(II).[23] Decomposition leads to a decrease in the nitrogen content and to the formation of mercaptides in the sorbent phase. The sulfur atom of the bound thiol group has two unshared electron pairs and therefore it is capable of the following interaction with electron acceptors.[13] So, the following stage of interaction is the coordination of a thiol group with one another ion of Ag(I), that, probably, leads to the anomalously high capacity of the sorbent for Ag(I), relative to ~2E_S (Table 2). Taking into account high ability of thiol ligands to bridge-formation[13,22] it is possible that bridging complexes in the sorbent phase of the type **4** are formed:



$$\mathrm{R-\underset{\overset{|}{Ag}}{S}\rightarrow\underset{\overset{|}{NO_3}}{Ag}\leftarrow\underset{\overset{|}{Ag}}{S}-R}$$

4

Perhaps, the thiol compounds of Ag(I) are unstable, they undergo further decomposition resulting in the formation of a sulphide of Ag(I) and partial reduction of Ag(I) up to metal. The probable mechanism of interaction of HS-S,N with silver nitrate may be described (Scheme 3).



$$\mathrm{R_2S + Ag^+ + NO_3^- \longrightarrow R_2S\rightarrow AgNO_3 \longrightarrow RS-Ag \xrightarrow{+AgNO_3} R-\underset{\overset{|}{Ag}}{S}\rightarrow AgNO_3 \longrightarrow Ag_2S + Ag}$$

Scheme 3

The equilibrium of the sorption of Ag(I) from solutions ≥0.2 M $AgNO_3$ is reached for 12−14 days, but from less concentrated solutions (0.01 M $AgNO_3$, 0.1 M HNO_3) Ag(I) is taken completely in 1-2 minutes.

Pd(II) is quantitatively taken with HS-S, N over a wide range of HCl concentrations at ambient temperature. Thus, the sorption capacity for Pd(II) grows from 1 up to 12.5 mmol/g with the rise in HCl concentration from 0.1 up to 4 M and is maintained maximum in the range of 4-8 M HCl. The sorption of Pd(II) from moderately acidic solutions (2 M HCl) under heating at 100 ^{0}C allows one to increase sorption capacity up to maximum. The time of achievement of sorption equilibrium for small initial concentrations of Pd(II) (0.01 M) is about 6 h in the weakly acidic solutions (0.1 M HCl), but in the more acidic solutions (≥1M HCl) Pd(II) is taken completely for 1 min at room temperature. It allows the use of the sorbent for rapid recovery of Pd(II) from acidic solutions (≥1 M HCl) at ambient temperature. This favourably distinguishes it from PMS, since for the quantitative sorption of Pd(II) by PMS for analytical purposes boiling for 1−2 h is required.

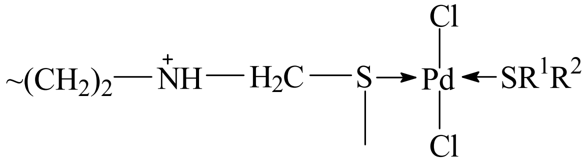
On the basis of the data of IRS and elemental analysis of the sorption products depending on an acidity of medium, contact time and of the dependence of the rate of the sorption of Pd(II) from an acidity of the solution we have assumed two mechanisms of interaction of Pd(II) with functional groups of HS-S, N depending upon the acidity of the medium:

1.The sorption of Pd (II) from weakly acidic solutions (< 0.5 M HCl) occurs by slow formation of an inner-sphere complex of the replacement type with deprotonated amino groups such as *trans*-$PdCl_2N_2$ (ν(Pd–N) =512 cm–^{1}, ν(Pd–Cl)=345 cm^{-1}). Subsequent replacement of chloride-ions in the internal coordination sphere by two sulfur atoms of thioether groups with the formation of the mixed-ligand aminothioether complex of the type *trans*-PdS_2N_2 occurs. Further formation of an aminomercaptide complex such as *trans*-$Pd(S_m)_2N_2$ (ν(Pd–N) =400 cm^{-1}, ν(Pd–S_m) =385 cm^{-1}) may be attributed to the destruction of coordination through sulfur atom polymer sites by *S*-dealkylation or hydrolysis.

2. For strongly acidic solutions (≥1 M HCl) the following mechanism for the sorption of Pd(II) is probable: rapid formation of ionic associates with protonated amino groups of the type $(RNH^+)_2[PdCl_4]$, further rapid inner-sphere replacement of two cloride-ions by atoms of thioether sulfur with formation of a complex such as *trans*-$PdCl_2S_2$, subsequent replacement of chloride-ions by the atoms of thioether sulfur accompanied by the destruction of sorbent by *S*-dealkylation or hydrolysis and final formation of the complex *trans*-$Pd(S_m)_2S_2$ (ν(Pd–S_m) =385 cm^{-1}, ν(Pd–S) =272 cm^{-1}).

The opportunity for interaction of $[PdCl_4]^{2-}$ with donor atoms of thioether sulfur in acidic solutions at room temperature on the mechanism realized for interaction of Pd(II) with PMS on heating in hydrochloric acid solutions[2,24] and resulting in the formation of the complex *trans*-$Pd(S_m)_2S_2$ isn't exclude. Thus, the acidity of a solution determines the mechanism of the sorption, composition of interior coordination sphere of sorption complexes, the value of sorption capacity and the rate of recovery of Pd(II).

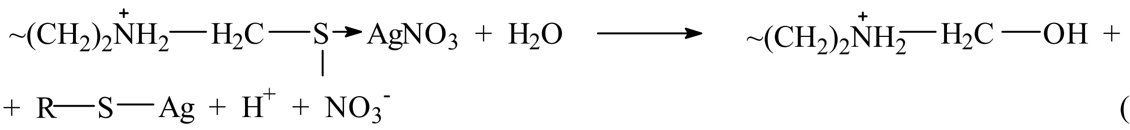
The destruction of HS-S,N after coordination of metal ions with sulfur atoms occurs under mild conditions and results in the formation of the corresponding mercaptides Cu(II,I), Ag(I), Pd(II). It is known, that the *S*-dealkylation of coordinated thioether groups in aliphatic monothioethers and aminothioethers proceeds spontaneously only for the complexes of Ag(I) and Au(III), but in the case of Pd(II) heating in dimethylformamide is nesessery.[22] Examples of *S*-dealkylation of coordinated ligands, containing amino groups in the α-position to the thioether sulfur are absent. Graft aminothioether groups of the sorbents, such as $R–NH–(CH_2)_n–S–R$, where n≥2, do not degrade on coordination with platinum metals ions.[2] Mild conditions of the degradation of HS-S,N during the interaction with Pd(II) in acidic solutions indicate that the mechanism of decomposition of the coordinated ligand on the C–S bond in the sorption complex **5** (where R^1 and R^2 - polymeric fragments of sorbent) is probably similar to the hydrolysis of



$$\sim(CH_2)_2-\overset{+}{N}H-H_2C-\underset{|}{S}\rightarrow \overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{Pd}}\leftarrow SR^1R^2$$

5

coordinated with Pd(II) or Pt(II) isothioamides such as $R^1{-}S{-}C(NHR^2)NR^2$ or isothioacetamides such as $[R^1{-}S{-}C(NH_2^+)R_2]Cl$ (R^1, R^2 - methyl or ethyl).[23,25] Coordination of such ligands with ions of platinum metals through sulfur atom is accompanied by a hydrolysis of the ligand on C–S bond under mild conditions (ambient temperature, the absence of hydroxyl-ions, neutral and even weakly acidic medium), and results in formation of mercaptides such as $Pt(SR^1)_2$. It is believed[23,25] that the redistribution of electron density in the coordinated ligand leads to increase of electrophilicity of the carbon atom bound with the coordinated sulfur atom. As a result the attack of this carbon atom by molecules of water and hydroxyl-ions is facilitated, and the hydrolysis of the ligand is accelerated. A similar mechanism of hydrolysis of aliphatic thioamide groups of sorbents coordinated with ions of platinum metals, results in the formation of inorganic sulfides of metals in the sorbent phase under mild conditions.[2] Indirect confirmation of the mechanism of hydrolytic decomposition of HS-S, N coordinated with Ag(I) on the suggesting reaction (Equation 7) may be considerable acidification of the solution from pH 3-4 up to pH~1 after recovery of Ag(I) from 0.2 M $AgNO_3$ solution at g:v=1:100 (g:mL), temperature 20 ^{0}C and contact time 2 h. The equilibrium 1 M $NaNO_3$ solution is characterized by value pH 5 after the contact with HS-S,N under the same conditions.



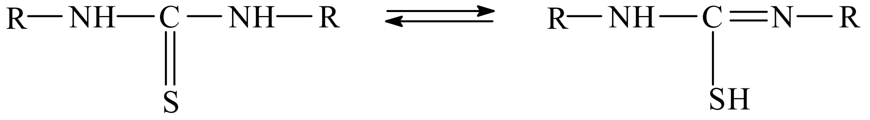
$$\sim(CH_2)_2\overset{+}{N}H_2-H_2C-\underset{|}{S}\rightarrow AgNO_3 + H_2O \longrightarrow \sim(CH_2)_2\overset{+}{N}H_2-H_2C-OH + $$
$$+ R-S-Ag + H^+ + NO_3^- \qquad (7)$$

Sorption of noble metals by poly-[*N,N'-bis*-(3-silsesquioxanylpropyl)thiocarbamide]

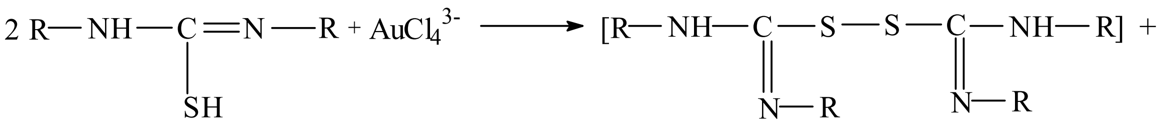
The hydrolytic polycondensation of organosilicon carbofunctional monomers $(RO)_3Si(CH_2)_nX$, where R - alkyl, n≥1, X - ionogenic or complexing group, is a simple and convenient method of preparation of organosilicon sorption materials. One of the most effective and useful S,N-containing organosilicon HS – poly[*N,N′-bis*-(3-silsesquioxanylpropyl)thiocarbamide], or PSTU-3 (Table 1,2), has been prepared by the hydrolytic polycondensation of *N,N′-bis*-[3-(triethoxysilyl)propyl]thiourea at 95-100 ^{0}C in an aqueous medium.[7]

The sorption ability of PSTU-3 toward 20 elements has been investigated. Depending upon the acidity of the solution the sorbent interacts with ions of transition metals by complexation, cation- or anion-exchange, and it also shows reducing properties. The sorption properties and selectivity of PSTU-3 are determined by the state of thiocarbamide functional groups and also by the nature and complexed forms of the metal in the solution.

Thiocarbamide functional group has three potential donor atoms capable of coordination with ions of soft transition metals. According to the structure it can act as neutral S- or N-ambidentate ligand or as S,N-bidentate chelating ligand. Alkyl substituents at the atoms of nitrogen change the electron-donor ability of sulfur atom, as well the reducing properties of thiocarbamide group in comparison with thiourea.[24] Reducing properties of PSTU-3 are relatively higher, than that of PMS. Using the methods of elemental and IRS analysis of sorption complexes the probability of reduction of Au(III) up to Au(I) and Pt(IV) up to Pt(II) in the phase of PSTU-3 has been established, when these metals are sorbed from hydrochloric solutions without heating. PMS at ambient temperature reduces up to the lowest oxidation state only Au(III),[26] but reduction of platinum metals (Pt(IV) up to Pt(II), Ir(IV) up to Ir(I), Os(IV) up to Os(II)) occurs only under heating.[24] The mechanism of reduction of Au(III) and Pt(IV) in the phase of PSTU-3 [5,7] is explained by the position of thione–thiol tautomeric-equilibrium of thiocarbamide group (Equation 8):



$$\mathrm{R{-}NH{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}NH{-}R \rightleftarrows R{-}NH{-}\underset{\underset{\displaystyle SH}{|}}{C}{=}N{-}R} \qquad (8)$$



$$\mathrm{2\,R{-}NH{-}\underset{\underset{\displaystyle SH}{|}}{C}{=}N{-}R + AuCl_4^{3-} \longrightarrow [R{-}NH{-}\underset{\underset{\displaystyle N{-}R}{\|}}{C}{-}S{-}S{-}\underset{\underset{\displaystyle N{-}R}{\|}}{C}{-}NH{-}R] +}$$

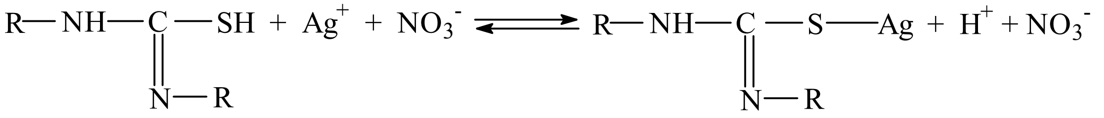
$$+\ \mathrm{AuCl_2^-} + 2\mathrm{H}^+ + 2\mathrm{Cl}^- \qquad (9)$$

Au(I) and Pt(II) reduced up to the lowest oxidation states are more soft Lewis acids, than Au(III) and Pt(IV)[21] and they interact with thiocarbamide groups by inner-sphere replacement. The reduction of Au(III) and Pt(IV) in the sorbent phase requires in confirming by X-Ray electron spectroscopy.

The selectivity of PSTU-3 toward ions of metals is in agreement with HSAB and is comparable to the selectivity of PMS, this characterizes which sorbent as a soft electron-donor reagent. The sorbent does not sorb ions of hard alkaline, alkaline-earth and rare-earth elements. In acidic solutions at $pH < 1$ the sorbent is highly selective toward Au(III), Ag(I), Hg(II) and platinum metals at the presence of 10^5-fold excess of heavy and non-ferrous metals (Table 5). Thus the efficiency of recovery of noble metals by PSTU-3 (the values of sorption capacity (Table 2) and high distribution coefficients - $(1.8–5.5)\cdot 10^3$ cm^3/g) is comparable to that of the best organopolymeric sorbents with graft complexing groups.[2] At ambient temperature from acidic solutions PSTU-3 quantitatively takes only Au(III), Ag(I), Hg(II), Pd(II), Pt(IV). For quantitative sorption of the kinetically inert complex forms of Ir(IV), Rh(III), Ru(III), Os(IV) the more rigid conditions (high acidity 3–12 M H_2SO_4, heating at 100 ^0C) are necessary as in the case of PMS.

Using the methods of elemental analysis and IR spectroscopy (1000–3500 cm^{-1}) of saturated sorption complexes has established the coordination mechanism of interaction of Ag(I) in nitric acid and Au(III), Pd(II), Pt(IV) in hydrochloric acid solutions with the thione-form of thiocarbamide groups of PSTU-3, dominated in acidic solutions.[24] The coordination mechanism of sorption of Ag(I) is confirmed by the large time of the achievement of sorption equilibrium (4 h in 0.5 M HNO_3 solution); for Au(III) – by the possibility of desorption only by the solutions of strong complexing agents (Table 5); for Au(III) and Pd(II) – by the replacement of two, and for Pt(IV) - four chloride-ions in interior coordination sphere of their chlorocomplexes. The shift of the bound ν(N−H) to the long-wave area on 40−50 cm^{-1} in the spectra of sorption complexes of Pd(II) and Pt(II) allows us to assume coordination of metals ions on one of the nitrogen atoms of thiocarbamide group. Sorption affinity of PSTU-3 toward soft metals in acidic solutions (Table 3) is similar to that for PMS and is characteristic for S-donor sorbents. The theoretical and experimental study of the complexes of thiourea and its derivatives with Pd(II), Pt(II), Pt(IV), show that *N,N′*-dialkylsubstituted derivatives are coordinated with these metals only on the sulfur atom.[22,24,25] Use of radiochemical and spectroscopic methods has established the formation of coordinately-unsaturated surface sorption complexes of Ag(I) with coordination through thione atoms of S in the graft thiourea groups, for the sorption of Ag(I) by chemically modified silica from solutions at pH 10–4 M HNO_3.[27] So, these publications show a high probability of coordination of noble metals with thiocarbamide groups of PSTU-3 through thione atoms of S. To establish reliably the nature of coordinated donor atoms and configuration of sorption complexes of noble metals a more detailed study of complexes by the methods of long-wave length IR and diffuse reflection spectroscopy is necessary.

With the decrease of the solution acidity (pH 1 to 12) the thiol-form of thiocarbamide functional groups begin to prevail. This form interacts with cations of transition metals Ag(I), Hg(II), Cu(II), Cd(II), Th(IV) and UO_2^{2+} by the cation-exchange mechanism (Equation 10):

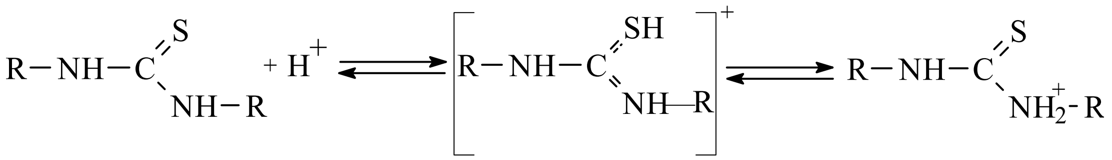


$$R-NH-\underset{\overset{\|}{N-R}}{C}-SH + Ag^{+} + NO_3^{-} \rightleftharpoons R-NH-\underset{\overset{\|}{N-R}}{C}-S-Ag + H^{+} + NO_3^{-}$$

(10)

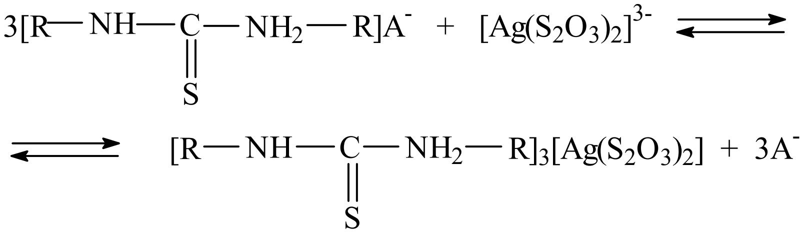
Thus, cations of heavy and non-ferrous metals are sorbed by PSTU-3 in a more acidic region (pH 1−5) in comparison with PMS (pH 4−7). In contrast to PMS, organosilicon HS quantitatively takes cations of Th(IV) and UO_2^{2+} (K_d=5900 and 1050 cm^3/g accordingly, pH 3−5). The sorption of Ag(I) and Hg(II) in the area of pH 1−12 is not selective in the presence of transition metals and realized by both cation-exchange and by coordination mechanisms.

In highly acidic solutions thiocarbamide ligands are protonated mainly at the sulfur atom with the formation of sulphonium cation[24,28] and to a much less degree - with the nitrogen atom. Authors[23] suggest the existence of equilibrium between S- and N-protonated forms (Scheme 4):



Scheme 4

Owing to the probability of formation of thiuronium salts by thiocarbamide groups of PSTU-3 in acidic thiosulphate solutions the sorption of Ag(I) occurs from such solutions both by complex-forming and by anion-exchange mechanisms (Equation 11):



$$3[R-NH-\underset{\overset{\|}{S}}{C}-NH_2-R]A^- + [Ag(S_2O_3)_2]^{3-} \rightleftarrows$$
$$\rightleftarrows [R-NH-\underset{\overset{\|}{S}}{C}-NH_2-R]_3[Ag(S_2O_3)_2] + 3A^- \qquad (11)$$

Probability of the anion-exchange sorption of species $[Ag(S_2O_3)_2]^{3-}$ is confirmed by the possibility of desorption of Ag(I) with HNO_3 solutions.[5]

The high selectivity and efficiency of PSTU-3 toward noble metals, and also possibility of regeneration define the scope of its application in analytical practice and hydrometallurgy. A series of progressive methods for the analysis of Au, Ag, Pd, Pt in various areas have been developed.

Conclusions

The selectivity and mechanism of interaction of the investigated complex-forming HS with ions of noble metals, as well the type of generated sorption complexes are determined by the structure and the state of functional groups of sorbent; by the nature of electron-donor atoms and ions of transition d-metal; by the equilibriums of complexation and hydrolysis of the complex forms of metal in the solution depending on an acidity, saline background and temperature of the solution. Weakly basic porous anionite An differs from thioether HS in smaller selectivity toward Pd(II), Pt(IV), Rh(III) in acidic solutions. It is rather effective for the rapid group concentrating of these metals at ambient temperature under the optimal conditions for the sorption on the anion-exchange mechanism. PMS is the most selective toward noble metals in hydrochloric and nitric solutions. Its main disadvantages are the slow kinetics of the sorption of noble metals and necessity of the heating for quantitative recovery of kinetically inert platinum metals. The introduction of weakly basic amino groups into polymeric chain of monothioether (HS-S,N) decreases selectivity of sorbent in acidic solutions in comparison with PMS, but allows rapidly and effectively to uptake acidocomplex anions of platinum metals from acidic solutions at ambient temperature due to the prompt anion-exchange with counter-ions of the protonated amino groups at the first stage of interaction. HS-S,N distinguishes from weakly basic anionites by the possibility of highly selective and effective recovery of Ag(I) by donor atoms of S in a wide range of HNO_3 concentrations. The close locating of N- and S-donor atoms through methylene group promotes the hydrolytic degradation of HS-S,N coordinated through S-atoms with ions of soft metals under mild conditions. This defines the mechanism of sorption of Ag(I) and anomalously high sorption capacity for Ag(I). The separation of N- and S-atoms through the ethylene group is represented optimal and sufficient for the stabilization of the coordinated ligand with conservation of labilizing activity of protonated amino groups and high sorption ability of S,N-containing sorbents.

The rows of the sorption affinity toward ions of soft transition metals are similar in the main for S- and S,N-containing sorbents PMS, HS-S,N and PSTU-3. According to HSAB they reflect an affinity of soft electron-donor atoms of S to ions of soft metals. All investigated sorbents are perspective for application in analytical practice of noble metals. The possibility of regeneration allows to suppose the usefulness of An, PHMTC and PSTU-3 in hydrometallurgy.

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