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Palladium(II) Extraction by Sulfur-Containing Calix[4,6]arenes from Hydrochloric Acid Solutions

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Abstract—The comparison of the extraction properties of calixarenes, thiacalixarenes, and calix[4,6]arene thioethers showed that methyl(thiamethyl)calix[4,6]arenes **3a** and **4a** have the highest extraction abilities. These extractants rapidly and completely extract palladium from hydrochloric acid solutions; regarding distribution factors achieved in the kinetic mode, they three to four orders of magnitude exceed their monodentate analogue, octylbenzyl sulfide (OBnS). Approaches are considered to enhance palladium extraction via generating mixed palladium species in low-acidity solutions and via intramolecular catalysis by the protonated oxygen atoms of alkoxy groups in the lower rim. For 1 M HCl, the kinetic order of diluent effects on palladium extraction was established. The substitution of sulfur atoms for bridging CH_2 groups was discovered to enhance palladium extraction by calix[4]arene thioether **3c**.

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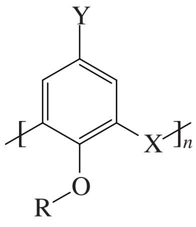
Extraction of palladium by organic sulfides (dialkyl sulfides and petroleum sulfides) from hydrochloric solutions is widely used in technologies for processing of platinum-metal concentrates [1, 2]; in the analytical chemistry of palladium, silver, and gold [2, 3]; and in refining palladium chips for deep decontamination from silver radionuclides [4] in chloride systems. The main limitation for use of these extractants is the low rates of palladium extraction from hydrochloric solutions. This is due to the low surface-active properties of organic sulfides and the inertness of the $PdCl_4^{2-}$ major species in the substitution of the extractant for chloride ion. It is known from [5–8] that the zone of the chemical reaction between palladium and R_2S in heterogeneous systems can be either in one of the conjugate phases or at their interface. Possible approaches to enhancing palladium extraction are increasing R_2S concentration in the starting aqueous phase [5], improving the surface-active properties of R_2S [6] and palladium complex species [7], and introducing anion-exchange additives into the organic phase to catalyze interfacial transfer of $PdCl_4^{2-}$ [8]. These ideas were used to study palladium extraction by macrocyclic calix[4,6]arene thioethers, which was described for hydrochloric solutions with $c_{HCl} > 0.5$ mol/L. Available data [9–11] refer to low-acidity solutions (pH 1–3), in which palladium exists as labile aquachloro complexes.

Compared to monodentate R_2S, polydentate calix[*n*]arene thioethers acquire new possibilities due to the chelation and dimensional effects resulting from complex formation: these effects improve the efficiency and selectivity of extraction of precious metals (palladium, silver, and gold) [9–14]. In addition, substitution of sulfur atoms for bridging CH_2 groups in the macrocyclic platform in calix[*n*]arene ethers (thiacalix[*n*]arenes) and calix[*n*]arene thioethers (thiacalix[*n*]arene thioethers) considerably widens the range of potential extractants. Thiacalix[*n*]arenes have recently generated great interest in the context of the participation of bridging sulfur atoms in chelation during cation-exchange extraction of many metals, including palladium, silver, and gold, from low-acidity solutions and also in the context of the feasibility of substitution of RO group in the upper rim and inhibition of classical reactions in the upper rim of the thiacalix[*n*]arene [15–18]. We have not found any data on the extraction properties of thiacalix[*n*]arene thioethers in the literature.



№	n	R	Y	X
1a^b	4	C_3H_7	H	CH_2
1б^b	4	H	t-C_4H_9	S
2a^a	4	CH_3	H	S
2б^c	4	n-C_4H_9	H	S
3a^b	4	n-C_3H_7	CH_2SCH_3	CH_2
3б^b	4	n-C_3H_7	$CH_2SC_4H_9$-n	CH_2
3в^b	4	n-C_3H_7	$CH_2SC_6H_4CH_3$-p	CH_2
4a^a	6	CH_3	CH_2SCH_3	CH_2
4б^a	6	CH_3	$CH_2SC_4H_9$-n	CH_2
5^b	4	H	$CH_2SC_6H_4CH_3$-p	S

^{a} *conformationally mobile*; ^{b} *cone*; ^{c} *1,3-alternate*

Scheme 1.

In this work, we compare the extraction characteristics of calix[4]arenes (**1a**), calix[4,6]arene thioethers (**3a–3**c, **4a**, and **4b**), and their thia derivatives (**1b**, **2a**, **2b**, and **5**) (Scheme 1); we also substantiate the choice of the most efficient extraction system for rapid recovery of palladium from hydrochloric acid solutions.

EXPERIMENTAL

The chemicals used were dibenzyl sulfide (DBnS), octylbensyl sulfide (OBnS) (pure grade), HNO_3 and HCl (both of high-purity grade), and organic solvents (toluene, CCl_4, and dichloroethane of chemically pure grade) after distillation.

Calixarene thioethers **3a–3**c, **4a**, **4**b [13], and **5** [26]; and thiacalixarenes **1**b and **2a–2**c [19, 20] were prepared as described elsewhere.

Solutions of extractants L in diluents (10^{-5} to -10^{-3} mol/L) were prepared from exactly weighed aliquots of calixarenes. The stock palladium solution was prepared by dissolving K_2PdCl_4, which was synthesized from metallic palladium (99.9%) as described in [21]. Working palladium solutions (10^{-4} to 10^{-3} mol/L) were prepared by diluting the stock solution to the required HCl concentration (0.01–6 mol/L).

Solutions of trioctylammonium chloride (QCl) in toluene were prepared by stirring solutions of trioctylamine in diluents with equal volumes of 1 M HCl for 20–30 min and then used for preparing mixtures with L.

Extraction was performed by vigorously stirring (at 100 rpm) of equal volumes of organic and aqueous phases at 298 K for 2–180 min. Palladium extraction being a non-steady-state process, effective distribution ratios were determined: $D_\tau = (c^0_{\mathrm{Pd}} - c_\tau)/c_\tau$, where c^0_{Pd} and c_τ are, respectively, the initial and current palladium concentrations in hydrochloric acid solutions for a fixed moment. The palladium concentration in aqueous solutions after extraction was determined by atomic absorption (Hitachi Z-800 spectrophotometer) with Zeeman background correction in air–acetylene flame or in an electrothermal atomizer, with a blank carried out at low palladium concentrations (on the level of 0.02 μg/mL).

In calculating observed rate constants from $k_{\text{н}} = 2.3\log(c^0_{\mathrm{Pd}}/c_\tau)$, Excel 97 and Origin 7.0 standard program packages were used for data processing.

RESULTS AND DISCUSSION

The test sulfur-containing calix[4,6]arenes contain three types of sulfur atoms (one bridging atom and two in $CH_2SC_6H_4CH_3$ and CH_2SAlk groups), which differ in their charge states. Presumably, the inductive and steric effects of substituents at sulfur atoms in polydentate macrocyclic ligands and their monodentate analogues vary symbatically. If so, diphenyl sulfide (DPS) is an analogue of thiacalixarenes; for calixarene thioethers **3**c and **5**, the analogue is DBnS; and for **3a**, **3**b and **4a**, **4b**, the analogue is OBnS. It was demonstrated in [5, 22] that the reaction of palladium with dialkyl sulfides is located in the aqueous phase (which is chloride [5] or nitrate—nitrite [22] solution). With account for the hydrophobicity of R_2S molecules, the general order of the influence of organic sulfides on the rate constants, complex-formation equilibrium constants, and extraction constants was experimentally established as follows: DPS $\ll$ DBnS < OBnS < R_2S (propyl > hexyl) [23, 24]. As applied to sulfur-containing calix[4,6]arenes, this order can be transformed as follows: **1b**, **2a**, **2b** $\ll$ **3c**, **5** < **3b**, **4b** < **3a**, **4a**. The experimental data below, in general, support this tendency.

Palladium Extraction by Thiacalix[4]arenes

For palladium, unlike for gold [13] and other metals, 7–8% recovery (D_{Pd} = 0.07–0.08) is observed in extrac-

Table 1. Palladium extraction by tolyl(thiomethyl)calix[4]arene (**3c**) and its thia analogue **5** from hydrochloric solutions to toluene

L	$c_L \times 10^3$, mol/L (c_{QCl})	$c^0_{Pd} \times 10^4$, mol/L	HCl	τ, min	D_τ	k_{obs}, s^{-1}
3c	6.65	6.8	0.01	10–60	130–800	$(8.0 \pm 2.0) \times 10^{-3}$
3c	6.65	9.1	0.1	10–60	80–2400	3.7×10^{-3}**
3c	6.65	7.2–8.4	1.0	10–60	0.15–3.1	$(3.7 \pm 0.7) \times 10^{-4}$
3c	6.65	7.1	3.0	10–60	0.2–5.8	$(5.0 \pm 0.9) \times 10^{-4}$
3c	6.65	7.4	6.2	10–60	0.5–12.8	$(6.9 \pm 0.6) \times 10^{-4}$
3c	5.4 (0.19)	7.7	1.0	30–180	2.2–3250	$(6.9 \pm 0.6) \times 10^{-4}$
3c	4.43	8.4	1.0	10–60	0.15–3.70	$(3.5 \pm 1.0) \times 10^{-4}$
3c	3.33	7.2–8.4	1.0	10–60	0.15–2.21	$(3.0 \pm 0.5) \times 10^{-4}$
3c	3.32 (0.14)	3.4	3.0	10–45	0.52–35.4	$(0.7 \pm 0.1) \times 10^{-3}$
3c	3.32 (0.7)	3.4	3.0	10–45	12.5–1820*	$(3.8 \pm 0.5) \times 10^{-3}$
3c	3.32 (1.4)	3.4	3.0	10–45	134–1820*	$(7.0 \pm 0.1) \times 10^{-3}$
3c	5.5	3.4	3.0	5–1300	0.3–519	$(1.4 \times 0.2) \times 10^{-4}$
5	2.83	7.2	1.0	5–30	0.7–3.1	$(1.8 \pm 0.8) \times 10^{-3}$
DBnS	26.5	9.1	0.1	60	30	3.7×10^{-4}**
	26.5	6.8	1.0	10–60	0.28–0.94	$(3.9 \pm 0.6) \times 10^{-4}$
	26.5	7.4	6.2	10–60	0.92	1.8×10^{-4}**

* Palladium concentration in the aqueous phase is below the detection limit.

** k_{obs} was estimated from two points.

tion from chloride solutions by conventional calixarene **1a** (from 1 M HCl) and *p*-methoxycalix[4]arene (from 0.1 M HCl). In transfer from **1a** to thia-substituted **1b**, the extraction efficiency almost does not change (D_{Pd} = 0.05–0.1). This means that bridging sulfur atoms do not participate in coordination to palladium during extraction; the donor ability of sulfur in **1b** only insignificantly differs from that in DPS, for which the $PdCl_4^{2-}$ extraction constant is 12 orders of magnitude lower than for $(C_6H_{13})_2S$ [24]. Palladium extraction by calix[4]- and thiacalix[4]arenes is due to the π-binding of the palladium complex species with the fused aromatic system of the macrocycle; the existence of this binding was verified by EXAFS spectroscopy in benzene solutions of $PdCl_2(R_2S)_2$ [25]. This interaction enhances both outer-sphere coordination of palladium to benzene rings and its inclusion into the macrocyclic cavity. Therefore, calix[4]arenes **2a** and **2b** in the 1,3-alternate and partial cone conformations almost do not extract palladium ($D < 0.01$).

The influence of the bridging sulfur atom on the gold [26] and palladium extraction properties of calix[4]arene thioethers functionalized in the upper rim was discovered in comparing the properties of **3c** and **3**. In going from **3c** to **5**, gold extraction is reduced by two orders of magnitude [26]; palladium extraction is, in contrast, enhanced (Table 1). For gold, the effect can arise from the reduction of electron density on the sulfur atom in the $-SC_6H_5CH_3$ group because of *p*-π interactions with the aromatic rings of the macrocycle. For palladium, in contrast, a rise in the π-donor ability of the aromatic system of the macrocycle enhances extraction. Thus, the above opposite effects on palladium and gold extraction generate the fundamental possibility of separating these metals with dominant palladium recovery, which is atypical of known S,N,O-coordinating extractants. For palladium and gold in the ratio 1 : 1, palladium refining from gold is 3–10 times.

Palladium Extraction by p-Tolyl(thiamethyl)calix[4]arene 3c

Palladium extraction by solutions of **3c** in toluene rises with acidity (1–6 M HCl), despite the increasing concentrations of competing chloride ions (Fig. 1a), but almost does not change for monodentate DBnS and OBnS when $c_{HCl} > 1$ mol/L (Fig. 1b). This difference can arise from the presence of a propoxy group in the lower rim; as a result of protonation, the propoxy oxygen atom acts as an intramolecular catalyst of anion-exchange $PdCl_4^{2-}$ transfer

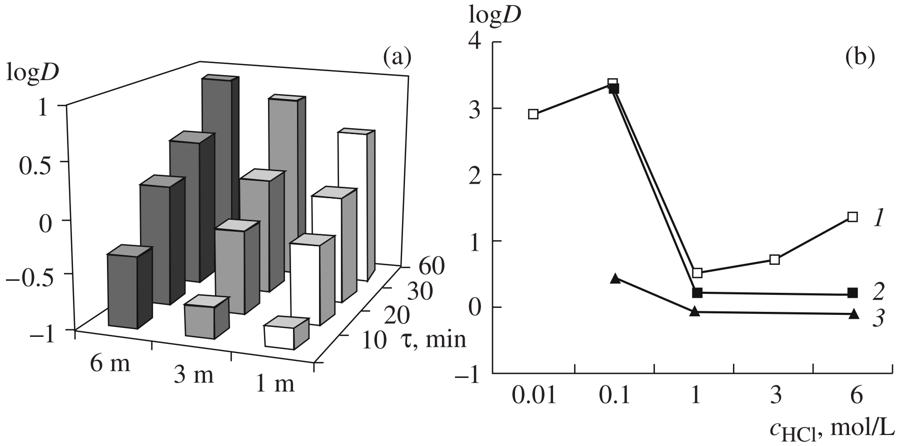


Fig. 1. Effect of HCl concentration on palladium extraction by solutions of **3c**, DBnS, and OBnS in toluene. Panel(a): 6×10^{-3} mol/L **3c** and 7×10^{-4} mol/L Pd. Panel (b): (*1*) 6×10^{-4} mol/L **3c**, (*2*) 2.65×10^{-3} mol/L OBnS, and (*3*) 7×10^{-3} mol/L Pd. $\tau = 60$ min.

$$PdCl^{2-}_{4(aq)} + LH_2Cl_{2(org)} \xrightarrow{\text{rapidly}} LH_2PdCl_{4(org)} + 2Cl^{-}_{(aq)}, \qquad (1)$$

which is followed by the replacement of chloride ions in the coordination surrounding of palladium:

$$LH_2PdCl_{(org)} \longrightarrow PdCl_2L_{(org)} + 2HCl_{(aq)}. \qquad (2)$$

Indeed, this species is absent in the electronic absorption spectra of extracts with **3c** because of the substitution of the extractant for chloride ion in the organic phase, and the position of the absorption band at 27000–28000 cm^{-1} is close to that in the spectra of $PdCl_2(R_2S)_2$ [27]. The protonation of the propoxy group in **3c** enhances the surface-active properties of the extractant. Therefore, the independence of the palladium extraction rate from 1 M HCl from the concentration of **3c** in the bulk of the organic phase (Table 1) results from the interaction between palladium and **3c** near or at the interface. The sulfur atom in R_2S having a far lower basicity than the oxygen atom in R_2O ($pK_a = -2.42$ for Et_2O and -6.8 for Et_2S [28]), the HCl concentration has no effect on palladium extraction by monodentate R_2S (Fig. 1b).

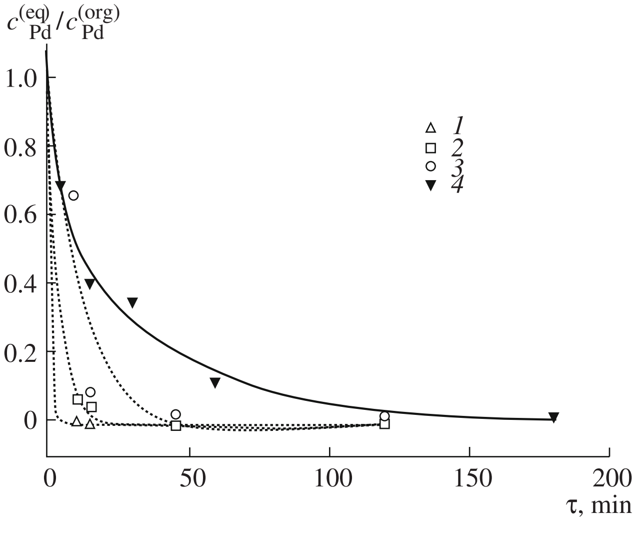


Fig. 2. Aqueous palladium concentration vs. time in extraction by solutions of **3c** in toluene. $c_{Pd} = 7 \times 10^{-4}$ mol/L, $c_L = 3.3 \times\times 10^{-3}$ mol/L and (*4*) 5.3×10^{-3} mol/L. c_{QCl} = (*4*) 0, (*3*) 1.4×10^{-4} mol/L, (*2*) 7.0×10^{-4} mol/L, and (*1*) 1.4×10^{-3} mol/L. W : O = 1 : 1.

The catalytic effect can be enhanced by introduction of trioctylammonium chloride QCl (an anion-exchange additive) (Fig. 2). The enhancement rises with increasing additive concentration: with increasing QCl concentration from 20 to 100% relative to the QCl/Pd = 2 stoichiometry, $E_{Pd} > 95\%$, respectively, after 45 and 15 min (without additive, after 180 min) (Table 1). We should note that anion-exchange palladium extraction

$$PdCl^{2-}_{4(eq)} + 2QCl_{(org)} = Q_2PdCl_{4(org)} + 2Cl^{-}_{(eq)}, \qquad (3)$$
$$K_{a0} = 6.3 \times 10^5 \ [24]$$

is insignificant in the range of c_{QCl} tested (calculated $D_{Pd} = 0.0014–0.14$); therefore, the additive has a catalytic effect.

For lower acidities (0.01–0.1 M HCl), high extraction efficiencies (Table 1) must be due to the presence, in the starting solution, of a nonsymmetrical complex species (possibly, $Pd(H_2O)Cl_3^-$ [5]) with its surface activity increased relative to $PdCl_4^{2-}$. Likely, it is for this reason that calix[4]arenes functionalized with SMe and S–C(S)NMe_2 in the lower rim rapidly extracted palladium introduced in the form of $PdCl_4^{2-}$ in nitrate

Table 2. Palladium extraction from HCl by alkyl(thiamethyl)calix[4,6]arenes in diluents

L	Diluent	$c_L \times 10^3$, mol/L	c_{HCl}, mol/L	$c^0_{Pd} \times 10^4$, mol/L	τ, min	D_τ	k_{obs}, s^{-1}
3a	Toluene	2.32	1.0	7.8	40–90	4100*	–
	«	3.5	1.0	7.8	40–90	4100*	–
	«	7.2	1.0	7.7	2–15	135–4100*	0.03 ± 0.01
4a	«	8.1	1.0	7.2	5–30	3800*	0.03**
	«	0.74	1.0	7.2	60	3800*	–
3b	«	0.33	1.0	7.8	40–90	2.0–7.3	$(4.2 \pm 0.3) \times 10^{-4}$
	«	0.64	1.0	7.8	40–90	3.6–14	$(6.6 \pm 1.3) \times 10^{-4}$
	«	1.2	1.0	7.8	40–90	8.1–4100*	$(9.2 \pm 1.6) \times 10^{-3}$
	«	7.0	1.0	7.8	2–60	1.3–4100*	$(5.6 \pm 0.3) \times 10^{-3}$
	CCl_4	2.68	1.0	7.2	2–60	760–3800*	0.055 ± 0.023
	«	6.52	1.0	7.8	5–10	4100*	–
	Dichloroethane	3.17	1.0	7.2	2–60	0.57–3800*	$(1.03 \pm 0.4) \times 10^{-3}$
	«	6.52	1.0	7.8	5–10	4100*	–
4b	Toluene	7.3	1.0	7.2	2–30	1.2–3800*	$(4.9 \pm 0.7) \times 10^{-3}$
	«	0.66	1.0	7.2	60	4.6	4.7×10^{-4}**
OBnS	«	26.8	0.1	9.1	10–60	7.5–2400	3.0×10^{-3}**
	«	26.8	1.0	6.9	10–300	0.33–3600	$(5.4 \pm 1.5) \times 10^{-4}$
	«	26.8	6.2	7.4	10–60	0.37–1.8	3.5×10^{-4}**

* Palladium concentration in the aqueous phase is below the detection limit.

** k_{obs} was estimated from two points.

solutions with pH 1–3 [9–12]. The trend in D_τ in this region for **3c** and DBnS is the same and caused by equilibria between palladium phases in the aqueous phase (Fig. 1b). These data supplement the increasing order of the kinetic efficiency of palladium species established for R_2S [22]: $PdCl_4^{2-} < Pd(H_2O)Cl_3^-$, and $Pd^{2+} < Pd(NO_2)_2 < PdNO_2^+$. For $PdCl_4^{2-}$ and $PdNO_2^+$, all other conditions being equal, the complete palladium extraction is achieved after 30 min and 10 s, respectively. Therefore, the minimum (Fig. 1b) in the acidity range 0.1 M < 1 M < 3 M, likely, appears because palladium exists as the inert species $PdCl_4^{2-}$ exclusively and because of the low degree of protonation of the oxygen atom of the propoxy group; that is, under these conditions, the concentration of **3c** in the aqueous phase can control the extraction efficiency.

Thus, due to the low donor ability of the sulfur atom and low extraction rates, tolylmethylcalix[4]arene is not efficient enough for concentrating palladium from hydrochloric acid solutions, although its thia derivatives are of interest for palladium separation from gold. In addition, with the identical concentrations of the sulfur atoms, **3c** only insignificantly exceeds DBnS in extraction from 1 M HCl because of complex formation sterically hindered by the bulky benzene ring.

Palladium Extraction by Alkyl(thiamethyl)calix[4,6]arenes

Palladium extraction by calix[4,6]arene thioethers, as by monodentate thioethers, depends on the phase contact time (Table 2, Fig. 3). With an excess of the extractant, the variation of the current palladium concentration in the aqueous phase with time is quite well fitted by the first-order rate equation

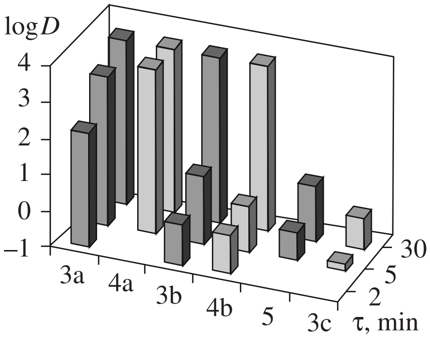


Fig. 3. Effect of the phase contact time on palladium extraction from 1 M HCl to solutions of calix[4,6]arene thioethers in toluene. $c_{Pd} = 7 \times 10^{-4}$ mol/L. $c_L = 6.6 \times 10^{-3}$ mol/L for **3a, 3b, 4a**, and **4b** and $c_L = 3.3 \times 10^{-3}$ mol/L for **3b** and **5**.

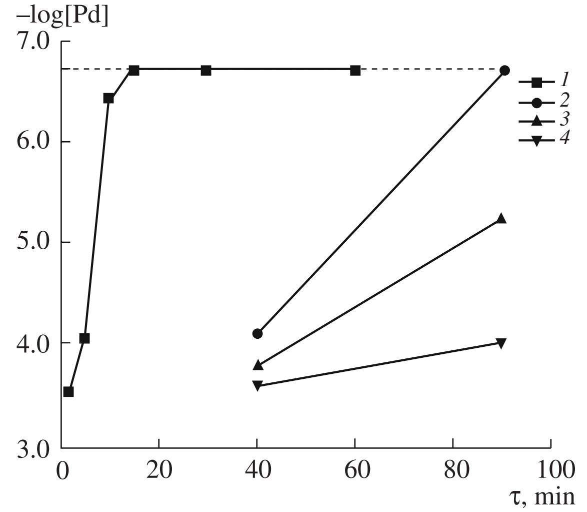


Fig. 4. Effect of the concentration of **3b** in toluene on palladium extraction from 1 M HCl. c_L = (*1*) 7.0 × 10^{-3}, (*2*) 1.2 × 10^{-3}, (*3*) 6.4 × 10^{-4}, and (*4*) 3.3 × 10^{-4} mol/L. c_{Pd} = 7.8 × 10^{-4} mol/L. The blank is shown by a dashed line.

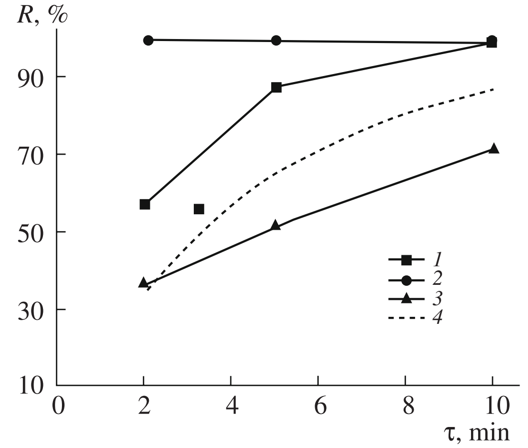


Fig. 5. Palladium(II) extraction from 1 M HCl to solutions of **3b** in diluents: (*1*) CCl_4 (*1*, $c_L = 2.68 \times 10^{-3}$ mol/L; (*2*) toluene, $c_L = 7.0 \times 10^{-3}$ mol/L; (*3*) DCE, $c_L = 3.17 \times 10^{-3}$ mol/L; and (*4*) toluene, estimated for $c_L = 3.17 \times 10^{-3}$ mol/L. $c_L = 3.3 \times 10^{-3}$ mol/L.

$$[\mathrm{Pd}]_{\mathrm{aq}} = c^0_{\mathrm{Pd}} \exp(-k_{\mathrm{obs}} \cdot \tau). \qquad (4)$$

In view of the fact that k_{obs} for extraction from 1 M HCl for methyl-substituted **3a** and **4a** is higher than for more hydrophobic butyl-functionalized **3b** and **4b** (Table 2) and with reference to data for **3c** (for 1 M HCl), we have enough reasons to think that palladium extraction by calix[4,6]arene thioethers under these conditions is controlled by the concentration of L in the aqueous phase according to

$$\mathrm{L}_{(\mathrm{aq})} \rightleftarrows \mathrm{L}_{(\mathrm{org})}, \quad K_{\mathrm{L}} = c_{\mathrm{L}}^{(\mathrm{org})}/c_{\mathrm{L}}^{(\mathrm{aq})}. \qquad (5)$$

In the same way, the rate-controlling reaction for R_2S is the substitution reaction

$$\mathrm{PdCl}^{2-}_{4(\mathrm{aq})} + \mathrm{L}_{(\mathrm{aq})} \xrightarrow{k_1} \mathrm{PdCl_2L}_{(\mathrm{aq})} + 2\mathrm{Cl}^-_{(\mathrm{aq})}, \qquad (6)$$

whose rate ($w = k_{\mathrm{H}} \times c_{\mathrm{L}}^{(\mathrm{aq})} c_{\mathrm{Pd}}$) depends on k_{obs} and K_L. With increasing alkyl radical volume at the S atom, the hydrophobicity of the molecule rises, the equilibrium aqueous concentration of L decreases, and the extraction efficiency is reduced in going from methyl- to butylcalix[4]arene thioethers (Table 2).

For **3b**, unlike for tolyl-functionalized **3c**, an increase in the concentration in the bulk of the organic phase enhances palladium extraction (Fig. 4). When $c_L > c_{Pd}$, the extraction efficiency increases with rising excess extractant concentration, and the residual aqueous palladium concentration ($\log[\mathrm{Pd}]_t$) acquires, with time, the level of the blank. Under these conditions, D_{Pd} is on the level of (3–4) × 10^3 for two- to fourfold molar excess of L (Table 2).

When $c_{Pd} : c_L \geq 1$, the extraction efficiency decreases as the extractant is saturated with palladium (Table 2). The limiting ratio Pd : L in the organic phase is two, corresponding to the generation of the complex $(PdCl_2)_2L$, in which there are two thioether groups per palladium atom, as in palladium nitrate complexes with **3a**–**3b** [14].

We could expect that transfer from conformationally rigid calix[4]arenes to labile calix[6]arenes would reduce steric hindrances due to conformational alteration. However, our data show that D_{Pd} changes only insignificantly in going from **3a** and **3b** to **4a** and **4b** (Table 2). Thus, changes in the cavity volume and conformational rigidity of calixarenes are not the key factors for the palladium extraction efficiency.

Alkyl(thiamethyl)calix[4]arenes in toluene provide the complete (>99.9%) palladium extraction in shorter times (2–5 min for **3a** and 30 min for **3b**) than monodentate R_2S with the same concentration of donor atoms (Table 2); for short times, D_{Pd} for **3a** and **3b** is three to four orders of magnitudes the respective values for OBnS and DBnS (Tables 1, 2).

The effect of the nature of the diluent on the extraction efficiency is determined by the distribution of L on account of different solvating abilities of diluents. In gold(III) extraction by calixarene thioethers [13, 26] and monodentate R_2S [2], it was demonstrated that the increasing polarity in the order CCl_4 < toluene, benzene < dichloroethane in equilibrium increases extraction constants due to the preferred solvation of $AuCl_3L$. In the case of palladium (Fig. 5), the highest extraction by **3b** for small extraction times is observed for CCl_4, and R_{Pd} for solutions of **3b** in dichloroethane and toluene for commensurate c_L are close (estimation for toluene solutions with c_L = 33 mmol/L was carried out on the assumption of a linear dependence of the extraction efficiency on c_L).

The increasing order of $R(D)_{Pd}$ (dichloroethane ≤ toluene < CCl_4) corresponds to the decreasing order of R_2S solvating abilities [29]. The highest palladium extraction by **3b** with CCl_4 as diluent is due to the lowest K_L and, thus, the highest aqueous concentration of L according to equilibrium (5). The rapid acquisition (in 2–5 min) of high D_{Pd} (up to 4×10^3; Table 2) and D_{Au} values [13, 16] from chloride solutions (1–3 M HCl) with the use of a three- to fourfold excess of **3a** in toluene provides a more than 99% overall extraction of these metals. Thus, the use of calixarene thioethers releases the main limitation inherent to monodentate R_2S and opens a possibility for organizing palladium extraction together with gold in a continuous mode, in particular, with the use of solid extractants. The nonsteady-state character of palladium extraction by calix[4]arene thioethers and the extremely low palladium concentrations in raffinates kept us from calculating extraction constants; they were determined using conjugate equilibria [27].

To conclude, we list the main strengths of calix[4,6]arene thioethers over monodentate R_2S:

(i) The possibility of chelation increases D_{Pd} by three to four orders of magnitude compared to palladium extraction with R_2S from chloride and nitrate–nitrite solutions [4, 14] and shortens the time of complete palladium recovery from 40–60 min to 2–5 min;

(ii) Additional enhancement of palladium extraction is possible due to intermolecular catalysis by the protonated oxygen atoms of alkoxy groups in the lower rim of calix[4,6]-arene thioethers for HCl concentrations higher than 2–3 mol/L;

(iii) The presence of bridging sulfur atoms in thiacalix[4,6]arene thioethers differently affects their reactivity to palladium and gold, creating prerequisites for the extraction separation of these metals.

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