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Extraction and separation of Pt(IV)/Rh(III) from acidic chloride solutions using Aliquat 336

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ABSTRACT

Extraction and separation of Pt(IV)/Rh(III) from chloride solutions using Aliquat 336 (Quaternary ammonium salt made by the methylation of mixed tri octyl/decyl amine) diluted in kerosene as an extractant/synergist alone and mixed with organophosphorous extractants as synergists/extractants were carried out from an aqueous feed containing 0.0005 mol L^{-1} Pt(IV)/Rh(III).Variation of hydrochloric acid concentration of aqueous phase from 0.005 to 10.0 mol L^{-1} increased the percentage extraction of platinum up to 5.0 mol L^{-1} there after it decreases. Whereas in the case of rhodium, from 0.005 to 1.0 mol L^{-1} acid range the percentage extraction was decreased from 1.0 to 10.0 mol L^{-1} acid range is favorable for extraction. Platinum(IV)/rhodium(III) separation factor of 279.2 was obtained at 1.0 mol L^{-1} HCl concentration with 0.005 mol L^{-1} Aliquat 336 and separation factor of 612.3 was obtained at 3.0 mol L^{-1} HCl concentration with 0.01 mol L^{-1} Aliquat 336. The present study optimized the various experimental parameters like phase contact time, effect of extractant, salts, temperature, loading capacity of extractant, stripping studies with various mineral acids/bases, recycling and reusing capacity of extractant up to ten cycles.

1. Introduction

Platinum is an extremely rare metal, occurring as only 0.003 ppb in the Earth's crust, and is 30 times rarer than gold. It is sometimes mistaken for silver but platinum is whiter in appearance. Platinum is often found chemically uncombined as native platinum and alloyed with iridium as platiniridium. Most often the native platinum is found in secondary deposits, platinum is combined with the other platinum group metals. In the nickel and copper deposits the platinum group metals occur as sulphides, tellurides, antimonides, and arsenides, and as end alloys with raw nickel or raw copper. The platinum arsenide, sperrylite, is a major source of platinum associated with nickel ores. Platinum exists in relatively higher abundances on the Moon and in meteorites. Correspondingly, platinum is found in slightly higher abundances at sites of bolide impact on the Earth that are associated with resulting post-impact volcanism, and can be mined economically [1,1a].

The most common use of platinum is as catalyst in chemical reactions. The most important application of platinum is in automobiles as a catalytic converter, which converts harmful emissions from the engine into less harmful gases. Platinum is also used in the petroleum cracking process, which breaks down crude oil molecules into smaller organic molecules, such as gasoline. PtO_2, also known as Adams' catalyst, is used as a hydrogenation catalyst, specifically for liquid vegetable oils. Platinum metal also strongly catalyzes the decomposition of hydrogen peroxide into water and oxygen gas.

Platinum is used as an alloying agent for various metal products, including fine wires, noncorrosive laboratory containers, medical instruments, jewelry, dental equipment, electrical contacts, and thermocouples. Platinum–cobalt, an alloy comprised of roughly three parts platinum and one part cobalt, is used to make extremely strong permanent magnets. Platinum-based anodes are used in ships, pipelines, and steel piers [1].

The industrial extraction of rhodium is complex as the metal occurs in ores mixed with other metals such as palladium, silver, platinum, and gold. It is found in platinum ores and obtained free as a white inert metal which is very difficult to fuse. The annual world production of this element is only about 25 tons and there are very few rhodium minerals.

The primary use of this element in automobiles as a catalytic converter, which converts harmful emissions from the engine into less harmful gases. The recycling of catalytic converter also became

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a valuable source for rhodium. Rhodium is used as an alloying agent for hardening and improving the corrosion resistance of platinum and palladium. These alloys are used in furnace windings, bushings for glass fiber production, thermocouple elements, electrodes for aircraft spark plugs, and laboratory crucibles. Other uses include: It is used as an electrical contact material due to its low electrical resistance, low and stable contact resistance, and its high corrosion resistance [2]. The high prices of precious metals like platinum group metals (PGMs) have ensured that there is continued interest in the development of new extractants for the commercial concentration and separation of these metals.

In chemical technology, the solvent extraction (SX) of metal chelates plays an important role in the purification of chemical reagents. This method is also frequently used in nuclear chemistry and technology for the separation of various radioisotopes and for the reprocessing of nuclear fuels.

The 1,3,4-thiodiazole-2-nonylmercapto-5-thiol was used to extraction and separation of Pd(II)/Pt(IV) and the metals can be stripped using thiourea/HCl solutions [3,3a]. The synergistic extraction of platinum from hydrochloric acid solutions was reported by isoamylalcohol + methylisobutylketone. At optimum conditions, the platinum extraction is over 99%; Al, Ca, Mg, Mn, Ni, Cr are quantitatively retained in the aqueous phase [4]. Eight systematically substituted 1,5-diphenyl formazans, dissolved separately in toluene, chloroform and dichloromethane, were investigated as liquid–liquid extractants. Consequently, in the stripping step with an acidified solution of thiourea, the rate of ligand substitution is also comparatively faster in the case of the 1:1-chelate. An effective separation of Pd(II) from an excess of Pt(IV) can be achieved by the iodo formazan (extraction time: 24 h, stirring time: 48 h) [5]. Solvent extraction of platinum(IV)/palladium(II) with tri-n-octylamine (TOA) in o-xylene from 4.0 mol L^{-1} (Na, H) (Cl, HSO_4) was investigated at 298 K in order to compare with similar extraction by trioctylphosphine oxide (TOPO) [6]. A novel sulfur containing solvent extraction reagent, 3,3-diethylthietane (DETE) was synthesized and its extraction mechanism of platinum(IV) from aqueous hydrochloric acid solutions was investigated at 30 °C in terms of the equilibrium distribution and extraction kinetics as well as its aqueous distribution and interfacial adsorption equilibrium [7]. The distribution behavior of ion associates of $PtCl_6^{2-}$ with quaternary ammonium cations (Q^+) between aqueous phase and two organic phases ($CHCl_3$ and CCl_4) was examined and the extraction constants ($\log K_{ex}$) were determined. A linear relation was found between $\log K_{ex}$ and the total number of C atoms in Q^+; from the slope of the line, the contribution of a methylene group to $\log K_{ex}$ is 0.6 [8]. The results indicate that amine Alamine 304 in chloride form extracts tetravalent platinum in chloride media. The extraction mechanism corresponds to an anion exchange, in which a complex of stiochiometric formula $(R_3NH^+)_2\ PtCl_6^{2-}$ is formed in the organic phase liberating at the same time Cl^- ions in the aqueous phase [9]. Some extractants are reported for extraction separation of Pt from Pd [10–20] but very less number of extractants is utilized for separation of platinum from rhodium [21–22]. The LLE literature reviewed showed that, despite a large number of studies, no system has been identified as yet to yield quantitative extraction of rhodium from concentrated solutions [23–27].

Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of mixed tri octyl/decyl amine, which is capable of forming oil soluble salts of anionic species at acidic or slightly alkaline pH. Aliquat 336 is composed of a large organic cation associated with chloride ion, $[R_3NCH_3]^+Cl^-$. Because the ammonium structure has a permanent positive charge, it can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason, Aliquat 336 finds application in environments from acid to slightly alkaline pH.

Solvent extraction of metals/acids such as mercury [28], amino acid enantiomers [29], hydrochloric acid [30], chromium(III) [31] and cobalt(II) [32] with Aliquat 336 was investigated. In spite of large number of studies on the extraction of transition metals and other acids with Aliquat 336, it has not been reported for the systematic solvent extraction and separation of tetravalent platinum/trivalent rhodium.

2. Experimental

2.1. Apparatus and reagents

Analysis of platinum(IV)/rhodium(III) was obtained using inductively coupled plasma optimal emission spectrometer (ICP-OES) Perkin Elmer Model Optima 2000 Dr. Stock solutions of $PtCl_4$ (Aldrich) of 98% purity, $RhCl_3 \cdot 3H_2O$ (Kojima Chemicals Co. Ltd.) were prepared in distilled water with addition of concentrated sulphuric acid to prevent hydrolysis of metal ions. The metal solutions used in SX studies were prepared from the stock solution. The commercial grade extractants Aliquat 336 was supplied by Cognis Corporation, USA, di-(2-ethylhexylphosphoricacid (D2EHPA) and 2-thylhexyl-phosphonic acid mono-2-ethyl hexyl ester (PC88A) was supplied by Daihachi Chemical Industry, Japan, bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) was supplied by Cytec, Canada and used as it is without purification. The present study we were used diluent as kerosene supplied by Junsei Chemicals Co. Ltd., Japan (boiling point: 180–270 °C, density: 0.80). All other reagents used were analytical reagent grade.

2.2. Extraction/stripping procedure

Extraction/stripping was carried out by shaking equal volumes (30 mL) of aqueous and organic phases (*A*:*O*) in separating funnels using a mechanical shaker at temperature 25 ± 1 °C for 1800 s, although it was proved that the extraction equilibrium was achieved within 300 s. The concentration of platinum(IV) in aqueous phase was analyzed by ICP-OES and the concentration in the organic phase was obtained by mass balance. These concentrations were used to obtain the distribution ration '*D*' ($D = [M_{org}/M_{aq}]$, where *M*: metals such as Pt(IV) or Rh(III)), the percentage of extraction ($\%E = D \times 100/D + 1$) and stripping efficiency '*S*' ($\%S = M_{aq}/M_{org} \times 100\%$). All the experiments were conducted at excepting that involving temperature effect and the general agreement with distribution values obtained was within ±5%.

3. Results and discussions

3.1. Effect of phase contact time for platinum(IV)/rhodium(III) extraction

The extraction behavior of platinum(IV)/rhodium(III) (0.0005 mol L^{-1}) from acid chloride (1.0 mol L^{-1}) solutions with 0.005 mol L^{-1} Aliquat 336 in kerosene has been measured at different phase contact times. The percentage extraction of platinum was increased with increase in phase contact time up to 300 s and further increase in contact time showed a stable behavior (65–78.5%). It is found that the equilibrium time for this system is 300 s (5 min). Time is not influenced the rhodium extraction; even 30 s is more than enough for metal equilibrium.

3.2. Effect of hydrochloric acid on platinum(IV)/rhodium(III) extraction

The effect of hydrochloric acid on the extraction of platinum(IV)/rhodium(III) was studied in the range of 0.005–10.0 mol L^{-1}. The effect of acid concentration on platinum(IV)/rhodium(III)