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EXTRACTION OF PALLADIUM

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It is known that a series of organic compounds containing in molecule SH-, NH- groups, including halogens, carboxylic acids and their derivatives, have the ability to form the innercomplex compounds under certain conditions. These compounds permit to carry out the extraction in acidic medium, that prevents the of process hydrolysis. They are not dissolved in water but are soluble in various solvents and form colored solutions and so may be used as an extractants. The main purpose of this paper is the study of palladium extraction ability for chlorinated naphthenic acids (CNA) synthesited in laboratory on the basis of industrial alkylphenols. Ammoniumacetate with various pH was used as a buffer to extract palladium from $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ 0.1 mkg/ml solution. The main task for the use of inert organic compound in extraction is the selection of reagent which dissolves it but does not form any compound. With this aim the influence of different solvents on their reagent was researched. The experiments show that chloronaphthenic acid is dissolved well in organic solvents. Its solution, for example in kerosene, is light-resistant, does not hydrolyze in water, alkalis and acids. So, chloronaphthenic recomendefor palladium extraction.

Keywords: *extraction, palladium, chloronaphthenic acid, diluent.*

doi

Introduction

A consistent and thorough study of the search and synthesis of new extract ants and their to extract ability the elements is important. Every work done in this area leads to the development of extraction chemistry and accelerates the resolution of practical issues.

From this point of view, a number of organic compounds have the ability to form internalcomplex compounds with metal ions under certain conditions. These are organic compounds, mainly with SH-, NH-groups in the molecule including halogens. Extraction became a modern technique to recover and separate noble metals, including palladium(II). E.g. [1], several reagents, including hydroxyl-oximes, alkyl derivatives of 8-hydroxyquinoline, hydrophobic amines and esters of pyridine carboxylic acids were proposed. Some of them are used in the industry. However in this case the extraction occurs very slowly that is caused by the nature of hydrophobic extractant with formation of symmetrical palladium complex.

The amine type extraction reagents are perspective for the separation of palladium from acidic nitrate solutions like industrial solutions waste. At the same time palladium

is effectively extracted by quaternary ammonium salts from the nitric acid solutions, tertiary amines offer low distribution coefficients. The effectiveness of extraction by these reagents increases considerably in the presence of small amounts of chloride ions [2].

The mechanism of palladium extraction from hydrochloric acid is well studied, less is known about the extraction from nitrate medium. At low chloride ions concentrations, it has been observed that with an increase of palladium concentration the distribution coefficient increases, and the mechanism of extraction is complex.

In was shown [3] that palladium(II) is efficiently extracted with (RS)-1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole from 0.2–5.0 M HNO_3 solutions and can be selectively separated from Ni(II), Cu(II), Pb(II), Fe(III), Ag(I), as well as from lanthanides(III) in 2–4 M HNO_3 solutions. The extraction of Pd(II) from 1 M HNO_3 solution proceeds via coordination mechanism; this is an endothermic process in the 10–30°C temperature range.

It was shown [4] by extraction methods and IR spectroscopy that thiocalixarenes 2 extract complex species $[\text{Pd}_n\text{L}_m\text{H}_{4-2n}]$ ($m = 1$,

$n = 1$ and 2) and $[(\text{PdA}_2)_n\text{L}_m\text{H}_4]$ ($\text{A} = \text{NO}_3^-$, $m = 1$, $n = 1-4$) from nitric acid solutions at pH 3. Extraction constants for these palladium species regarding of experimental data were calculated.

A comparison [5] was made between the separate extraction and coextraction of neodymium and palladium from nitric acid solutions with bifunctional phosphorylated thiocalixarene (TCPO) and model of monofunctional extractants – phosphorylated calixarene (CPO), thiocalixarene (TCA) and their mixtures – for mutual influence evaluation of S- and PO-donor sites of the extractants. The results of the extraction with TCA–CPO mixtures are of interest for a simplified process (PUREX) and a process being developed (CARBEX) as applied to extraction of neodymium and palladium from nitric acid solutions and their separation from carbonate solutions after removing of neodymium.

In [6] studied the extraction of chloropalladium complexes by solutions of trioctylmethylammoniumdi(2,4,4-trimethylpentyl)dithiophosphinate in toluene over in wide range of aqueous acidities. Distribution factors and spectroscopic studies of extraction products showed that $(\text{R}_4\text{N})[\text{Pd}_2\text{Cl}_4\text{A}]$ complexes are formed in the organic phase. Thus, if the concentration of the dialkyldithiophosphinic acid increases, then palladium di-(2,4,4-trimethylpentyl)dithiophosphinate is formed in the organic phase.

So, various derivatives of organic acids, have been studied as extractants for the extraction and separation of palladium from acid solutions.

Successful solution of the problem of protecting the biosphere, reducing the negative impact of industrialization on the state of the environment are directly related to the development of effective analysis methods. And the above mentioned extractants for the selective determination of palladium do not always satisfy the requirements for the lower boundaries of the determined contents. These extractants are often unstable reagents can be gradually oxidized by air. Taking into account

the above indicated, it was interesting to study the distribution of palladium over effective extractant solutions, which are highly soluble in organic solvents. Our task was to effectively determine the composition of the extracted compounds.

The aim of this work is to study the extraction ability of chlorinated naphthenic acids synthesized in the laboratory on the basis of industrial alkyl phenols, to determine the composition of the extracted palladium compound, and to study its physicochemical properties.

Experimental part

Ammonium acetate buffer was used to obtain a $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ salt solution with a density of 0.1 mg/ml [7–11]. The solutions were concentrated using concentrated HCl in a water bath before the experiment. Then the solutions were diluted to achieve the required concentrations (C) of metal and acid. The fixed values of chloride ion concentration and ionic strength in aqueous solutions were adjusted using lithium chloride so that $C_{\text{LiCl}} + C_{\text{HCl}} = 3 \text{ mol/l}$.

The solutions containing palladium used in the extraction were prepared according to the procedure described in [7–11]. Chloronaphthenic acid (CAN) (molecular weight 198 g, d_4^{20}) in kerosene were used as extractant.

Extraction was carried out in diving funnels at equal volumes of aqueous and organic phases at 20°C. The concentration of palladium in solutions was determined by the photometric method, and in organic phases – by the difference between the concentrations of palladium in the initial solution and in the aqueous phase after extraction.

The optical density of the solutions was determined by IR spectrometer. To assess the degree of extraction used the following quantitative values in the organic and aqueous phases:

$$R = \frac{q_{\text{org}}}{q_w^0} = \frac{C_{\text{Pd,org}} \cdot v_{\text{org}}}{C_{\text{Pd,org}} \cdot v_{\text{org}} + C_{\text{Pd,w}} \cdot v_w} \quad (1)$$

The share of the substance remained in the aqueous phase was determined by the formula

$$\alpha_w = \frac{q_{\text{org}}}{q_w^0} = \frac{C_{\text{Pd},w} \cdot v_w}{C_{\text{Pd,org}} \cdot v_{\text{org}} + C_{\text{Pd},w} \cdot v_w} \quad (2)$$

To determine the solubility of the synthesized CNA in organic solvents, there was experimentally chosen an inert solvent which, by dissolving the extractant, would not form a compound. For this, the effects of solvents of different grades were tested.

Results and discussion

Extraction was performed using chloronaphthenic acid by studying the distribution of palladium between two immiscible phases (water and an organic solvent). In this case, the extraction obeys the Gibbs phase rule: $N+F=K+2$, where N is the number of phases, F is the number of degrees of freedom; K is the number of components. Therefore, at constant temperature and pressure, the studied system was monovariant ($F=1$). In this case, if the concentration of dissolved palladium in one phase is constant, then its concentration in the other phase is also constant.

It was established that the synthesized by us chloronaphthenic acid, on the one hand, allows extraction to be carried out in an acidic medium, thereby preventing hydrolysis. On the other hand, the extractant increases the selectivity of the palladium extraction process. The reagent gives soluble colored solutions, which is important for their use, in particular in extraction chemistry.

The third light filter was used during all measurements. The largest optical density was obtained for palladium extraction by CNA compound with kerosene. Therefore, kerosene is taken as an organic solvent useful in subsequent experiments.

Another of no small importance condition is studying the dependence of optical densities on the duration of stirring 5 ml mixture of 1N H_2SO_4 , 0.5 ml of reagent CNA (0.1 mol), 5 ml of kerosene. For this, the mixture was

thoroughly shaken for 1–15 minutes (Figure 1). Then the optical density of the solution was measured by separating the organic phase.

Fig. 1. The dependence of palladium by CNA of extraction degree on stirring time.

After phase separation, the optical density of the solution was measured by the photocolorimetric method. It was established that the dependence of the optical density of palladium formed by CNA at various concentrations ($[\text{Pd}^{2+}] = (2-4) \cdot 10^{-4} \text{ M}$ with time (1–24 h) remains constant. In other words, the synthesized reagent does not change its optical density for 24 hours, regardless of the concentration of palladium. This indicates that it creates a stable complex with palladium.

To establish optimal conditions for the formation of a palladium compound with CNA, the dependence of the degree of palladium extraction on the pH of the medium was studied. With an increase in pH from 1 to 5.0, the main concentration of palladium (100–95%) is transferred to the organic phase. An increase in the concentration of $[\text{OH}]^-$ ions in solution leads to a decrease in the percentage of palladium extraction.

The experimental data of the dependence of the extraction of palladium by CNA on the concentration of mineral acids are shown in Figure 2.

It was discovered that in solutions from 0.01 to 1 N during the extraction, palladium passes into the organic phase. Starting from 2 N, the percentage of extracts decreases. For example, the extraction percentage in chlorous acid 5 N makes up 37.7% (Figure 2, curve 1).

Fig. 2. Dependence of the extraction of palladium by CNA on the concentration of mineral acids in the aqueous phase: 1 – HCl, 2 – H₂SO₄, 3 – H₃PO₄.

In sulfuric acid medium from 0.01 N to 6 N, palladium passes into the organic phase. Starting with a concentration of 7 N sulfuric acid, the extraction percentage is gradually reduced. Extraction at 7 N, was 95%, and this indicator remains constant till concentration of orthophosphoric acid 10 N ~70% (Figure 2, curve 2).

Conclusion

Thus, it was detected that CAN has the ability to form complexes with palladium in acidic medium under certain conditions, that allows to prevent, hydrolysis. Being soluble in various solvents, it forms colored solutions and can be used in extraction chemistry. Solution of CAN in kerosene is light-resistant, does not hydrolyze in water, alkalis and acids. Palladium extraction by this reagent depends on the ratio and organic phases. This makes it possible to vary the extraction characteristics in palladium-containing systems. Reagent is recommended by us for palladium extraction.

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PALLADIUMUN EKSTRAKSİYASI**S.R.Mamedova, Z.A.Cabbarova**

XNT-ları müəyyən şəraitdə turş mühitdə palladium ilə kompleks birləşmələr əmələ gətirir, bu da hidrolizin qarşısını almağa imkan verir. Müxtəlif həlledicilərdə həll olaraq rəngli məhlullar alınaraq ekstraktsiyada istifadə edilə bilər. XHK-nın kerosində məhlulu, işığa davamlı, suda, qələvi və turşularda hidroliz etmir. Palladiumun bu reaktivlə ekstraktsiya dərəcəsi sulu və üzvi fazaların nisbətindən asılıdır. Bu, palladiumun tərkibli sistemlərdə hasilat xüsusiyyətlərini dəyişdirmək üçün imkan yaradır. Reagent palladiumun ekstraktsiyası üçün tövsiyə edilə bilər.

Açar sözlər: ekstraktsiya, palladium, xloronften turşuları, həlledici.

ЭКСТРАКЦИЯ ПАЛЛАДИЯ**С.Р.Мамедова, З.А.Джаббарова**

Обнаружено, что ХНК обладают способностью образовывать комплексы с палладием в кислой среде при определенных условиях, что позволяет предотвратить гидролиз. Будучи растворимым в различных растворителях, образуют окрашенные растворы и могут быть использованы в экстракции. Раствор ХНК в керосине, устойчив к воздействию света, не гидролизуются в воде, щелочах и кислотах. Степень экстракции палладия этим реагентом зависит от соотношения водной и органической фаз. Это создает возможности для варьирования экстракционных характеристик в системах, содержащих палладий. Реагент может быть рекомендован для экстракции палладия.

Ключевые слова: экстракция, палладий, хлорнафтеновые кислоты, растворитель.