

Application of quaternary phosphonium salts as extractants of Ru(III) and Rh(III) from model aqueous solutions

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Introduction

In the recent years there is a growing interest in the reactive extraction of PGM (Platinum Group Metal) ions and noble metals from secondary sources (e.g. spent catalysts) from aqueous chloride solutions using organic phases containing various extractants [1, 2]. PGM prices at the global market remain high, due to a high demand, energy-consuming and expensive mining process, as well as depleting natural resources [3].

PGMs have unique physical and chemical properties, such as a high melting and boiling point, high chemical resistance and good catalytic properties. Therefore, they are widely used in chemical (Pt, Pd, Ir, Ru), automotive (Pt, Pd, Ru, Rh), electrical and electronic industries (Pt, Rh, Ru, Ir), as well as in medicine (Pt, Ru) and dentistry (Pd, Pt, Ru). At the same time, these PGM application fields generate a very high amount of waste containing PGMs that should be recycled [3].

To this moment, the following extractants were proposed in the literature for the extraction of rhodium (III) and ruthenium (III): organophosphorus compounds (e.g. Cyanex 921, Cyanex 923, Cyanex 471, Cyanex 272) [4–6], diisopentyl sulfide [7], aliphatic tertiary amines or quaternary ammonium salts [8, 9], tributyl phosphate [5], as well as derivatives of 4-pyridone [10]. Phosphonium ionic liquids (studied by our team) proved to be very promising extractants for Pd(II) and Pt(IV) in terms of reaction kinetics and efficiency [11–14]. The preliminary studies on the extraction of Rh(III), Ru(III) and Pt(IV) using trihexyl(tetradecyl)phosphonium bromide proved that this quaternary phosphonium salt is a very effective extractant for Pt(IV), while the extraction of Rh(III) and Ru(III) may differ, depending on the “freshness” of aqueous solutions [2].

The aim of the studies presented was to use the phosphonium ionic liquids selected (ILs) for extracting Ru(III) or Rh(III). Furthermore, the effect of the contact time of aqueous and organic phases, HCl concentration and extractant concentration in organic phase on extraction process of Ru(III) and Rh(III) with organic phases containing selected phosphonium ILs with trihexyl(tetradecyl)phosphonium cation and the following anions: chloride (Cyphos IL 101), bromide (Cyphos IL 102), bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and bis(trifluoromethylsulfonyl)imide (Cyphos IL 109) was also studied.

Experimental part

Materials

Quaternary phosphonium salts with the trihexyl(tetradecyl) phosphonium cation: chloride (Cyphos IL 101), bromide (Cyphos IL 102), bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and bis(trifluoromethylsulfonyl)imide (Cyphos IL 109) supplied by Cytec Industries Inc. and diluted with toluene were used as the extractants of Rh(III) and Ru(III) ions from aqueous solutions. The solutions of individual

extractants Cyphos IL 101, IL 102, IL 104 or IL 109 at a concentration of 0.005 M were used as the organic phases. Aqueous solutions (feeds) contained 0.0025 M Ru(III) or Rh(III) in 0.1 or 3 M HCl. Salts of the metals studied in the form of chlorides were used (from IMC Platinum Group Chemicals and Sigma Aldrich). The tests were conducted with fresh solutions prepared at the day of the tests.

Extraction and stripping

The extraction was carried out in 50 cm³ glass separatory funnels. Equal phase volumes (5 cm³ each) were shaken for 20 minutes at 20±2°C. Then, they were left to separate. Metal ions were stripped from the loaded organic phase using 0.05 and 0.5 M NH₃, 5 M HCl or 0.1 M thiourea in 0.5 M HCl. The content of Rh(III) and Ru(III) ions in the aqueous phase, before and after extraction, as well as in the aqueous phase after stripping, was determined by means of atomic absorption spectrometry AAS (Hitachi Z-8200) at a wavelength of 369.2 and 349.9 nm for Rh(III) and Ru(III), respectively.

Results

The effect of phase contact time and feed composition on Rh(III) and Ru(III) extraction

The effect of phase contact time on the equilibrium state of Rh(III) and Ru(III) extraction was studied. The equilibrium of the extraction of Ru(III) (Fig. 1) and Rh(III) (Fig. 2) is reached quickly – after 5 minutes of shaking, both for 0.1 M HCl and 3 M HCl solution.

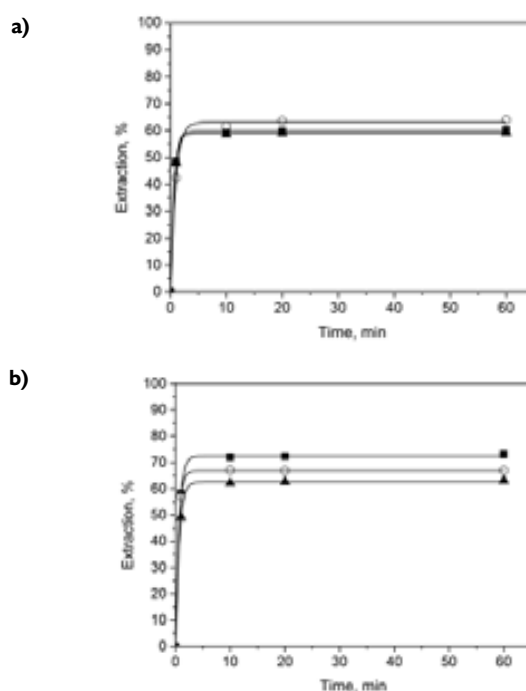


Fig. 1. Extraction of Ru(III) from: a) 0.1 M HCl; b) 3 M HCl with (■) IL 101, (○) IL 102, (▲) IL 104, vs. contact time

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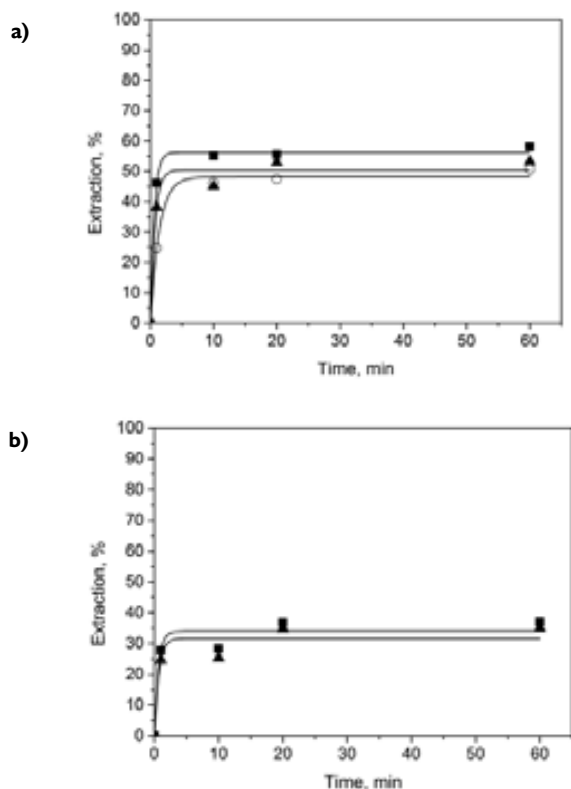


Fig. 2. Extraction of Rh(III) from: a) 0.1 M HCl; b) 3 M HCl with (■) IL 101, (○) IL 102 or (▲) IL 104 vs. contact time

Extraction efficiency for Ru(III) is much higher than for Rh(III), while the highest extraction efficiency (approx. 70%) was achieved for the Ru(III) extraction from 3 M HCl solution to the organic phase containing IL 101 usunąc (Fig. 1b). The Ru(III) extraction from 0.1 M HCl using IL 101, IL 102, IL 104 gives almost the same efficiency (approx. 60%). No significant effect of the HCl concentration in the feed on the Ru(III) extraction was observed.

The best Rh(III) extraction (55%) occurs from the 0.1 M HCl solution using Cyphos IL 101 (Fig. 2a). As the HCl concentration decreases, the Rh(III) extraction efficiency decreases, and it drops below 40% for the 3 M HCl solution, when using both Cyphos IL 101 and 104 (Fig. 2b).

Table I

The initial extraction rates of Ru(III) and Rh(III) with 0.005 M Cyphos IL 101 or Cyphos IL 104 from feed of various concentrations of HCl

Initial HCl concentration in feed, M	Extractant type	Ru(III) rate · 10 ⁵ mol/dm ³ ·s	Rh(III) rate · 10 ⁵ mol/dm ³ ·s
0.1	IL 101	1.43	1.59
	IL 104	1.42	1.31
3	IL 101	1.71	0.95
	IL 104	1.44	0.85

Table I presents the values of initial transfer rates of metal ions to the phase containing IL, which were estimated based on the slope of the linear equation of the metal ion concentration as a function of time at the beginning of the extraction (first 5 minutes). Ru(III) and Rh(III) ion transfer rates from the 0.1 M HCl solution to the organic phase containing IL 101 or IL 104 are similar and equal approx. $1.5 \cdot 10^{-5}$ mol/dm³·s. In case when the initial phase is the 3 M HCl solution, the Rh(III) ion transfer rate is almost twofold lower than for Ru(III), which is also reflected in twofold lower efficiency of the Rh(III) extraction.

Effect of the phosphonium ionic liquid used on the efficiency of Ru(III) and Rh(III) extraction

The phosphonium ionic liquids used have different ions, which affects their hydrophobicity. The authors of the paper [15] concluded,

based on the study on water solubility of phosphonium ionic liquids, that hydrophobicity of these compounds increases depending on the type of an anion according to the following series: Cyphos IL 104 ~ Cyphos IL 101 < Cyphos IL 102 << Cyphos IL 109.

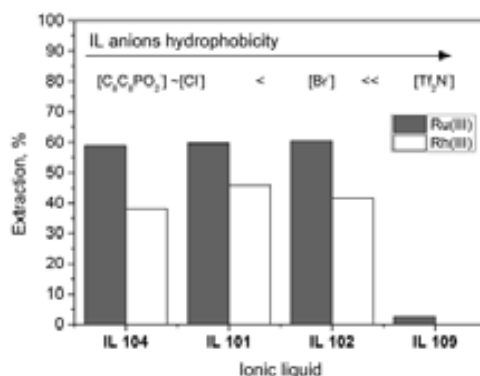


Fig. 3. Percentage extraction of Ru(III) or Rh(III) from 0.1 M HCl solution with four ILs. Feed: $2.5 \cdot 10^{-3}$ M Ru(III) or Rh(III) in 0.1 M HCl; organic phase: $5 \cdot 10^{-3}$ M IL in toluene

It was found that the Ru(III) extraction using each of the ILs is more effective than the Rh(III) extraction. Ru(III) extraction efficiency stays at the same level (approx. 60%) regardless of the ionic liquid used (except for IL 109). Cyphos IL 101 proved to be the best Rh(III) ion extractant (45% extraction). Cyphos IL 109 is the least effective extractant, both for Ru(III) and Rh(III). The ability observed to extract Ru(III) and Rh(III) can be linked to varying hydrophobicity of IL, which is determined by anions (Fig. 3). The most hydrophobic of all the extractants, IL 109, is the most difficult to react with hydrophilic hydrated chlorocomplexes of the ions studied. Other phosphonium ionic liquids undergo the reaction of the exchange of an ionic liquid anion (more hydrophilic than IL 109) much more easily than anion chlorocomplexes of the ions studied.

Stripping of Ru(III) and Rh(III) from the loaded organic phases

As a result of the Ru(III) or Rh(III) ion extraction from feeds containing 0.1 M HCl, the organic phases were loaded with metal ions. We studied the effect of various strippants (Tab. 2): 0.05 and 0.5 M NH₃, 5 M HCl or 0.1 M thiourea in 0.5 M HCl on the stripping of Ru(III) and Rh(III) ions from the loaded organic phases containing Cyphos IL 101 or IL 104 as an extractant.

Table 2

Percentage stripping of Rh(III) and Ru(III) from the loaded organic phases containing Cyphos IL 101 or IL 104

IL	C [*] _(org) , mg/dm ³	Strippant	C _{(w)R} , mg/dm ³	R, %
Rh(III)				
101	107,5 ± 7.7	0.05 M NH ₃	8,0 ± 0.2	7.4
		0.5 M NH ₃	24,7 ± 0.2	23.0
		5 M HCl	5,8 ± 0.1	5.4
		0.1 M thiourea in 0.5 M HCl	10,2 ± 0.1	9.5
104	93,4 ± 1.3	0.05 M NH ₃	17,3 ± 0.2	18.5
		0.5 M NH ₃	34,3 ± 1.1	37.8
		5 M HCl	7,1 ± 0.4	7.6
		0.1 M thiourea in 0.5 M HCl	15,0 ± 0.6	16.1
Ru(III)				
101	208,6 ± 0.9	0.05 M NH ₃	3,9 ± 0.1	1.9
		0.5 M NH ₃	6,7 ± 0.1	3.2
		5 M HCl	151,0 ± 1.5	72.4
		0.1 M thiourea in 0.5 M HCl	121,4 ± 4.6	58.2
104	202,7 ± 1.7	0.05 M NH ₃	10,0 ± 0.1	4.9
		0.5 M NH ₃	8,9 ± 0.1	4.4
		5 M HCl	143,1 ± 1.3	70.6
		0.1 M thiourea in 0.5 M HCl	147,2 ± 2.3	72.6

C^{*}_(org) – metal concentration in organic phase after extraction, C_{(w)R} – metal concentration in aqueous phase after stripping, R – stripping percentage

After the extraction, the organic phase contained approx. 100 mg/dm³ of Rh(III) ions. The highest stripping percentage was obtained using the 0.5 M NH₃ solution as a strippant and corresponded to approx. 20% or 40% percent of Rh(III) from the organic phase containing IL 101 or IL 104, respectively. The maximum concentration of Rh(III) in the aqueous phase after the stripping was 34 mg/dm³. In case of the stripping of Rh(III) using 0.1 M thiourea in the 0.5 M HCl, the Rh(III) concentration in the aqueous phase was two times lower than the Rh(III) concentration in the aqueous phase after the stripping using the 0.5 M ammonia solution. However, when the 5 M HCl solution was used as a strippant, concentration of Rh(III) ions in the aqueous phase was five times lower than the Rh(III) concentration after the stripping with the 0.5 M ammonia solution.

After the Ru(III) extraction, the metal ion concentration in the organic phase was approx. 200 mg/dm³. The ammonia solution (at 0.05 and 0.5 M concentrations) proved to be an ineffective strippant; the Ru(III) concentration in the aqueous solution after the stripping was at a maximum of 10 mg/dm³ (less than 5% of the stripping). 5 M HCl solution proved to be the best stripping for Ru(III). After the stripping of Ru(III) from the loaded organic phase containing IL 101, the metal concentration in the aqueous phase was approx. 150 mg/dm³, which corresponds to stripping efficiency of approx. 70%. 0.1 M thiourea in 0.5 M HCl was equally effective for Ru(III). After the stripping from the organic phase containing IL 101, the metal concentration in the aqueous phase was approx. 120 mg/dm³, which corresponds to stripping efficiency of approx. 60%.

Summary and conclusions

The studies conducted indicate that the best extractant for Ru(III) ions is Cyphos IL 101. The increase in the HCl concentration in the feed has a positive effect on the transport of Ru(III) ions to the organic phase, which is reflected in the increase in the extraction rate (from 60% to 70%). Moreover, the initial extraction rate of Ru(III) changes advantageously with the increase in the HCl concentration in the feed (Tab. I). The similar results were obtained for ionic liquids IL 102 and IL 104. Extraction efficiency for Rh(III) using the ionic liquids studied reaches 45% at most (IL 101) from the solution of the low HCl concentration and decreases with the increase in the acid concentration in the feed.

Cyphos IL 109 is the least effective extractant, both for Ru(III) and Rh(III), which results from high hydrophobicity of the bis(trifluoromethylsulfonyl)imide anion and a difficulty in reacting with hydrophilic chlorocomplexes of the ions extracted.

The best strippant of Rh(III) ions was the 0.5 M ammonia solution, while for Ru(III) ions it was the 5 M HCl solution and 0.1 M thiourea solution in 0.05 M HCl.

The results presented serve as the basis for further research on the development of the extraction-stripping method for separating Ru(III) from Rh(III) ions in aqueous chloride solutions.

Acknowledgments

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Literature

- Regel-Rosocka M., Rzelewska M., Baczyńska M., Janus M., Wiśniewski M.: *Removal of Palladium(II) from aqueous chloride solutions with Cyphos phosphonium ionic liquids as metal ion carriers for liquid-liquid extraction and transport across polymer inclusion membranes*. Physicochem. Probl. Miner. Process. 2014, 51, 2, 621–631.
- Rzelewska M., Baczyńska M., Regel-Rosocka M., Wiśniewski M.: *Trihexyl(tetradecyl)phosphonium bromide as extractant for Rh(III), Ru(III) and Pt(IV) from chloride solutions*. Chem. Pap. 2016, 70, 4, 454–460.
- Godlewska-Zytkiewicz B., Pyrżyńska K.: *Platynowce – zastosowanie i metody oznaczania*. Malamut. Warszawa 2012, 11–26.
- Gupta B., Singh I.: *Extraction and separation of platinum, palladium and rhodium using Cyanex 923 and their recovery from real samples*. Hydrometallurgy 2013, 134–135, 11–18.
- Kedari S., Coll M.T., Fortuny A., Górska E., Sastre A. M.: *Liquid-liquid extraction of Ir, Ru and Rh from chloride solutions and their separation using different commercially available solvent extraction reagents*. Sep. Sci. Technol. 2005, 40, 1927–1946.
- Mhaske A. A., Dhadke P. M.: *Extraction separation studies of Rh, Pt and Pd using Cyanex 921 in toluene – a possible application to recovery from spent catalysts*. Hydrometallurgy 2001, 61, 143–150.
- Zhang C., Huang K., Yu P., Liu H.: *Ionic liquid based three-liquid-phase partitioning and one-step separation of Pt(IV), Pd(II) and Rh(III)*. Sep. Purif. Technol. 2013, 108, 166–173.
- Górska E., Coll M. T., Fortuny A., Kedari C. S., Sastre A. M.: *Studies on the selective separation of Ir(IV), Ru(III) and Rh(III) from chloride solutions using Alamine 336 in kerosene*. Solvent Extr. Ion Exch. 2007, 25, 65–77.
- Panigrahi S., Dash T., Natharma K. C., Sarangi K.: *Extraction of ruthenium using both tertiary and quaternary amine from chloride media*. Sep. Sci. Technol. 2014, 49, 545–552.
- Druskovic V., Vojkovic V., Antonic T.: *Extraction of ruthenium and its separation from rhodium and palladium with 4-pyridone derivatives*. Croatica Chem. Acta. 2005, 78, 4, 617–626.
- Cieszyńska A., Regel-Rosocka M., Wiśniewski M.: *Extraction of palladium(II) ions from chloride solutions with phosphonium ionic liquid Cyphos IL101*. Pol. J. Chem. Technol. 2007, 9, 2, 99–101.
- Cieszyńska A., Regel-Rosocka M., Wiśniewski M.: *Ekstrakcyjne metody wydzielenia i rozdzielenia metali szlachetnych*. Przem. Chem. 2011, 90, 8, 1579–1585.
- Cieszyńska A., Wiśniewski M.: *Extraction of palladium(II) from chloride solutions with Cyphos®IL 101/toluene mixtures as novel extractant*. Sep. Purif. Technol. 2010, 73, 202–207.
- Cieszyńska A., Wiśniewski M.: *Extractive recovery of palladium(II) from hydrochloric acid solutions with Cyphos IL 104*. Hydrometallurgy 2012, 113–114, 79–85.
- Freire M. G., Carvalho P. J., Gardas R. L., Santos L. M. N. B. F., Marrucho I. M., Coutinho J. A. P.: *Solubility of water in tetradecyltriethylphosphonium-based ionic liquids*. J. Chem. Eng. Data 2008, 53, 2378–2382.

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