Liquid-liquid extraction of Pt(IV) from hydrochloric acid solutions using PPG 425 – NaCl – H₂O system

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Abstract. Today, metal extraction from e-waste is beneficial from both an environmental and economic point of view. Natural resources of metals, especially platinum group metals, are limited. At the same time, the amount of waste containing many valuable elements continues to grow. In this work, we studied the extraction of Pt (IV) from hydrochloric acid solutions using polypropylene glycol 425 (PPG 425). In the course of the experimental work, the dependence of the platinum extraction degree on the influence of hydrochloric acid concentration and medium pH in the polypropylene glycol 425 – sodium chloride – water system have been established. The maximum recovery (distribution coefficient > 3.5) has been achieved in the presence of 2 M HCl in an aqueous two-phase system (ATPS), which allows the use of the proposed system for the extraction of platinum from leaching solutions.

Keywords: extraction, aqueous two-phase system, platinum, green chemistry, e-waste

1. Introduction

The growing attention to the problem of environmental conditions associated with the continuous increase in the production of electronic equipment, such as computers, cell phones, household appliances, prompted researchers to develop new technologies for the processing of huge amounts of waste electronic and electrical equipment [1]. Essential components of e-waste, particularly in the field of information technology and communication equipment, are non-ferrous metals (Fe, Zn, Al, Mn, etc.) [2], as well as precious metals (Au, Ag, Pt, Pd) [3], and rare elements (In, Sb, Te, Ta, rare earth elements (REE), etc.) [4]. It is interesting to note that electronic waste may be secondary "ores", as they may contain higher concentrations of valuable metals than primary natural resources [5]. The hydrometallurgical method is the most promising one for metal extraction from electronic waste. Traditional liquid extraction has proven its effectiveness in extracting organic acids from aqueous media [6-8], metals from nitrate [9,10], and chloride [11,12] leaching solutions. Belova et al. proposed extraction systems based on binary extractants for the effective extraction of rare-earth elements from aqueous solutions [13-15]. Xu Z-X et al. used imidazolium-based task-specific polymeric ionic liquid (CP-AMIN) for separation of Pt(IV), Pt(II), and Pd(II) and associated metal ions from hydrochloric acid media [16].

In recent years, systems that do not contain any flammable, toxic, or volatile compounds have been developed and used in the extraction process [17,18]. Several works are devoted to the application of such systems in the extraction of biological compounds [19], organic acids [20,21], known work on
the production of nanomaterials in aqueous two-phase systems [22,23]. ATPS based on polymers as a new type of environmentally safe extraction systems have been proposed in the extraction and separation technology of rare-earth [24], heavy [25], precious [26], nonferrous [27-29], and other metals [30,31] by many scientific groups.

For example, Bulgariu L and Bulgariu D offered ATPS based on PEG and sulfate salts in the presence of iodide for selective extraction of Hg(II), Cd(II), and Zn(II) ions from the aqueous solution. The efficiency of metal ion extraction under study depends on many factors, including the nature of inorganic salt, the amount of introduced iodine, pH of the initial salt solution, etc [32]. Zakhodyaeva Yu A et al. introduced potassium rhodanide into the PEG 1500 - (NH₄)₂SO₄ - H₂O system to separate a mixture of metals contained in the leaching solution of used batteries [33] Water-soluble polymers (polyethylene glycols, polypropylene glycols, copolymers) and inorganic salts are usually used to form aqueous two-phase systems. Polyethylene (propylene) glycols are non-ion, biodegradable, non-toxic polymers with low volatility and are widely used in the cosmetic, food, pharmaceutical, and chemical industries. Unlike PEG, polypropylene glycol can form ATPS with sodium chloride at room temperature. This system allows for the extraction of metals from acidic chloride solutions. The elements of the platinum group, especially Pt, are important metals that are used in the manufacture of catalysts, technological devices, reactors, jewelry, electronics. In the present work, we studied for the first time the extraction of platinum(IV) from model hydrochloric acid solutions with the use of PPG 425 without introducing additional extracting agents. The results of studies of the effect of hydrochloric acid concentration on Pt⁴⁺ distribution coefficients are presented.

2. Experimental details
2.1. Reagents and equipment

The following reagents were used in the work: Pt dissolved in 5% HCl (Sigma-Aldrich, St. Louis, MO, USA), hydrochloric acid (chemically pure Chimmed, Moscow, Russia), poly(ethylene glycol) with a molecular weight of 1500 produced by Fluka (Shanghai, China), sodium chloride (chemically pure, Chimmed, Moscow, Russia). Distilled water was used for the preparation of solutions.

The following equipment was used in the work: temperature-controlled shaker (Enviro-Genie SI-1202, Scientific Industries, Inc., Bohemia, NY, USA), analytical balance with an accuracy of 0.0001 g (HR-100AZ, AND Company, Seoul, Korea), centrifuge (CM-6MT, SIA ELMI, Riga, Latvia), Cary-60 spectrophotometer (Agilent Tech., Santa Clara, CA, USA), pH-meter (Starter 5000, OHAUS, Parsippany, NJ, USA) with a combined STMICRO5 RU glass electrode calibrated against buffers with the pH-values 1.68, 4.01, 7.00, and 10.01 (at 298.15 K).

2.2. Experiment method

All experiments were performed at a temperature of 298.15 K and an atmospheric pressure of ~100kPa. For platinum extraction, PPG 425 (30 wt %) - NaCl (8 wt %) - H₂O system was chosen. Precisely weighed amounts of polymer and salt, as well as necessary amounts of hydrochloric acid and extractable metal, were placed in graduated tubes, dissolved in distilled water, and mixed until a two-phase system was formed. The tubes were then placed in a temperature-controlled shaker and stirred at 45 rpm at a constant temperature for 30 minutes to achieve thermodynamic equilibrium. The samples were centrifuged at 2500 rpm for 10 minutes for complete phase separation. The volumes of the upper and lower phases were fixed, then the pH and metal concentration were determined in the phases. Figure 1 shows the scheme of the extraction experiment.
Figure 1. Schematic of the platinum(IV) extraction process in PPG 425 – NaCl – H₂O ATPS.

The concentration of metal in the initial solution and the equilibrium polymer and salt phases after extraction was determined using a spectrophotometric method based on the formation of a platinum complex with tin chloride, which has an absorption band at a wavelength of 403 nm. The error of determination was <5%.

The distribution coefficient (D) of platinum was calculated by the formula (1):

\[ D = \frac{[Pt]_{t,ph}}{[Pt]_{b,ph}}. \]  

where \([Pt]_{t,ph}\) - concentration of metal in the upper phase, \([Pt]_{b,ph}\) - is the concentration of metal in the lower phase. All experiments were repeated 3 times each.

3. Results and Discussion

3.1. Interphase distribution of Pt(IV) in PPG 425 – NaCl – H₂O system.

When studying the extraction of platinum in an aqueous two-phase system, the influence of the salt phase acidity on the interphase distribution of the metal under study is of interest. Thus, the influence of equilibrium values of a salt phase pH on the efficiency of platinum(IV) extraction in the (PPG 425 (30 wt %) - NaCl (8 wt %) - H₂O) system in a range of pH 0-2 (figure 2) is studied.
Figure 2. Dependence of Pt(IV) distribution coefficient on equilibrium pH values of the bottom phase in the presence of HCl: [Pt]_{init} = 0.0001 mol/L.

From the received extraction data, it is visible, that at a decrease in the value of a salt phase acidity increase in distribution coefficients Pt^{4+} occurs. A decrease in the pH value of the salt phase leads to an increase in hydrophobicity of the polymer phase [34], which in turn contributes to the extraction of hydrophobic anion PtCl_{6}^{2-}. The maximum distribution coefficient (> 3.5) was obtained at pH ~ 0. In hydrometallurgical processes, platinum group metals are contained in hydrochloric acid leaching solutions, where the HCl content may vary depending on the conditions of the process, the initial concentration of metals, and acid. Figure 3 shows the results of the influence of hydrochloric acid initial concentration on the platinum (IV) extraction in the range from 0 to 2 mol/L in the PPG 425 - NaCl - H_{2}O system.

Figure 3. Influence of hydrochloric acid concentration on platinum(IV) extraction in PPG 425 - NaCl - H_{2}O system: [Pt]_{init} = 0.0001 mol/L.

Further increase in acid concentration leads to the homogenization of the extraction system. The figure shows that the maximum distribution coefficient is achieved at HCl concentration ~2 mol/l. A similar effect was observed in Mhaske A A et al. in the work on extraction of this metal, where Cyanex 921 was used as an extractant [35].

Conclusions
Thus, we studied the interphase distribution of Pt(IV) in the aqueous two-phase PPG 425 - NaCl - H_{2}O system. We have studied the interphase distribution of Pt(IV) in the aqueous two-phase PPG 425 - NaCl - H_{2}O system. We have studied the acidity of the salt phase and the initial concentration of hydrochloric acid on the metal extraction. It is established that a reduction of the medium pH the metal distribution coefficient increases; at acid concentration ~1.5 mol/l the maximum distribution of platinum in the polymer phase is achieved. It has been shown that an aqueous two-phase system based on polypropylene glycol 425 can be used for the effective extraction of Pt ions from chloride solutions.

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