ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 4, pp. 624–632. © Pleiades Publishing, Ltd., 2013.
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Extraction of Palladium(II) from Hydrochloric Acid Solutions with Triacylated Ethyleneamines

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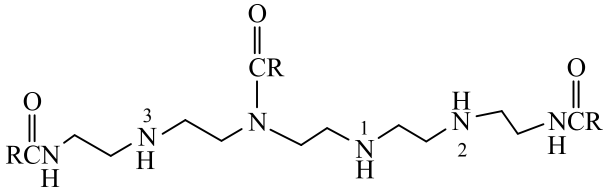
Received April 9, 2012

Abstract—Extraction of palladium(II) from hydrochloric acid solutions with novel efficient extractants, triacylated ethyleneamines, was studied. The most effective extraction of palladium(II) was observed from 0.5–1 M HCl solutions. Extraction of palladium(II) from 1 M HCl solutions was found to occur through mixed (coordination and anion-exchange) mechanism. In the field of dominance of the anion-exchange mechanism of the extraction of palladium(II) with triacylated pentaethylenehexamine the concentration constant of palladium(II) extraction was calculated, and thermodynamic parameters of extraction were evaluated.

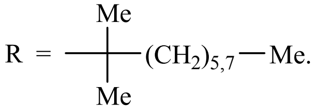
DOI: 10.1134/S1070363213040026

In the last decade the interest appeared to amides as extractants of platinum metals. *N*-Disubstituted monoamides and *N*,*N*'-tetrasubstituted diamides are characterized by low efficiency and low selectivity of extraction of palladium(II), platinum(IV), and rhodium(III) from hydrochloric acid solutions at the optimal acidity of the aqueous phase of 5–7 M HCl and the absence of tin(II) chloride as a labilizing agent [1–3]. However, functionalized amides containing pyridine or thioether groups, secondary or tertiary amine groups in the structure are highly efficient and selective extractants of platinum metals [4–10]. We have developed a simple one-pot method for the synthesis of functionalized di- and triamides based on the cheap and available industrial chemicals: ethyleneamines and synthetic α,α'-branched C_{10}–C_{14} carboxylic acids [10, 11]. Bis-acylated diethylene triamine obtained by this method effectively extracts gold(III), palladium(II), platinum(II), platinum(IV), rhodium(III), ruthenium(III), and iridium(IV) from hydrochloric acid solutions, and triacylated ethyleneamine extracts rhodium(III) [6–10]. It is known that aliphatic polyamines extract palladium(II) more efficiently than monoamines [12]. However, an increase in the number of secondary amino groups in bis-acylated ethyleneamines causes an increase in their solubility in aqueous solutions of hydrochloric acid [11]. The introduction of additional α,α'-branched acyl group into the fragment of ethyleneamine of bisamide molecule allows to reduce significantly the solubility of the extractant in an aqueous hydrochloric acid medium (more than 7 times) [10, 13, 14].

The purpose of this work was to study the extraction properties of the novel triacylated ethyleneamines obtained by condensation of pentaethylenehexamine fraction and more accessible and cheaper fraction of heavy polyamines with a narrow fraction of α,α'-branched $C_{10,12}$ carboxylic acids (triamides L_1 and L_2, respectively) with respect to palladium(II) when extracting from hydrochloric acid solutions.



L_1



$$R = \overset{\text{Me}}{\underset{\text{Me}}{-\!\!\!\!+\!\!\!\!-}}(CH_2)_{5,7}\!-\!Me.$$

The synthesized triamides L_1 – triacylated pentaethylenehexamine and L_2 are high boiling mixtures of isomers and homologues.

Triamide L_2 contains predominantly triacylated pentaethylenehexamine fraction (~70–75%). Since triamides are polyfunctional reagents containing in their structure the amine and amide groups, to estimate the influence of the amide groups on the extraction of palladium(II) we have synthesized bis-acylated ethylenediamine L_3 containing only amide groups as a model reagent.

$$\overset{\displaystyle O}{\underset{}{\overset{\|}{RC}}}\underset{H}{N}$$

All reagents are resistant to acid (2.5 M H_2SO_4) and alkaline (pH_{eq} ~ 11, NaOH) hydrolysis at ambient temperature [10, 13, 14]. They are well soluble in alcohols, aromatic hydrocarbons, chloroform, carbon tetrachloride (0.1–0.5 M), moderately soluble in saturated hydrocarbons (<0.1 M), and almost insoluble in water. Triamides L_1 and L_2 are characterized by similar values of amine numbers (Table 1).

The values of protonation constants $\log K_1 = 8.33$, $\log K_2 = 6.27$ for L_1 and $\log K_1 = 8.17$, $\log K_2 = 6.12$ for L_2 obtained by the potentiometric titration method (60% aqueous 2-propanol, 0.5 M $NaClO_4$) indicate that in the triamide molecule two amine nitrogen atoms are sufficiently basic and the acid-base properties of the reagents are similar. This was confirmed by the study of the extraction of hydrochloric acid. The equilibration time of the acid extraction with the reagents L_1 and L_2 does not exceed 1 min, so the extraction was carried out with a time of phases contact $\tau = 5$ min. Figure 1 shows the dependence of the ratio of the concentration of hydrochloric acid in the extract (without the acid recovered by diluent) and the initial concentration of the reagent $Z = c_{HCl\ org}/c_L$ on the equilibrium concentration of hydrochloric acid in the aqueous phase. In both reagents two amine nitrogen atoms (presumably 1 and 2) are completely protonated at acid concentration in aqueous phase above 0.1 M in accordance with reaction (1).

$$L_{org} + 2H^+_{aq} + 2Cl^-_{aq} \rightleftarrows L{\cdot}2HCl_{org}. \quad (1)$$

The third amine nitrogen atom reacts considerably with hydrochloric acid at the acidity of the aqueous phase at least of 1 M. Apparently, it is fully protonated when acidity of aqueous phase is more than 2 M. Further increase in acidity leads to the superstoichiometric HCl extraction with the reagents.

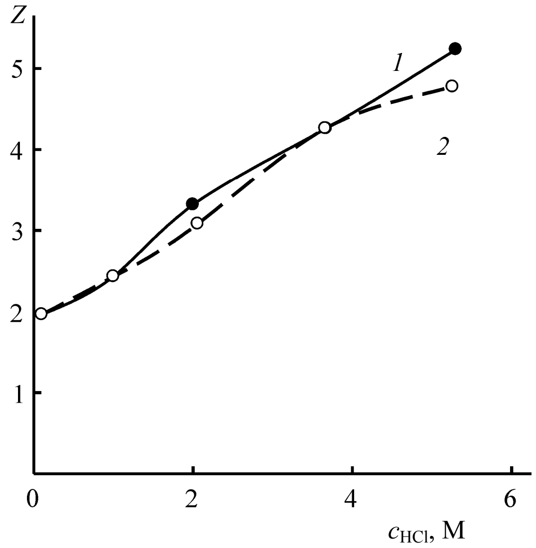


Fig. 1. Dependence of extraction of HCl with the reagents L_1 (*1*) and L_2 (*2*) on the acidity of aqueous phase (c_L = 0.06 M, toluene with 15 vol % of *n*-octanol as diluent).

To study the extraction of palladium(II) from HCl solutions we used solutions of triamide salts $L{\cdot}2HCl$ in diluents providing prevention of the third phase formation in metal extraction. The diluents were CCl_4 with 15 vol % of *n*-octanol for L_1 and toluene with 15 vol % of *n*-octanol for L_2. The equilibrium time of extraction of palladium(II) with the reagents L_1 and L_2 does not exceed 2.5 and 8 min, respectively (Fig. 2). Extraction of palladium(II) with the reagents L_1 and L_2 was studied at the time of phases contact of 5 and 15 min, respectively. Figure 3 shows the dependence of the extraction of palladium(II) with the reagents L_1–L_3 on the initial acid concentration in the aqueous phase. The triamides L_1 and L_2 most effectively extract palladium(II) from 0.5–1 M HCl solutions. The metal

Table 1. Spectral parameters and amine numbers of synthesized compounds

Reagent	IR spectrum, cm^{-1}			^{13}C NMR spectrum δ, ppm (NHC=O)	Amine number, mg HCl g^{-1}
	ν(N–H) of amide and amine groups	I amide band	II amide band		
L_1	3343	1638	1533	177.87–178.27[a]	97.1
L_2	3337	1639	1531	177.86–178.19[a]	95.6
L_3	3336	1639	1533	179.69, 182.90	

[a] Set of signals.

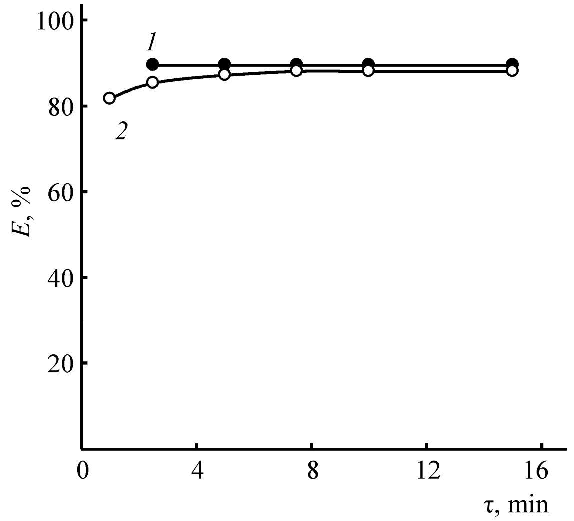


Fig. 2. Dependence of extraction degree of palladium(II) from 1 M HCl solution with the reagents L_1 (*1*) and L_2 (*2*) on the time of phases contact. (*1*) $c_{Pd} = 0.0114$ M, $c_L = 0.015$ M; (*2*) $c_{Pd} = 0.0104$ M, $c_L = 0.012$ M.

extraction decreases with increasing acidity of the aqueous phase. At the concentration of HCl 0.1 M the formation of the third phase was observed. Like *N*,*N*-dioctylacetamide [1] and *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-tetradecylmalonamide [2], diamide L_3 extracts palladium(II) from HCl solutions with a low efficiency even when using a tenfold excess of the reagent concentration relative to the metal concentration in the aqueous phase. The extraction of palladium(II) with diamide decreases with increasing acidity of the aqueous phase from 0.1 to 1 M HCl and in the range of 1–6 M HCl does not exceed 5%. Further acidification to 10 M of HCl is accompanied by an increase in the extraction of metal ions up to 24%. The study of extraction properties of triamides toward palladium(II) was carried out at the acid concentration in the aqueous phase of 1 M, wherein the metal ions extraction with the amide groups of the reagents is negligible, and palladium(II) exists in the aqueous phase in the form of $PdCl_4^{2-}$ [15].

The steepness of the initial parts of the extraction isotherms of palladium(II) (Fig. 4) indicates a high extraction affinity of triamides to the metal ions. The value of solvate number determined by the extraction equilibrium shift method from the initial parts of extraction isotherms (Fig. 5) is equal to 1 for both reagents in the range of equilibrium concentrations of palladium(II) in the aqueous phase *X* of 0.0005–0.0013 M. Consequently, we can assume that in a region far from saturation of the organic phase the extracted compounds have a composition Pd:L = 1:1. It is known that the extraction of palladium(II) with tetraoctylethylenediamine hydrochloride from 1–3 M HCl solutions occurs through anion-exchange mechanism with the formation of ionic associates $[R_4N_2(CH_2)_2H_2]PdCl_4$ [12]. Fast extraction of palladium(II) with triamides, the presence of a broad absorption band of *d*–*d*-transition $^1A_{1g}\rightarrow{}^1A_{2g}$ of $PdCl_4^{2-}$ ion (D_{4h}) with maximum at 473–475 nm [16] in the electronic spectra of the extracts corresponding to the initial section of the isotherms, a decrease in the distribution ratio of the metal with increasing total concentration of chloride ions in the aqueous phase at constant acidity of aqueous phase, the value of the slope of log $D = f(\log [Cl^-])$ dependence close to –2 (Fig. 6) suggest the predominance of anion-exchange mechanism of palladium(II) extraction in the area far from saturation. Anion-exchange extraction based on the protonation features of the reagents [Eq. (1)] may be described by the following Eq. (2).

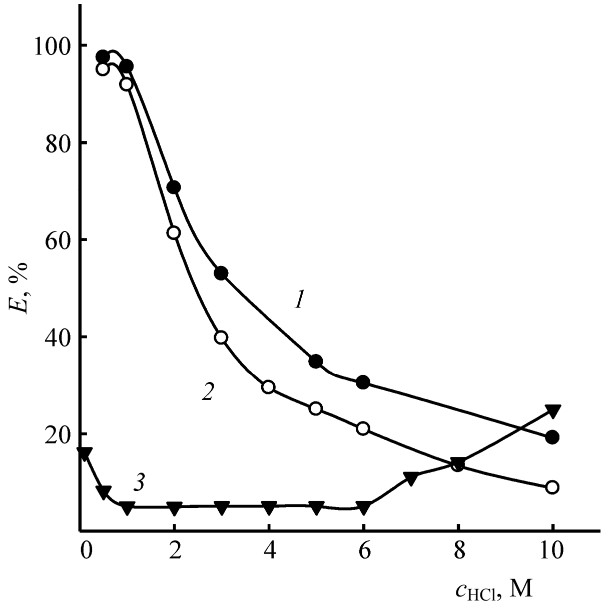


Fig. 3. Dependence of extraction degree of palladium(II) with the reagents L_1 (*1*), L_2 (*2*) and L_3 (*3*) on the initial concentration of HCl in aqueous phase. (*1*) $c_{Pd} = 0.0067$ M, $c_L = 0.015$ M, CCl_4 with 15 vol % of *n*-octanol as diluent, τ = 5 min; (*2*) $c_{Pd} = 0.0067$ M, $c_L = 0.010$ M, toluene with 15 vol % of *n*-octanol as diluent, τ = 15 min; (*3*) $c_{Pd} = 0.0054$ M, $c_L = 0.050$ M, toluene as diluent, τ = 15 min.

$$PdCl_{4\,aq}^{2-} + L{\cdot}2HCl_{org} \rightleftarrows (LH_2)PdCl_{4\,org} + 2Cl^-_{aq}, \quad (2)$$

The value of solvation number determined by the saturation method (Fig. 4) is 0.84–0.85 for L_1 (c_L = 0.010 and 0.015 M) and 0.75–0.77 for L_2 (c_L = 0.010

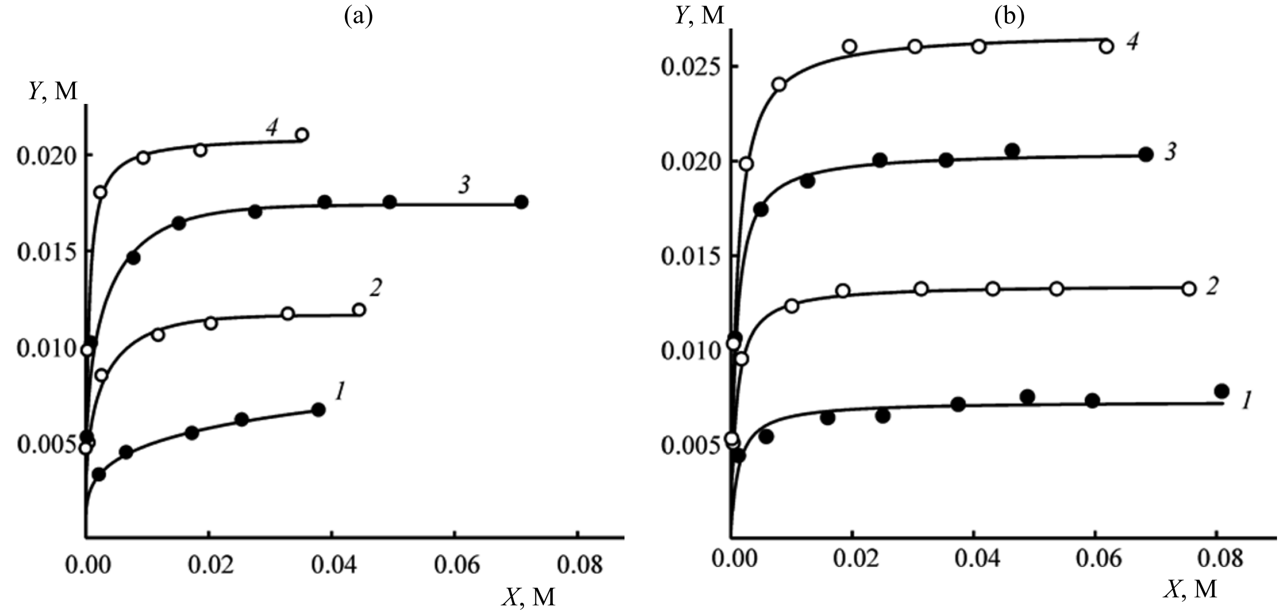


Fig. 4. Extraction isotherms of palladium(II) from 1 M HCl solutions with the reagents L_1 (a) and L_2 (b). X and Y are equilibrium concentrations of palladium(II) in aqueous and organic phase, respectively. c_L, M: (*1*) 0.005, (*2*) 0.010, (*3*) 0.015, and (*4*) 0.022.

and 0.020 M). Therefore, we can assume that at saturation of the organic phase triamides interact with palladium(II) through mixed (anion-exchange and coordination) mechanism with the participation of protonated and unprotonated amino groups. A lower value of solvation number of the reagent L_2 and its higher efficiency (Fig. 4) are caused by the larger content of free amino groups due to the presence of 10% of triacylated polyamines of following type in its composition:

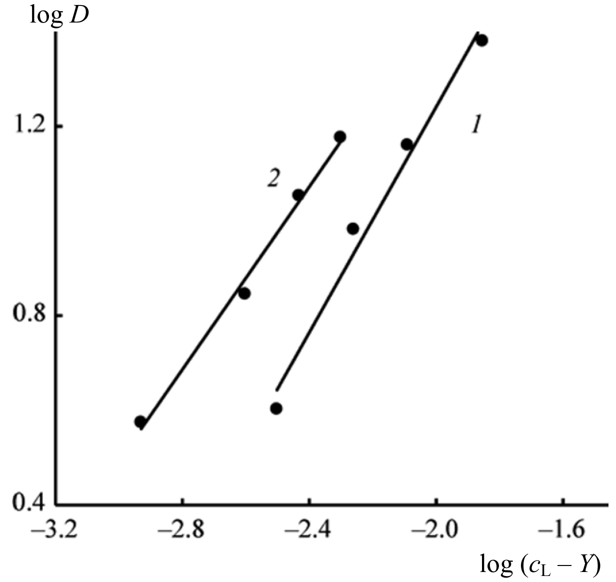


Fig. 5. Dependence of distribution ratio of palla-dium(II) on the concentration of free extractant (c_L–Y) for extraction with the reagents L_1 (*1*) and L_2 (*2*) from 1 M HCl solutions [c_L is the initial reagent concentration, M, Y is the equilibrium concentration of Pd(II) in organic phase, M]. (*1*) $X = 0.0005$ M, slope = 1.19, $r^2 = 0.981$; (*2*) $X = 0.0010$ M, slope = 0.97, $r^2 = 0.993$.

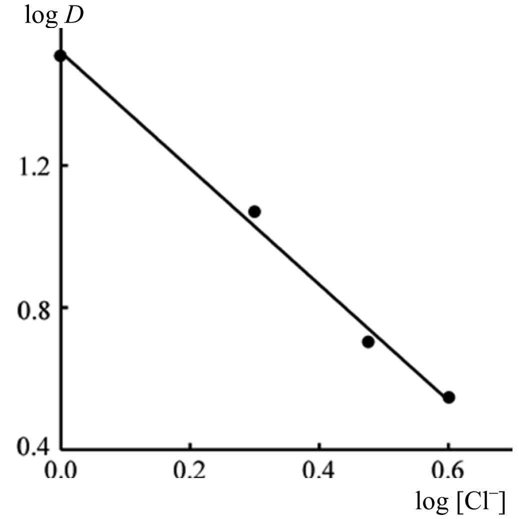
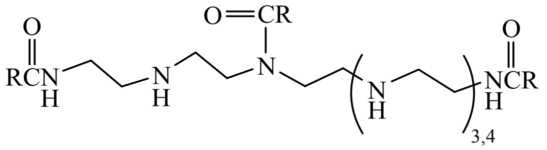
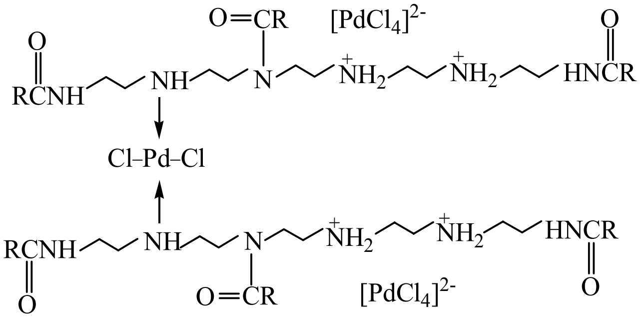


Fig. 6. Dependence of distribution ratio of palladium(II) on the concentration of chloride ions for extraction with the reagent L_1 from 1 M HCl solutions. [Cl^-] is the concentration of chloride ions in aqueous phase, g-ion l^{-1}; $c_{Pd} = 0.0096$ M, $c_L = 0.080$ M; slope = –1.63, $r^2 = 0.993$.



The mixed extraction mechanism under saturation conditions is confirmed by the data of electronic spectroscopy of extracts and IR spectroscopy of palladium(II) extracted compounds. The absorption bands in the electronic spectra of extracts are poorly resolved. The spectra of extracts contain a broad absorption band of *d–d*-transition of $PdCl_4^{2-}$ ion with the maximum at 475 nm ($\varepsilon \sim 78$ and ~ 69 for the reagents L_1 and L_2, respectively), indicating the presence of ionic associates, and low-intensive absorption bands (shoulders) with the maxima at 400 and 345 nm (L_1) and at 400, 360 and 340 nm (L_2), which can be attributed to the spin-allowed *d–d*-transitions of planar coordination compounds of palladium(II) with a symmetry lower than D_{4h} [16]. It is found that there are no significant changes of positions and intensities of the amide I and II absorption bands in the IR spectra of salt forms $L_{1,2}\cdot 2HCl$, $L_1\cdot 3HCl$ and of ion associate, obtained in palladium(II) extraction from 2.5 M HCl solution with $L_1\cdot 3HCl$ (chloroform), and of palladium(II) extracted compounds with the reagents L_1 and L_2, obtained under conditions of saturation of the organic phase at the acidity of 1 M HCl, in comparison with those in the spectra of triamides (Table 1). This indicates that the amide groups of triamides are not protonated and, probably, do not interact with palladium(II) under the extraction conditions at the acidity of the aqueous phase of 1–2.5 M. A broad diffuse absorption band with maxima at 2733–2660 (shoulder) and 2443–2357 cm^{-1} (shoulder) in the spectra of reagents hydrochlorides and palladium(II) ion associate can be attributed to the stretching vibrations ν(N–H) of the protonated secondary amino groups, and absorption band of medium intensity at 1701–1699 cm^{-1} in these spectra corresponds to $\delta(NH_2^+)$ [17]. In the spectrum of the ion associate an intensive absorption band at 330 cm^{-1} attributable to ν(Pd–Cl) of $PdCl_4^{2-}$ ion [18] is observed. The presence of the absorption band of the protonated amine groups with the maxima at 2730–2650 and 2478–2370 cm^{-1} and as a shoulder $\delta(NH_2^+)$ at 1690 cm^{-1} in the spectrum of palladium(II) extracted compound with the reagent L_1 confirm the existence of the protonated ethyleneamine groups. The spectrum of extracted compound with L_1 contains an intensive band of ν(Pd–Cl) of $PdCl_4^{2-}$ ion at 331 cm^{-1} and a weak absorption band at 350 cm^{-1}, which can be attributed to ν(Pd–Cl) of the complex of the type *trans*-$PdCl_2L_2$ (L = pyridine, alkylamine) [18]. This confirms the mixed mechanism of palladium(II) extraction by $L_1\cdot 2HCl$ and shows a significant predominance of ionic associates in the compound isolated from saturated extract. Since the rate of extraction of palladium(II) through the anion exchange mechanism is much higher than in the case of coordination mechanism, the formation of the coordination units including the unprotonated nitrogen atoms in compound with Pd:L_1 = 3:2 and suggested structure shown below is probably impeded due to electrostatic repulsion of the associated ions $PdCl_4^{2-}$.



In the far IR region the spectrum of palladium(II) extracted compound with L_2 is more complex. The absorption bands of medium intensity at 566, 554, and 451 cm^{-1} and of low intensity at 480 cm^{-1} observed in this spectrum can be attributed to ν(Pd–N), and two intensive absorption bands at 371 and 338 cm^{-1} can be assigned to ν(Pd–Cl) of palladium(II) coordination compounds with triethylenediamine groups of the extractant [18, 19]. The medium-intensive absorption bands at 3202, 3119 and 3040 cm^{-1} observed in the spectrum of this compound can be attributed to ν(N–H) of the secondary eamine groups whose nitrogen atoms are coordinated with palladium(II) ions [20]. In the spectrum of palladium(II) extracted compound with the reagent L_1 only a slight increase in the intensity of absorption at 3200–3190 cm^{-1} was observed. Thus, the IR spectral data show much greater contribution of the coordination mechanism in the extraction of palladium(II) with triamide L_2, which is indirectly confirmed by the slower rate of the metal extraction with this reagent (Fig. 2).

The values of the concentration constant of the anion-exchange extraction of palladium(II) with triamide L_1, described by Eq. (2), in the area of equilibrium concentrations of palladium(II) in the aqueous phase X = 0.0005–0.0013 M and the initial concentrations of the reagent c_L = 0.005–0.022 M (Table 2) were calculated by Eq. (3).

$$\tilde{K} = [(\mathrm{LH_2})\mathrm{PdCl}_{4\,\mathrm{org}}][\mathrm{Cl}^-_{\mathrm{aq}}]^2/([\mathrm{PdCl}^{2-}_{4\,\mathrm{aq}}][\mathrm{L\cdot 2HCl_{org}}]) = Y[\mathrm{HCl_{aq}}]^2/\{X(c_{\mathrm{L}} - Y)\}. \quad (3)$$

Here Y, M is the equilibrium concentration of palladium(II) in the organic phase, $[\mathrm{Cl}^-_{\mathrm{aq}}] = [\mathrm{HCl_{aq}}]$, M is the concentration of chloride ions, which is equal to the concentration of hydrochloric acid in the aqueous phase, $(c_{\mathrm{L}} - Y)$, M is the concentration of free extractant (in a salt form) in the organic phase.

Figure 7 shows that extraction of palladium(II) with triamides $\mathrm{L_1}$ and $\mathrm{L_2}$ increases slightly with increasing temperature in the range of 13–43°C. The value of enthalpy change $\Delta H = 7.5$ kJ mol^{-1} for anion-exchange extraction of palladium(II) from 1 M HCl solution with triamide $\mathrm{L_1}$ was determined from the slope of the linear dependence $\ln \tilde{K} = f(1/T)$ (Fig. 7) according to the integral form of van't Hoff equation (4).

$$\ln \tilde{K} = -\Delta H/(RT) + \mathrm{const}. \quad (4)$$

The values of the thermodynamic parameters of anion-exchange extraction $\Delta G = -18.1$ kJ mol^{-1} and $\Delta S = 87$ J mol^{-1} K^{-1} were evaluated at 20°C. The positive value of entropy change ΔS of the endothermic process indicates that the extraction is determined by the entropy factor.

Triamides $\mathrm{L_1}$ and $\mathrm{L_2}$ are highly selective toward palladium(II) when extracting from the hydrochloric acid solutions with a moderate saline background. Palladium(II) can be separated from the associated elements like iron(III) at acidity of aqueous phase of 0.1–2.0 M HCl, from copper(II) in the region of 0.2–2.5 M HCl, from cobalt(II) at the acidity of 0.1–5.5 M HCl, which are not extracted in the indicated ranges of HCl concentration [13]. The reagents may be used in the extraction-stripping cycling. Using triamide $\mathrm{L_1}$ as an example, it was shown (Table 3) that a solution of the thiourea in 0.1 M HCl is the best stripping agent for palladium(II).

The comparison of the extraction ability of triamides $\mathrm{L_1}$, $\mathrm{L_2}$ and known aliphatic amines toward palladium(II) revealed that the studied reagents are significantly more effective than the secondary and tertiary amines, and reagent $\mathrm{L_2}$ is comparable with *N*,*N*,*N'*,*N'*-tetraoctylethylenediamine (Table 4). Higher efficiency of triamides (at lower concentrations) compared with bis-acylated diethylenetriamine (Table 4) is due to the greater number of amino groups in the investigated triamides.

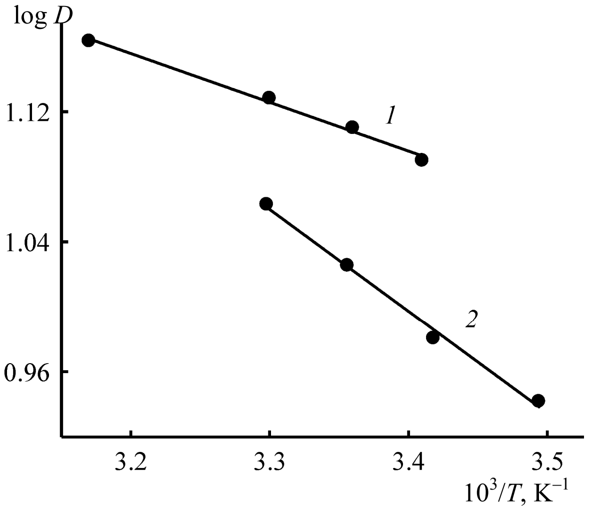


Fig. 7. Temperature dependence of distribution ratio of palladium(II) for extraction with the reagents $\mathrm{L_1}$ (*1*) and $\mathrm{L_2}$ (*2*) from 1 M HCl solutions. (*1*) $c_{\mathrm{Pd}} = 0.014$ M, $c_{\mathrm{L}} = 0.022$ M, $r^2 = 0.993$; (*2*) $c_{\mathrm{Pd}} = 0.0113$ M, $c_{\mathrm{L}} = 0.015$ M, $r^2 = 0.999$.

Thus, triacylated ethyleneamines $\mathrm{L_1}$ and $\mathrm{L_2}$ are inexpensive and effective extractants for palladium(II) and can be recommended for its extraction from the technological hydrochloric acid solutions with a moderate salt background.

Table 2. Concentration constants of palladium(II) extraction from 1 M HCl solutions with triamide $\mathrm{L_1}$ at 20°C

Initial concentration of reagent c_{L}, M	Equilibrium concentration of palladium(II), M		$\tilde{K}\times10^{-3}$
	X	Y	
0.005	0.0005	0.0022	1.57
	0.0008	0.0026	1.44
0.010	0.0005	0.0048	1.85
	0.0008	0.0057	1.78
	0.0010	0.0062	1.63
	0.0013	0.0067	1.63
0.015	0.0005	0.0073	1.92
	0.0010	0.0096	1.78
	0.0013	0.0103	1.78
0.022	0.0005	0.0120	1.71
	0.0008	0.0140	1.64
	0.0010	0.0158	1.55

$\tilde{K}_{\mathrm{av}}$ 1.69±0.09[a]

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[a] The confidence interval of the concentration constants of extraction was calculated using the Student's t-distribution for $P = 0.95$.

Table 3. Stripping of palladium(II) at A:O = 1:1 and time of phases contact of 10 min (concentration of L_1 0.015 M)

Concentration of Pd(II) in extract, M	Stripping solution	Stripping, %
0.0141	1 M $HClO_4$	6.7
0.0141	100 g l^{-1} $NaHCO_3$	38.8
0.0124	1 M thiourea in 0.1 M HCl	79.0

EXPERIMENTAL

IR spectra were recorded on a Specord M80 spectrophotometer in the range of 4000–200 cm^{-1} for the samples as a thin film or mulls in mineral oil. The NMR spectra were taken on a Bruker AM 300 spectrometer (300 MHz, solvent *d*-chloroform). Recording electronic absorption spectra of the extracts of palladium(II) relative to the diluent and spectrophotometric determination of the concentration of palladium(II) in aqueous solutions were performed on a Specord M40 spectrophotometer.

For the synthesis of extractant the following reagents were used: a narrow fraction of α,α'-branched synthetic $C_{10,12}$ carboxylic acids (a mixture of 2,2-dimethyloctanoic and 2,2'-dimethyldecanoic acids in a ratio of ~1:1) with average molecular weight M_{av} 186; ethylenediamine (bp 117–118°C); technical pentaethylenehexamine (M 232), and the fraction of heavy polyamines (M_{av} 272). All reagents were produced by JSC "Caustic" (Sterlitamak). The fraction of heavy polyamines is a mixture of tetraethylenepentamine (10–15%), pentaethylenehexamine (70–75%), and hexaethyleneheptamine (10–20%) fractions, each of them consists of 3–4 difficultly separable isomers: linear, branched, and cyclic ethyleneamines. All reagents, except for ethylenediamine, were used without further purification.

Synthesis of triacylated ethyleneamines (triamides) L_1 and L_2 *(general procedure).* To 4.65 g of pentaethylenehexamine or 5.44 g of heavy polyamines fraction (0.02 mol) was added with stirring 11.2 g of a fraction of α,α'-branched carboxylic acids (0.06 mol). The mixture was heated at 100±10°C for 1 h in a round bottom reactor in a nitrogen atmosphere under constant stirring. Then the temperature was raised to 210±20°C and maintained for 4 h with removal of water formed during the condensation of an ethyleneamine with a carboxylic acid. The resulting reagent was cooled under nitrogen to room temperature, dissolved in chloroform, and washed successively with 5 M hydrochloric acid (three times) to remove impurities of the starting ethyleneamines, ammonia buffer solution (pH 9–10, three times) to remove the unreacted α,α'-acids, and with saturated aqueous solution of NaCl. Then chloroform was distilled off. Yield L_1 11.6 g (78.8%), L_2 11.1 g (71.7%).

Synthesis of bis-acylated ethylenediamine L_3. To 3 g (0.05 mol) of predistilled ethylenediamine (bp 117–118°C) was added with stirring 21.39 g (0.115 mol) of the fraction of α,α'-branched carboxylic acids. The mixture was heated at 100±10°C for 1 h under nitrogen atmosphere with constant stirring. Then the temperature was raised to 230±10°C and maintained so for 4 h. The obtained compound was cooled under

Table 4. Dependence of palladium(II) extraction from the nature of extractant at A:O = 1:1

Organic phase		Aqueous phase		E, %	Reference
extractant (diluent)	c_L, M	c_{HCl}, M	c_{Pd}, M		
R_2NH (toluene)[a]	0.005	1.0	0.0053	31.1	[12]
$R_3N\cdot HCl$ (toluene)[a]	0.005	1.0	0.0053	38.9	[12]
$R_2N(CH_2)_2NR_2\cdot 2HCl$ (toluene)	0.005	1.0	0.0053	76.9	[12]
$L_1\cdot 2HCl$ (CCl_4, 15 vol % *n*-octanol)	0.005	1.0	0.0056	59.8	
$L_2\cdot 2HCl$ (toluene, 15 vol % *n*-octanol)	0.005	1.0	0.0056	78.9	
Bis-acylated DETA (toluene)	0.020	0.5	0.0068	89.0	[6]
$L_1\cdot 2HCl$ (CCl_4, 15 vol % *n*-octanol)	0.015	0.5	0.0067	97.4	
$L_2\cdot 2HCl$ (toluene, 15 vol % *n*-octanol)	0.010	0.5	0.0068	91.8	

[a] R is *n*-octyl.

nitrogen to room temperature, dissolved in chloroform, and washed with ammonia buffer solution (pH 9–10) three times to remove an excess of α,α'-branched acids, then three times with a solution of 5 M hydrochloric acid to remove the unreacted ethylenediamine and possible byproduct, monoamide derivative of ethylenediamine. After washing with saturated aqueous solution of NaCl the chloroform was distilled off. Yield 18 g (90.9%).

Triamides L_1 and L_2 are brown viscous liquids with a characteristic amine odor, reagent L_3 is viscous light yellow liquid. Structure of the reagents was confirmed by IR and ^{13}C NMR spectroscopy (Table 1), by the structure of the initial ethyleneamines, and by the results of the study of complexation of triamides with copper(II) ions [10]. Amine numbers of triamides were determined by potentiometric titration with 0.1 M hydrochloric acid in 60% aqueous isopropanol.

Study of extraction. Solutions of reagents were prepared by diluting of the accurately weighed samples in toluene, carbon tetrachloride, or chloroform (analytical grade) using *n*-octanol (pure) as a modifier. Solutions of triamides hydrochlorides L·2HCl were used to study the extraction of palladium(II).

Concentration of triamides L_1 and L_2 in diluents was determined by potentiometric titration with a standard solution of hydrochloric acid (free base) or NaOH (salt form), as well as by determination of extraction capacity of the reagents toward zinc(II) [10, 11]. The concentration of the extracted hydrochloric acid in the organic phase was determined by potentiometric titration with a standard 0.1 M NaOH solution. Potentiometric study was performed on a pH meter OP-211/1 with a combined glass electrode in 60% aqueous 2-propanol, supporting electrolyte – 0.5 M $NaClO_4$.

HCl and NaCl (chemically pure) and $PdCl_2$ (pure) were used for preparation of aqueous solutions of hydrochloric acid and palladium(II). The concentration of palladium(II) in hydrochloric acid solutions was spectrophotometrically determined with tin chloride(II) [15], in the back-extracts the determination was performed similarly after decomposition of back-extract aliquot with aqua regia followed by transformation of palladium(II) into the chloride salt [15]. The metal concentration in the organic phase was calculated as the difference between the initial concentration of the aqueous solution and of the raffinate.

Extraction of palladium(II) and hydrochloric acid and also stripping of the metal were carried out in the separatory funnels at a temperature of 21±1°C under vigorous stirring at a volume ratio of the aqueous and organic phases of 1:1. The time of the phases contact required to reach the extraction equilibrium was determined by preliminary experiments. Time for phase separation after extraction of HCl with triamides and palladium(II) with diamide L_3 does not exceed 3 and 6 min, respectively. For phase separation after the extraction of palladium(II) with triamides we used centrifugation for 5 min on a Model T5 centrifuge (JANETZKI). To study the temperature dependence of the palladium(II) extraction we used a thermostated separating funnels where the temperature was maintained by a thermostat with an accuracy of ±0.2°C.

The palladium(II) compounds extracted with triamides L_1 and L_2 under conditions of organic phase saturation at $c_{\text{Pd}} = 0.067$, $c_{\text{HCl}} = 1$, and $c_{\text{L}} = 0.020$ M were precipitated from extract with hexane, washed with hexane, and dried in air. They are viscous red-brown (L_1) and bright yellow (L_2) substances. The ion associate of palladium(II) with salt form $L_1 \cdot 3HCl$ was isolated from the extract obtained by contacting the 0.067 M solution of palladium(II) in 2.5 M HCl with chloroform solution of 0.025 M L_1 pre-equilibrated with 2.5 M HCl aqueous solution. The electronic spectrum of the extract (Pd:L_1 = 1:1.25) is characterized by the absorption band of *d–d*-transition of $PdCl_4^{2-}$ ion with a maximum at 471 nm (ε 149). After evaporation of chloroform, the ion associate is red-brown powder.

ACKNOWLEDGMENTS

This work carried out within the OKhNM-5 Program of Department of Chemistry and Materials Science of Russian Academy of Sciences.

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