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Extractive Recovery and Separation of Palladium(II) from Model Hydrochloric Solution from Refining Shop with Di-*n*-Heptyl Sulfide and Penconazole

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Abstract—Extractive method for recovery of palladium(II) from a model palladium-rich hydrochloric solution from a refining shop was suggested. It was found that palladium(II) is fully extracted with di-*n*-heptyl sulfide and penconazole from 3 M hydrochloric solutions with high salt background, with the optimal phase contact duration being 20 and 5 min, respectively. As reagent dilutions served toluene and chloroform. Palladium(II) was back-extracted with a 15% aqueous ammonia and a saturated aqueous solution of sodium rhodanide. The optimal conditions of palladium(II) extraction and its separation from the accompanying platinum(IV) and copper(II).

Keywords: palladium, extraction, di-*n*-heptyl sulfide, penconazole

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One of topical and complicated tasks of modern hydrometallurgy of noble metals is the processing of concentrated technological solutions of platinum-group metals. In refining of palladium, technological solutions, as a rule, contain, together with the main metal, other platinum-group metals (PGMs) and also non-ferrous, ferrous, rare, and other metals in a wide range of concentrations. In the classical precipitating method of refining, palladium is separated from other metals as a diamine dichloride, but this method fails to provide the 100% extraction of the metal.

The liquid extraction in hydrometallurgy is a promising alternative technological method that can effectively extract and selectively separate PGMs from aqueous solutions. Compared with precipitating method in refining, the extraction has no such shortcomings as considerable expenditure of reagents, long process duration, and coprecipitation of other metals. The extractive method provides high recovery, selectivity and is distinguished by simplicity of implementation, high output capacity, possible automation of the occurring processes, and repeated use of the extractive agent. The method is preferable for obtaining high-purity metals. The

application of the extractive method is largely determined by the presence of the modern set of available reagents and by the rational choice of these when solving any particular problem. It should be noted, however, that not all of the presently used extractive agents possess a high efficiency and selectivity with respect to metals.

Sulfur-, nitrogen-, and sulfur-nitrogen containing reagents have been studied and suggested as effective extractive agents for noble metals at Ufa Institute of Chemistry—Subdivision of the Ufa Federal Research Centre of the Russian Academy of Sciences in the last decades [1–3]. The extraction of palladium(II) from hydrochloric and nitrate solutions, and also that of platinum(IV), gold(III), rhodium(III), copper(II), and other metals from hydrochloric solutions with certain derivatives of 1,2,4-triazole have been studied [4, 5].

Organic sulfides (dialkyl sulfides R₂S and oil sulfides) have found wide application in the technology and analysis of noble metals. Processes have been developed for concentration and refining of palladium from chloride and nitrate solutions, together with a set of extractive-instrumental methods for determining microscopic amounts of noble metals in complex objects [6, 7].

Hydrometallurgical processes at Russia's refining plants yield technological solutions that are palladium concentrates [8]. Together with the macroscopic base (palladium), these solutions, as a rule, contain platinum, copper, and other noble, nonferrous, ferrous, heavy, and rare metals at a high salt background and acidity. The extraction of palladium and its selective separation from the accompanying metals in solutions of this kind is a rather topical technological problem.

The goal of our present study was to develop an extractive method or separation of palladium(II) from platinum(IV) and copper(II) with di-*n*-heptyl sulfide and (*RS*)-1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole from a model palladium-rich solution from a refining shop.

EXPERIMENTAL

A solution simulating in a simplified way the concentrate of a technological solution from a refining shop was prepared for study. The solution contained: 120.0 g L⁻¹ of palladium, 30.7 g L⁻¹ of platinum, and 1.76 g L⁻¹ of copper in 3 M HCl. The salt background was 60.0 g L⁻¹ of NaCl. The model solution was prepared by dissolution of weighed portions of hexachloroplatinic acid H₂PtCl₆·6H₂O (pure), palladium chloride PdCl₂ (pure), copper chloride CuCl₂·2H₂O (chemically pure), and sodium chloride (chemically pure) on a hydrochloric acid (chemically pure) solution.

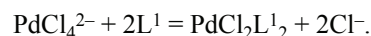
As extractive agents for metals served a 2.3 M (60 vol %) solution of di-*n*-heptyl sulfide (L¹ reagent) and a 2.0 M (56 vol %) solution of (*RS*)-1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole (penconazole, L² reagent). These reagents are products of large-tonnage manufacture and fully satisfy the requirements to industrial extractive agents. The reagents were characterized and their physicochemical properties were described in [3, 9]. Toluene (pure) and chloroform (chemically pure) served as reagent diluents.

The extraction was performed in 10-mL thermostated glass separation funnels at 20 ± 0.1°C. No third phase was formed in the course of extraction, the phase stratification occurred within 5 min after the agitation was terminated. When the extraction was complete, the raffinate was separated from the extracts and analyzed for the content of metals. Palladium(II) was back-extracted with 15% aqueous ammonia and a saturated aqueous solution of sodium rhodanide (chemically pure). The concentration of platinum-group metals in the stock model solutions

and in the raffinates was determined on a GBC SensAA atomic-absorption spectrometer in an acetylene-air flame (lamps with a hollow cathode made of the metals being analyzed, analytical wavelength of 247.6 nm in determining palladium, 265.9 nm for platinum, and 324.7 nm for copper), and that in extracts, from the difference of concentrations in the stock solution and raffinates. The determination error did not exceed 5 rel %.

DISCUSSION OF RESULTS

It was found in preliminary experiments that the extraction equilibrium in recovery of palladium(II) with L¹ reagent (toluene as diluent) does not exceed 20 min. Palladium(II) is extracted by the coordination mechanism with a disolvate formed due to the substitution of chlorine ions with donor sulfur atoms from the reagent:



According to the stoichiometry of the reaction, 0.52 g (0.0022 M) of L¹ reagent is required for extraction of palladium from 1 mL of a model solution containing 0.12 g (0.0011M) of palladium. In practice, palladium(II) was extracted with a 2.3 M reagent solution (5% excess) at a 1 : 3 ratio between the aqueous and organic phases and phase contact duration of 20 min. Under these conditions, palladium(II) was quantitatively extracted [$E_{\text{Pd(II)}} = 100\%$] and the accompanying platinum(IV) and copper(II) fully remained in the aqueous solution, which is evidenced by the results of an analysis of the raffinate. The low rate of platinum(IV) extraction by organic sulfides is due to the low rate of substitution of chlorine ions in the kinetically inert ion PtCl₆²⁻.

Of particular importance in the concentration of the metal that is a macroscopic base is the completeness of its back-extraction. Our experiments demonstrate that palladium(II) is quantitatively back-extracted from the organic phase [degree of back-extraction, $E_{\text{Pd(II)}} = 100\%$] with 15% aqueous ammonia (1 : 1 ratio between the aqueous and organic phases). Further, palladium can be precipitated from the raffinate with, e.g., a hydrochloric acid solution as Pd(NH₃)₄Cl₂.

A similar experiment on the extractive separation of palladium(II) was performed with chloroform as diluent. The results obtained demonstrated that, with chloroform, the separation coefficient $\alpha_{\text{Pd/Pt,Cu}}$ is not less than 22 × 10³. Based on these results, L¹ reagent can be recommended for application in the classical extractive scheme of

refining to recover palladium(II) from technological solutions and perform its selective separation from platinum(IV) and copper(II), with toluene and chloroform serving as diluents.

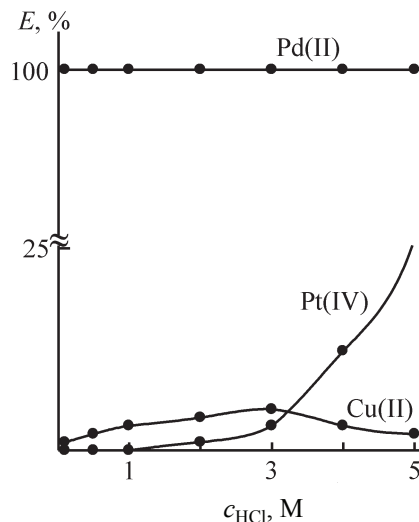
With appropriate conditions chosen, the role of extractive agents can be played by, e.g., dihexyl or dioctyl sulfide.

Thus, dialkyl sulfides are the optimal extractants for palladium, which successfully fit in the classical refining scheme and can be used to process not only lean solutions, including wastewater, but also rich palladium solutions from refining shops.

In contrast to dialkyl sulfides, derivatives of 1,2,4-triazole are not used as extractants in the hydrometallurgy of noble metals. It has been found previously that 1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]-methyl}-1*H*-1,2,4-triazole, (*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-yl-1,2,4-triazol-1-yl-methyl)-pentan-3-ol, and (*RS*)-1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole (L^2 reagent) are promising extractants and effectively extract under the optimal conditions some noble, ferrous, and nonferrous metals from nitrate and hydrochloric solutions [9].

We studied for the example of L^2 reagent the possibility of extracting palladium(II) from the model technological solution under study. The dependences of the degree of metal extraction by the given reagent on the hydrochloric acid concentration in the aqueous phase are presented in the figure.

It follows from these dependences that palladium(II) is effectively extracted with L^2 reagent in a wide range of acid concentrations in the aqueous phase (0.1–5 M HCl). Under these conditions, the reagent forms a hydrochloric acid due to the protonation of the nitrogen atom in position 4 of the 1,2,4-triazole ring, and the extraction occurs by the interphase anion exchange mechanism [10]. In contrast to palladium(II), copper(II) is not extracted in a wide range of acidities of the aqueous phase, and the degree of platinum(IV) extraction grows only slightly with the acidity increasing to more than 3 M HCl. Therefore, at 0.1–3 M HCl and phase contact duration not exceeding 5 min, palladium(II) can be selectively separated from copper(II) and platinum(IV). On raising the acidity of the raffinate after separating palladium(II) to 4–6 M and making the contact duration 20 min, platinum(IV) can be selectively separated with the given reagent from copper(II) [11].



Degree of extraction of palladium(II), platinum(IV), and copper(II) with L^2 reagent vs. the acidity of the aqueous phase at a phase contact duration of 5 min. $c_{Pd(II)} = c_{Pt(IV)} = 0.011$ M, $c_{L^2} = 0.025$ M; $c_{Cu(II)} = 0.020$ M, $c_{L^2} = 0.060$ M.

The extraction of palladium(II) from a 3 M hydrochloric model technological solution with a solution of L^2 reagent in toluene was performed at a 1 : 1 ratio between the aqueous and organic phases. The optimal concentration of L^2 reagent was calculated on the basis of the extraction mechanism indicating that the ionic associate $(HL^2)_2PdCl_4$ is the form being extracted.

In a single extraction stage at a phase contact duration of 5 min, the degree of palladium(II) extraction was 93%, with platinum(IV) and copper(II) fully remaining in the aqueous phase. After the phase separation, palladium(II) was back-extracted from the extract with a saturated aqueous solution of sodium rhodanide (20 : 1 ratio between the aqueous and organic phase, phase contact duration 3 min). The degree of metal ion re-extraction was no less than 99.5%.

To additionally extract palladium(II) from the resulting raffinate, a second extraction stage was performed. A fresh portion of L^2 reagent was used. The process was performed at a 2 : 1 ratio between the aqueous and organic phases and phase contact duration of 5 min. According to the results of an analysis, no palladium(II) was found in the raffinate after the second extraction stage. The raffinate containing only platinum(IV) and copper(II) can be further processed by the classical extraction scheme, and other accompanying metals, components of the industrial technological solution, can be separated in the stages of back-extraction and extract washing.

Consequently, with toluene used as diluent, it is impossible to fully recover palladium(II) under the extraction conditions under study. Therefore, we used chloroform as a reagent diluent to examine the possibility of separating palladium(II) from the concentrate in a single stage. An experiment, similar to that described above, on extraction of palladium(II) from a model concentrate with a solution of L² reagent in chloroform demonstrated that, at a 1 : 1 ratio between the aqueous and organic phases and phase contact duration of 5 min, the degree of palladium(II) extraction in a single stage was not less than 99.8%, with platinum(IV) and copper(II) fully remaining in the aqueous phase. Consequently, the replacement of a diluent in the extractive system makes it possible to optimize the technological problem and separate palladium(II) in a single stage, which is technologically rational and economically favorable. Despite that chlorine-containing diluents are commonly not used in hydrometallurgy, this compound can be recommended as an alternative simplifying the separation process, e.g., in closed-type extractors.

Thus, the complicated problem of palladium(II) recovery from high-concentration technological solutions can be solved by using the extraction method with readily available sulfur- and nitrogen-containing reagents.

CONCLUSIONS

An extraction method is suggested for selective recovery of palladium(II), macroscopic base of a model hydrochloric concentrate from a refining shop, with di-*n*-heptyl sulfide and (*RS*)-1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole, with its simultaneous separation from platinum(IV) and copper(II). The use of a 1,2,4-triazole derivative adequately fits into the classical extraction scheme in the stage of palladium separation. Palladium(II) can be fully back-extracted from extracts with an ammonia solution or a saturated aqueous solution of sodium rhodanide, and the reagents can be repeatedly used on being washed.

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REFERENCES

1. Afzaletdinova, N.G. and Murinov, Yu.I., *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 12, pp. 1597–1603.
2. Anpilogova, G.R., Khisamutdinov, R.A., Golubyatnikova, L.G., and Murinov, Yu.I., *Russ. J. Gen. Chem.*, 2017, vol. 87, no. 1, pp. 132–138.
3. Golubyatnikova, L.G., Anpilogova, G.R., Khisamutdinov, R.A., and Murinov, Yu.I., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 2, pp. 310–316.
4. Golubyatnikova, L.G., Khisamutdinov, R.A., Lobov, A.N., and Murinov, Yu.I., *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 4, pp. 491–498.
5. Anpilogova, G.R., Khisamutdinov, R.A., Golubyatnikova, L.G., and Murinov, Yu.I., *Russ. J. Appl. Chem.*, 2016, vol. 89, no. 2, pp. 206–211.
6. Bukhbinder, G.L., Korda, T.M., Demidova, M.G., Gus'kova, E.A., and Torgov, V.G., *J. Anal. Chem.*, 2009, vol. 64, no. 6, pp. 593–601.
7. Torgov, V.G., Korda, T.M., Demidova, M.G., Gus'kova, E.A., and Bukhbinder, G.L., *J. Anal. Chem.*, 2009, vol. 64, no. 9, pp. 877–885.
8. Sidorenko, Yu.A., *Zh. Ross. Khim. O-va im. D.I. Mendeleeva*, 2006, vol. L, no. 4, pp. 6–12.
9. Golubyatnikova, L.G., Mulagaleev, R.F., Khisamutdinov, R.A., and Murinov, Yu.I., *Russ. J. Appl. Chem.*, 2017, vol. 90, no. 9, pp. 1475–1479.
10. Khisamutdinov, R.A., Murinov, Yu.I., and Shitikova, O.V., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 6, pp. 696–978.
11. Khisamutdinov, R.A., Anpilogova, G.R., Golubyatnikova, L.G., Baikova, I.P., and Murinov, Yu.I., *Russ. J. Inorg. Chem.*, 2012, vol. 57, pp. 120–127.