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Solvent Extraction of Differently Charged Aquanitro Forms of Rhodium (III) with Reference to the Recovery of the Fission Rhodium from Nitrate-Nitrite Solutions

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Abstract

The approach to the search for efficient solvent extraction systems for fission rhodium is substantiated experimentally on the basis of characterization of the prevailing forms of rhodium differing in charge sign (cationic, anionic and neutral) in nitrate-nitrite solutions and their reactivity toward the coordination and anion-exchange extractants. The most promising processes are those involving coordination extraction of the $[Rh(NO_2)_3(H_2O)_3]$ form, which is relatively stable in nitric solutions and can be obtained by nitration of the initial solutions. Rhodium is solvent extracted by 96–98 % from the solutions containing this form within short time of contact between the phases in the region of low acidity. It is shown that the joint recovery of rhodium and palladium and their high separation from a number of the accompanying fission elements can be achieved using alkyl aniline.

INTRODUCTION

It is reasonable to carry out the recovery of fission platinum metals (Rh, Pd, Ru) and Tc during reprocessing the spent nuclear fuel (SNF) by inclusion into glassy matrices in order to increase the reliability of localization and storage of radioactive wastes [1]. In addition, SNF is considered as a potential renewable industry-caused source of the indicated platinoids [2, 3]. Unlike palladium and ruthenium, in the solvent extraction processing of SNF, rhodium is completely conserved in high-level wastes (HLW) of PUREX process after the recovery of the main actinoids into TBP. This is due to the low reactivity of complex forms of rhodium in the nitrate-nitrite medium of HLW (diversity of forms with potential ligands NO_2^-, NO_3^-, H_2O, OH^-, inertness in the reactions of their substitution, tendency to form polynuclear forms). The status of rhodium in HLW remains almost unknown till present, and it cannot be subjected to *a priori* prediction.

In the works carried out previously, search for extractants for rhodium was performed with model solutions (as a rule, nitrate ones) which do not provide a full imitation of HLW because of the presence of radiolytic HNO_2 (up to 10 mmol/l [4]). As the data reported in [5-11] suggest, no efficient extractants for rhodium recovery from nitric media have been found yet. In addition, uncertainty concerning the state of Rh(III) in the initial solutions may be seen in these works. The major part of the reported data are considered to be related to solvent extraction of rhodium from the solutions of its aquaion $[Rh(H_2O)_6]^{2+}$ (dissolution of hydrated rhodium (III) oxide in HNO_3) [6–11]. However, the data obtained recently provide evidence that the main species for HNO_3 concentration below 5 mol/l are polynuclear oligomers with μ-OH and μ-NO_3 coupled bridges [15]. In [5], the initial solution was obtained from $RhCl_3$; it most likely contained a mixture of aquachloride forms on unknown composition. In nitrate-nitrite solutions, the uncertainly of a set of $[Rh(NO_2)_m(H_2O)_{6-m}]^{(m-3)-}$, $1 \leq m \leq 6$, on the one hand, is due to a method of obtaining initial solutions for solvent extraction (nitration by nitrogen oxides or $NaNO_2$, dissolution of $K_3[Rh(NO_2)_6]$ salt) and conditions (HNO_3 concentration, temperature, duration of the procedure); on the other hand, it is due to the processes of aquation of nitro complexes [16, 17] during the storage of these solutions and during solvent extraction itself; in turn, the rates of these processes are dependent on the acidity of the aqueous medium and on temperature. So, from the viewpoint of the definiteness and reproducibility of the composition of nitric solutions containing rhodium, the available literature data on solvent extraction are to a substantial extent chancy.

The goal of the present work is experimental substantiation of the approach involving determination of the predominant complexes among the $[Rh(NO_2)_m(H_2O)_{6-m}]^{(m-3)-}$ and $[Rh_n(\mu\text{-OH}, \mu\text{-NO}_3)_{n-1}(H_2O)_{2n+4}]^{(n+2)+}$ forms in nitrate-nitrite media, creation of these forms in imitate solutions, and search for solvent extraction systems of the coordination and anion exchange classes for the recovery of rhodium from these solutions.

EXPERIMENTAL

The reagents used in the work were: HNO_3, $NaNO_3$, $NaNO_2$ $AgNO_3$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ $La(NO_3)_3 \cdot 6H_2O$(“kh. ch.” – chemically pure grade), $RhCl_3 \cdot 4H_2O$ (“ch.” – pure grade) and metallic Pd (99.9 %), Sb (Su-000), Se (“os.ch.” – 22-4 specially pure grade) and Te (TV-4). Some compounds were synthesized according to the known procedures: $H_2MoO_4 \cdot H_2O$ according to [18], $Na_2[RuNO(NO_2)_4OH]$ according to [19]. Tetra-*n*-octylammonium nitrate (TOAN), tri-*n*-octylaminoxide (TOAO), di-*n*-hexylsulphide (DHS), di-*n*-hexylsulphoxide (DHSO), triphenyl phosphine (TPP), tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butyl phosphate (TBP, “ch.”), para-*n*-octylaniline (OA) and technical-grade alkylaniline (AA, with C_7–C_9 alkyl) were tested as extractants. Diluents for the extractants were toluene, nitrobenzene (“kh.ch.”), metanitro(trifluoromethyl)benzene (MNTFMB) and technical-grade triethyl benzene (TEB) containing 99.2 % of the mixture of isomers.

Standard nitric solutions of the elements were prepared by dissolving the weighed portions of metals in concentrated (for Pd and Sb) or diluted (for Fe, Se and Te) HNO_3; weighed portions of the salts ($AgNO_3$, $La(NO_3)_3 \cdot 6H_2O$ and $H_2MoO_4 \cdot H_2O$) were dissolved in a 3 M solution of HNO_3. In the case of ruthenium, the weighed portion of $Na_2[RuNO(NO_2)_4OH]$ was decomposed under boiling in a 8M solution of HNO_3 for 1 h; then the solution was evaporated till humid salt and dissolved in diluted HNO_3. For rhodium, the reference solutions of definite composition were freshly prepared solutions $Na_3[Rh(NO_2)_6]$ [20] in water (type A), $Na_3[Rh(NO_2)_3(H_2O)_3]$ in a solution of 3M HNO_3 (type B) and a mixture of $[Rh_2(\mu\text{-OH}, \mu\text{-NO}_3)(H_2O)_8]^{4+}$ and $[Rh_3(\mu\text{-OH},\mu\text{-NO}_3)_2(H_2O)_{10}]^{5+}$ in a solution of 3M HNO_3 (type C). For intermediate forms of rhodium, since individual solutions cannot be obtained, we estimated the trends of changes in rhodium solvent extraction from a mixture of forms as the mean number of coordinated ions decreased within the range between the references.

Solvent extraction was carried out in tubes or in thermostated separating funnels with the phase volume ratio *r* equal to 1. The phases were mixed by intense manual jogging for $\tau = 5$ min or by means of mechanical rotation of the tubes in a thermostat with the frequency of 2–4 s^{-1} with lengthy contact between phases.

Concentrations of elements in the conjugated phases were determined by means of atomic absorption with HITACHI Z-8000 instrument in flame or with a graphite atomizer. Spectrophotometric investigation of the aquation of $[Rh(NO_2)_6]^{2-}$ was performed with Specord M40 instrument, potentiometric measurements in solutions were made with Anion 410 ionomer using a glass electrode ESL-63-07 and a silver chloride reference electrode EVL-1M 3.1 with the electrolytic bridge filled with the aqueous solution of KNO_3.

In order to determine the equilibrium constant of HNO_3 extraction with alkyl aniline (K_{AE}), we applied the two-phase potentiometric titration procedure placing 50 ml of the

TABLE 1

Solvent extraction of rhodium from solutions I–IV based on 3 M HNO_3 solutions. C_{Pd}, mg/l: 385 (I), 180 (II), τ = 1 h

Extractant	Diluent	T, K	Solution	C_{Rh}, mg/l	E_{Rh}, %
Solution of 0.05 M TOAN	Toluene	295	I	36	0
			II	20	0
Solution of 0.05 M OA	Toluene	295	I	36	0
			II	20	0
Solution of 0.05 M OA	Nitrobenzene	323	III	470	4
			IV	180	70
Solution of 0.05 M OA	MNTFMB	323	III	470	0
			IV	180	56

aqueous solution of 3.2 M $NaNO_3$ and 1 ml of the solution of 1.15 M AA in triethyl benzene. A mixture of phases was titrated with an aqueous solution containing 3.2 mol/l $NaNO_3$ and 0.096 mol/l HNO_3 with a step of 0.5 ml. The effective potential of the aqueous phase E_{ef} was measured directly in the emulsion after the addition of each portion of the titrant. The measuring system was calibrated by titrating 1 ml of TEB under identical conditions. During calibration, the equilibrium and analytical concentrations of the added acid coincided with each other: ($[H^+] = C_{HNO_3}$), and the dependence of the effective potential on pH was linear ($E_{ef} = a - b \cdot \mathrm{pH}$) with the determined parameters $a = (215.2 \pm 0.5)$ mV and $b = (55.5 \pm 0.3)$. On this basis, using the E_{ef} values measured during AA titration, we calculated the equilibrium values of $\mathrm{pH} = (a - E_{ef})/b$ in the aqueous phase, and then the equilibrium concentrations of the bound and free AA forms in the organic phase, respectively: $[LHNO_3]_o = (C_{HNO_3} - [H^+])/r$ and $[L]_o = C_L - [LHNO_3]_o$. . The K_{AE} value was determined as the arithmetic mean of the set of values of the constant which were determined in the points of the titration curve for the conditions when the $[L]_o/C_L$ ratio is 20 to 80 %. The error of the constant was characterized by the confidence interval for the confidence probability 95 % for the number of measurements $N = 14$.

SOLVENT EXTRACTION OF POLYNUCLEAR AQUAFORMS OF RHODIUM FROM SOLUTIONS

Nitric solutions of the B type (see above) were prepared by two methods. The solutions I and II (Table 1) were obtained as a result of two sequential stages of treatment of the solid solution Rh : Pd = 1 : 1 in concentrated HNO_3, solution III was obtained by the decomposition of $Na_3[Rh(NO_2)_6]$ in concentrated HNO_3 in an open system, followed by dilution with water [15]. The main forms of Rh(III) in these solutions are represented by a mixture of two- and three-nuclear cations $[Rh_2(\mu\text{-}OH, \mu\text{-}NO_3)(H_2O)_8]^{4+}$, and $[Rh_3(\mu\text{-}OH,\mu\text{-}NO_3)_2(H_2O)_{10}]^{5+}$. In solution IV, which is a product of nitration of solution III by nitrogen oxides, a substantial part of polynuclear forms was decomposed with the formation of a mixture of mononuclear lower nitro forms $[Rh(NO_2)_m(H_2O)_{6-m}]^{(m-3)-}$, $m < 3$. Rhodium is not recovered from solutions I–III (see Table 1) by an anion-exchange (TOAN) or coordination (OA) extractant, including an increase in the concentration of OA by an order of magnitude or temperature elevation from 295 to 323 K. At the same time, after the decomposition of oligomers, the coordination extraction of rhodium from the solution of a mixture of lower nitro aquacations proceeds up to 60–70 %.

So, a search for solvent extraction systems for rhodium recovery from nitric solutions seems not very promising. Such solutions require special preliminary treatment in order to destroy the polynuclear forms of rhodium, in particular by nitrating the solutions with nitrogen oxides without adding new salt components.

SOLVENT EXTRACTION OF THE ANIONIC AQUANITRO FORMS OF RHODIUM

In the row of complex anions $[Rh(NO_2)_m(H_2O)_{6-m}]^{(m-3)-}$, $4 \le m \le 6$, an individual solution A can be obtained for the high-

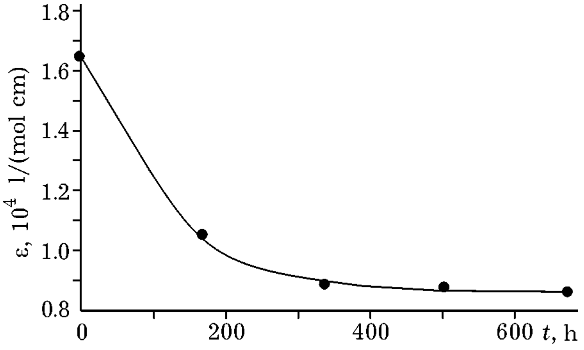

Fig. 1. Changes in the extinction coefficient ε of the aqueous solution during spontaneous aquation of $[Rh(NO_2)_6]^{3-}$ at T = 295 K (ν = 38 000 cm^{-1}).

er nitro form ($m = 6$) in neutral aqueous medium. A stepwise spontaneous aquation process goes on with time in such a solution:

$$[Rh(NO_2)_m(H_2O)_{6-m}]^{3-m} + H_2O$$
$$\rightarrow [Rh(NO_2)_{m-1}(H_2O)_{6-m+1}]^{3-m+1} + \qquad (1)$$

where $1 \le m \le 6$. Spectrophotometric investigation showed that the consumption of $[Rh(NO_2)_6]^{3-}$ during aquation (Fig. 1) is described by the kinetic equation for a first-order irreversible reaction. It was found that the rate constant for the 1st step of aquation ($m = 6$) is $k_1 = 2.36\ 10^{-6}\ s^{-1}$ and half-life is $t_{1/2} \approx 80$ h. These data were used to calculate the molar fraction of $[Rh(NO_2)_6]^{3-}$ (α_6) during estimating the depth of aquation in the solutions exposed for some time before extraction in order to obtain a mixture of nitro forms in them.

The anion exchange extraction of rhodium generally corresponds to the equation

$$\{[Rh(NO_2)_m(H_2O)_{6-m}]^{3-m}\}_w + (3-m)\{QNO_3\}_o$$
$$\rightarrow \{Q_{3-m}[Rh(NO_2)_m(H_2O)_{6-m}]\}_o$$
$$+ (3-m)\{\quad\}_w \qquad (2)$$

In addition, the ions formed during aquation participate in a competitive exchange:

$$\{\quad\}_w + \{QNO_3\}_o \rightarrow \{QNO_2\}_o + \{\quad\}_w \qquad (3)$$

In weakly polar organic media, the salts of quaternary ammonium bases (QAB) exist in the form of associates $(R_4NX)_p$. As suggested by the data for other QAB salts [21, 22], for the case of 0.05 mol/l TOAN solution (Q = $\{(R_4N)_pX_{p-1}\}^+$, R = C_8H_{17}, X =) in tolu-

TABLE 2

Solvent extraction of rhodium from aqueous solutions of the anionic forms of its aquanitro complexes
C_{TOAN} = 0.05 mol/l, C_{DHS} = 0.34 mol/l, C_{TBP} = 50 vol. %, T = 295 K, τ = 1 h

Extractant	C_{Rh}, mg/l	C_{NaNO3}, mol/l	α_6	D_{Rh}	E_{Rh}, %
TOAN	92.5	0	0.818	460	99.8
		0.5		0.54	35
		1		0.19	16
		2		0.05	5
		3		0	0
TOAN	185	0	0.997	>500	100
			0.818	460	99.8
			0.242	141	99.3
			0.058	167	99.4
			0.014	153	99.4
			0.003	83	98.8
			0.001	53	98.1
TOAN + DHS	185	0	0.997	>500	100
			0.058	230	99.6
			0.014	230	99.6
DHS	185	0	0.997	0.12	11
			0.058	0.12	11
			0.014	0.19	16
DHS + TBP	185	0	0.997	0.28	
TBP	185	0	0.997	0.12	11
			0.242	0.19	16
			0.058	0.16	14
			0.19	0.19	16

TABLE 3

Effect of $[Rh(NO_2)_6]^{3-}$ aquation degree on solvent extraction of rhodium by the solutions of 0.05 M TOAN and 0.05 M OA in toluene with the addition of sulphaminic acid into the system. T = 295 K, τ = 1 h

Experiment No.	Extractant	Rh/SAF	t, days	C_{Rh}, mg/l	$[Rh]_w$, mg/l	D_{Rh}
1	TOAN	0	1	130	<1	>130
2		0	9	130	14	8.3
3		0[a]	9	130	112	0.16
4		1	4	150	79	0.90
5		2	22	180	86	1.1
6		2[b]	1	130	60	1.2
7		4	22	170	73	1.3
8		6	22	170	60	1.8
9		8	22	162	45	2.6
10		10	22	162	40	3.0
11		10[c]	1	108	64	0.69
12		12	22	160	35	3.6
13		12	36	160	74	1.2[d]
14				74	65	0.14[e]
15	OA	0	1	130	105	0.24
16		1	4	150	122	0.23
17		2	22	180	130	0.38
18		2[b]	1	130	103	0.26
19		4	22	170	118	0.44
20		6	22	170	122	0.39
21		8	22	162	122	0.33
22		10	22	162	116	0.40
23		10[c]	1	108	88	0.23
24		12	22	160	115	0.39

Note. t is the time from the preparation of solution till the start of solvent extraction

[a] 3 mol/l HNO_3 was added into the aqueous phase directly before the start of solvent extraction.

[b] The solution was heated for 20 min at a temperature of 323 K.

[c] The solution was heated for 2 h at a temperature of 368 K.

[d, e] The 1st and the 2nd steps of extraction, respectively.

ene, the association degree p should be much larger than 2 ($C_{QX} = C_{TOAN}/p$). As it could be expected, rhodium is well recovered from fresh aqueous solution of $Na_3[Rh(NO_2)_6]$ by the anion-exchange TOAN; however, extraction is sharply suppressed when $NaNO_3$ is added into the aqueous phase, and decreases gradually during the aquation of $[Rh(NO_2)_6]^{3-}$ (Table 2). The effect of $NaNO_3$ is due to the shift of equilibrium (2) to the left under the action of an increasing concentration of NO_3^- ions. A decrease in recovery with aquation can be explained according to eqn. (3) by binding the extractant in more strong ion pairs QNO_2, as well as by the additional formation of ions in the oxidation of by the dissolved oxygen. Nevertheless, for a small extent of aquation (for 3–4 days), the fraction extracted exceeds 98 %, in spite of a ten-fold decrease in the distribution coefficient D_{Rh}. By elimination of the effect of nitrite ions due to their interaction with sulphaminic acid (SAA), a trend to increasing rhodium extraction is observed during aquation as the SAA/Rh ratio increases (Table 3). However, for a large aquation extent, which is achieved by lengthy exposure of the aqueouos solution of $Na_3[Rh(NO_2)_6]$ or its heating, the fraction of the forms with $m < 4$ not recoverable with TOAN increases in the material balance for Rh (see Table 3). The coordination extraction of rhodium with OA, DHS and TBP from the aqueous solutions of aqua nitro complexes is inefficient due to the slow kinetics of the process. The observed (non-equilibrium) distribution ratios D_{Rh}^* change within the range 0.2–0.4 independently of the composition of the forms varying during aquation (see Tables 2 and 3).

So, the anion exchange extractants are unsuitable for the recovery of complex anions $[Rh(NO_2)_m(H_2O)_{6-m}]^{(m-3)-}$ $(4 \le m \le 6)$ directly from nitrated HLW because of the high concentration of nitrate ions in these solutions (about 2–3 mol/l). Deep denitration of HLW can hardly be reasonable from the technological viewpoint. In addition, QAB salts are not selective with respect to rhodium. Some perspectives can be expected for the coordination and mixed extractants; however, in order to verify the situation, additional investigations of the versions of solvent extraction systems and of the conditions for the processes involving them are required.

SOLVENT EXTRACTION FROM SOLUTIONS OF TRIAQUATRINITRO RHODIUM

The $[Rh(NO_2)_3(H_2O)_3]$ form is relatively stable. A decimolar solution of this form in 3 M HNO_3 remains almost unchanged for at least a week [17]. Because of this, any acidic nitrate-nitrite solutions of rhodium (III) including HLW, with different compositions of the forms, can be drawn to the state at which the only prevailing form in solution is *cis*-$[Rh(NO_2)_3(H_2O)_3]$. The solutions of B type were obtained as a result of the treatment of $Na_3[Rh(NO_2)_6]$ with diluted nitric acid and contained 0.1 mol/l Rh; before solvent extraction, they were diluted till the required concentrations of Rh and HNO_3.

The results of testing rhodium recovery from $[Rh(NO_2)_3(H_2O)_3]$ solutions with some coordination extractants under different conditions are shown in Fig. 2. The concentrations of HNO_3 and extractant (L), diluents (S), temperature and duration of solvent extraction were varied. The recovery with the indicated O- and N-containing weakly basic extractants, independently of the degree of their protonation, is possible only according to the coordination mechanism, because the initial form $[Rh(NO_2)_3(H_2O)_3]$ is electrically neutral; only cationic forms of rhodium are probable to appear during its aquation. This is confirmed by

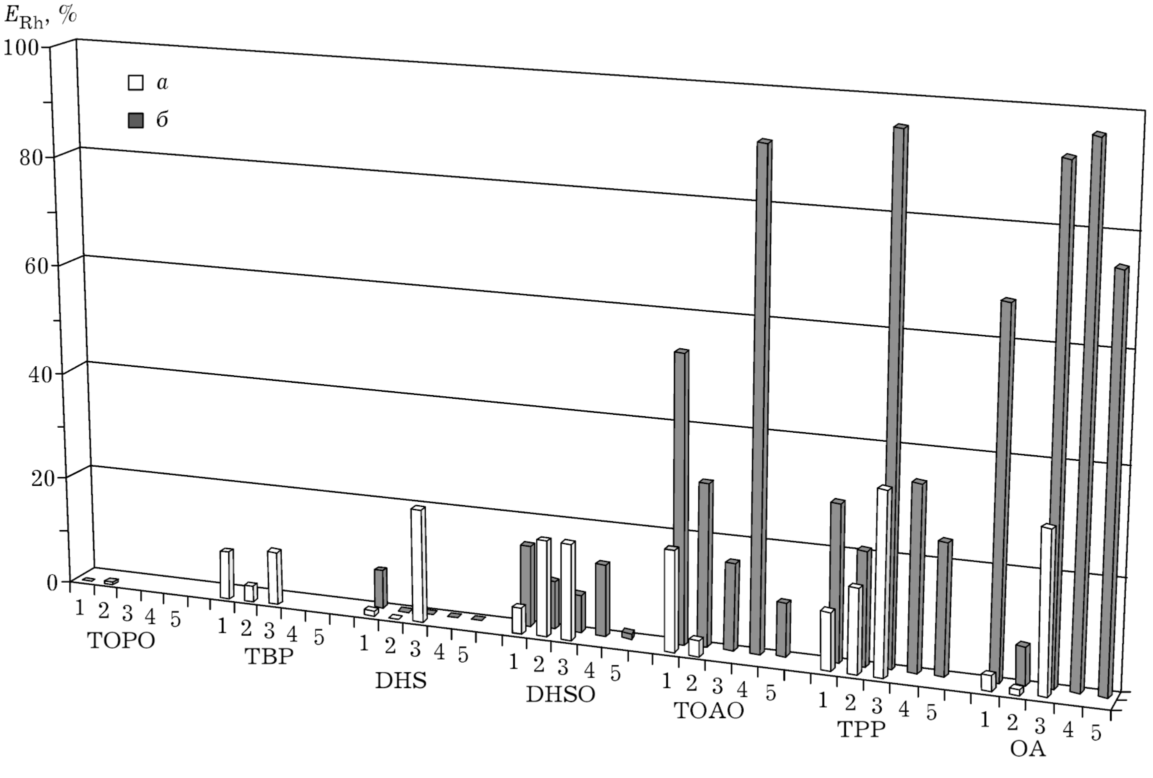

Fig. 2. Coordination extraction of rhodium from nitric solutions of $[Rh(NO_2)_3(H_2O)_3]$ (C_{Rh} = 206 mg/l): *a* − toluene, C_L = 0.1 mol/l; *b* − nitrobenzene, C_L = 0.45 mol/l, C_{TBP} = 50 vol. %; *1* − C_{HNO_3} = 0.5 mol/l, T = 293 K, τ = 1 h; *2* − C_{HNO_3} = 3 mol/l, T = 293 K, τ = 1 h; *3* − C_{HNO_3} = 3 mol/l, T = 293 K, τ = 24 h; *4* − C_{HNO_3} = 0.5 mol/l, T = 323 K, τ = 1 h; *5* − C_{HNO_3} = 3 mol/l, T = 323 K, τ = 1 h.

TABLE 4

Solvent extraction of rhodium with 1 M OA solution in triethyl benzene from nitric solutions of $[Rh(NO_2)_3(H_2O)_3]$. C_{Rh} = 200 mg/l, τ = 5 min

Experiment No.	T, K	C_{HNO_3}, mol/l	$[Rh]_w$, mg/l	E_{Rh}, %
1	291	3	135	32
2[a]			132	34
3[a,b]			120	40
4		0.5	107	46
5[a]			107	46
6[a,b]			118	41
7	342–326	3	120	40
8[a]			118	41
9[b]		0.5	13	93
10			6.0	97
11[a]			7.0	96

[a] HNO_3 solutions saturated preliminarily with OA were used.

[b] Recovery with pure TEB (without OA).

[c] The aqueous phase contained 2.5 mol/l $NaNO_3$ along with 0.5 mol/l HNO_3.

an increase in the fraction extracted occurring due to an increase in the duration of phase mixing and temperature elevation. An exception is the system with DHSO for which the fraction-extracted values for 1 and 24 h are the same and decrease about 2 times while temperature rises from 293 to 323 K. In addition, DHSO recovers rhodium from the solutions with higher acidity 3–4 times better, though the fraction extracted is not high: about 18 %, which is also opposite to the trend for the systems with other extractants. The highest recovery characteristics in test experiments were observed for TOAO, TPP and OA at elevated temperature (see Fig. 2). Octyl aniline and its analog alkyl aniline were chosen for more detailed investigation.

$NO_3^- \rightleftarrows$

Rhodium extraction with a solution of 1M OA in triethyl benzene for a short time of contact (5 min) was studied. In some experiments, the dilution of a standard solution B till the necessary concentration of Rh and the acid was carried out with the solutions of 0.5 and 3 mol/l HNO_3 saturated preliminarily with OA. Before solvent extraction, these solutions were kept for one day for the reaction between $[Rh(NO_2)_3(H_2O)_3]$ and AO distributed into the acid to proceed. The results are shown in Table 4.

Solvent extraction with pure TEB (experiments No. 3 and 6) provides unambiguous evidence of the presence of a heterogeneous equilibrium of OA (L) distribution between the phases:

$$\{L\}_s \overset{\text{rapidly}}{\qquad} \{L\}_o \tag{4}$$

Since OA is a primary amine and possesses base properties (see below), the acid-base equilibrium also occurs in the system:

$$\{L\}_o + \{H^+ + \qquad\}_s \overset{\text{rapidly}}{\qquad} \{LHNO_3\}_o \tag{5}$$

The occurrence of process (5) is confirmed by a decrease in the fraction extracted with an increase in the acidity of the aqueous phase (experiments No. 1, 2 and 4, 5; 7, 8 and 10, 11; 8 and 9), which is explained by a decrease in the concentration of non-protonated form of OA, while does not participate in rhodium extraction process (experiments No. 9 and 10). The absence of the effect of preliminary saturation of the aqueous phase on the mean rate of solvent extraction (E_{Rh}/τ) indicates that the equilibria (4) and (5) are rapidly established (experiments No. 1 and 2, 4 and 5, 7 and 8, 10 and 11). Since the initial form of rhodium $[Rh(NO_2)_3(H_2O)_3]$ and the coordinating OA are electrically neutral, the extractable complex should be also non-charged in a weakly polar medium of the diluent (in particular, it is known that in chloride systems [] (where L is dialkyl sulphide) is extracted with thio ethers [23]. The corresponding system of equilibria is as follows:

$$\{[Rh(H_2O)_3(NO_2)_3] + 3L\}_w \overset{\text{slowly}}{\quad} \{[RhL_3(NO_2)_3]\}_w \qquad (6)$$

$$[RhL_3(NO_2)_3]\}_w \overset{\text{rapidly}}{\quad} \{[RhL_3(NO_2)_3]\}_o \qquad (7)$$

The occurrence of the process (7) and its high rate are indicated by similar efficiency of the recovery of rhodium complexes with OA from aqueous solution into pure TEB and into the solution of OA in TEB at different temperatures and HNO_3 concentrations (experiments No. 3, 6 and 7, 8). Therefore, only one of the stages of the sequential substitution of coordinated water by L can be slow for the total reaction (6) which limits the solvent extraction rate.

So, the example of OA shows that extractants based on alkyl substituted anilines are able to extract rhodium from nitric solutions of $[Rh(NO_2)_3(H_2O)_3]$ quantitatively and rapidly, but only at elevated temperature and low acidity of the aqueous phase. Technical-grade AA is cheaper and more readily available for practical application.

EFFICIENCY AND SELECTIVITY OF SOLVENT EXTRACTION WITH ALKYL ANILINE

The constant of heterogeneous acid-base equilibrium (5) determined on the basis of the data for two-phase titration of AA with nitric acid (Fig. 3) $K_{AE} = [LHNO_3]_o/\{C_{NaNO_3} \cdot [H^+] \cdot [L]_o\}$ is (1.43 ± 0.02) 10^3 M^{-2} at 291 K and ionic force $I = 3.2NaNO_3$. As suggested by K_{AE} value, alkyl aniline extracts the acid in the amount of C_{HNO_3} - $[H^+] \approx C_L r$ from the aqueous phase. In excess of AA ($C_{HNO_3} < C_L r$), the acidity of the aqueous phase decreases till pH of water.

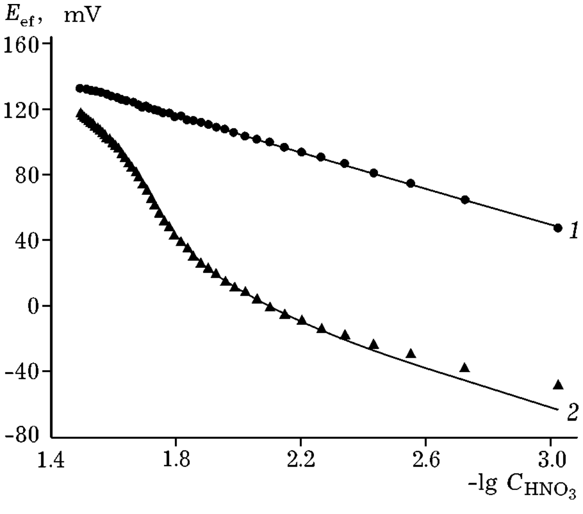

Fig. 3. Calibration curve (*1*) and the curve of two-phase titration of solution of 1.15 M AA in triethyl benzene by a 0.096 M HNO_3 aqueous solution (*2*) at T = 291 K and I = $3.2NaNO_3$.

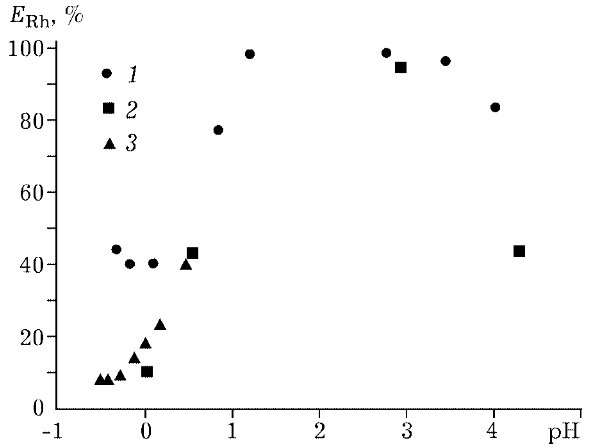

Fig. 4. Effect of the equilibrium pH of the aqueous phase on solvent extraction of rhodium from nitric solutions of $[Rh(NO_2)_3(H_2O)_3]$ by the solutions containing 1.15 mol/l alkyl aniline (*1, 2*) and 1.15 mol/l alkyl anilinium nitrate (*3*) in triethyl benzene (C_{Rh} = 200 mg/l, T = 308 K, τ = 5 min): *1, 3* – the 1st step of solvent extraction, *2* – the 2nd step.

A strong dependence of the rhodium fraction extracted from nitric solutions of $[Rh(NO_2)_3(H_2O)_3]$ on the equilibrium concentration of $[H^+]$ in the aqueous phase calculated taking into account equilibrium (5) is shown in Fig. 4. Solvent extraction was carried out in one and two steps, and also with the use of two initial solutions of the extractant (C_L = 1.15 mol/l) taken in the form of the free alkyl aniline (L) and transformed preliminarily into alkyl anilinium nitrate ($LHNO_3$). In spite of this, all the experimental points form a unified dependence. Maximal rhodium fraction extracted (96–98 %) within 5 min at 308 K is observed within a limited range of acidity: 1.2 < pH < 3.5. A decrease in the fraction extracted in the region pH < 1.2 qualitatively corresponds to a decrease in the concentration of free AA, which is connected with the acidity of the aqueous phase by the equation $C_{HNO_3} - [H^+] = r(C_L - [L]_o)$. In order to reveal the reasons of a sharp decrease in the fraction extracted at pH > 3.5, it is necessary to carry out special investigations. It may

TABLE 5

Separation effects for the solvent extraction of metals by a 1.15 M AA solution in triethyl benzene from nitrate-nitrite solutions containing 3 (I) and 1 mol/l HNO_3 (II). T = 308 K, τ = 5 min

Metal	C_M, g/l	lg D_M*		lg $\beta_{Rh,M}$	
		I	II	I	II
Rh	0,21	−0.11	1.79	0	0
Pd	0.52	3.82	3.94	−4.0	−2.2
Ru	1.00	−0.28	0.53	0.2	1.3
Ag	0.05	0.36	0.40	−0.5	1.4
Sb	0.013	−2.33	−1.64	2.2	3.4
Te	0.30	−4.30		4.2	
Se	0.02	<−2.8		>2.7	
Mo	1.6	<−2.0		>1.9	
La	2.5	<−1.7		>1.6	
Fe	1.2	<−3.4		>3.3	

be assumed that a reason is the start of hydrolysis of $[Rh(NO_2)_3(H_2O)_3]$ and the formation of non-extractable polynuclear forms of Rh(III).

Factors of rhodium separation from a number of elements present in the HLW ($\beta_{Rh,\ M}$) were estimated on the basis of efficient distribution ratios D_M^* determined for the extraction with alkyl aniline from individual nitric solutions of the elements. Rhodium was present in the initial solution in the form of $[Rh(NO_2)_3(H_2O)_3]$. About 10^{-2} mol/l $NaNO_2$ was added into each nitric solution of other elements before solvent extraction. The results shown in Table 5 indicate that one can perform deep separation of Rh from non-precious elements and partially from Ru and Ag using AA. Palladium is extracted with AA 2–4 orders of magnitude better than rhodium. Separation of Ag and Pd from Rh can be achieved at the stage of stripping within a short time because these metals, unlike rhodium, are rapidly and completely stripped with ammonium.

CONCLUSION

The analysis of literature data and the results obtained in the present study on the extraction oppositely charged and neutral aqua nitro forms of rhodium allow concluding that a neutral form *cis*-$[Rh(NO_2)_3(H_2O)_3]$ is promising for the solvent extraction recovery of rhodium from nitric solutions. It is this form for which the coordination extraction is possible due to the substitution of water molecules by extractant ligands (organic sulphides, phosphines, aromatic amines, *etc.*) or due to the addition of oxygen-containing ligands to (phosphoryl-containing and other organic oxides) to water molecules. Solvent extraction of this form is unaffected by the concentration of nitrate ions; however, in order to achieve high rate, elevated temperature is required. In some cases rhodium fraction extracted is higher than 90 %. Among the tested extractants, alkyl anilines are promising. Solvent extraction occurs *via* the coordination mechanism and is characterized by high selectivity of the recovery of precious metals (Pd, Rh, Ag, Ru) with respect to non-precious ones. Rhodium separation from palladium and silver is possible at the stage of stripping of the latter two metals with ammonia. A substantial disadvantage of alkyl aniline is the fact that high rhodium fraction extracted (96–98 %) within a short time of contact between the phases (5 min at 308 K) is achieved only within a limited range of aqueous phase acidity: 1.2 < pH < 3.5. The data obtained on solvent extraction of rhodium can be considered only as the start of investigations which are to be continued.

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