

Extraction and separation studies of platinum(IV) with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol in hydrochloric acid medium

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ABSTRACT

A novel method is proposed for the extraction of microgram level concentration of platinum(IV) from hydrochloric acid medium with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant. The platinum(IV) from the organic phase is stripped with water and estimated spectrophotometrically with stannous chloride. The effect of acid, reagent concentration and various foreign ions has been investigated. The method affords the binary separation and determination of platinum(IV) from the alloys and synthetic mixture. The method is highly selective, simple and reproducible.

Keywords: platinum(IV), solvent extraction, MBIMTT, Spectrophotometry

INTRODUCTION

The abundance of platinum in the earth's crust is $8 \times 10^{-11}\%$. Platinum is a good catalyst and in petroleum and chemical process. Platinum is widely used in jewellery and it has wide application in automotive exhaust-gas control converters and is of immense importance to the electronic industries. The increasing application of the platinum(IV) in the industrial process next to their extremely scarcity due to their natural abundance and the complexity of the process used for its extraction and refining, therefore it is of paramount importance in the development of separation method to recover platinum metal.

Liquid-liquid extraction is one of the most efficient method used to separate, concentrate and purify metal ions and organic compounds[1-5]. Solvent extraction has become an effective technique in the recovery and separation of palladium[6-13]. The aqueous chemistry of these metals is extremely complex. The important tendency of these metals is to form chlorocomplex in chloride medium. Solvent extraction technique of separation uses the difference in kinetic behavior for the formation of extractable species as well as the strength of electrostatic interactions of their chlorocomplexes with liquid anion exchanger. The inertness of the chlorocomplex of platinum in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported platinum(IV) are triphenyl phosphine[14], trioctylamine[15] N-benzyl aniline[16], bis (2-ethylhexyl) hydrogen phosphate[17] C₈₋₁₀ alkyl aniline hydrochloride[18], organoammonophosphate[19] N-n-octylaniline[20] n-octylaniline[21] The methods reported are not so reliable for routine application because these methods suffer due to the drawbacks such as operating condition (emulsion formation leading to problem for the separation, slow equilibrium) and ionic exchanger, nature of diluents, critical pH range etc.

One coordination chemistry property of Pt(IV) is that it prefer to coordinate most strongly with polarizable atoms such as sulfur, phosphorous and nitrogen. These ligands are 'soft' bases according to the empirical Pearson classification [22]. Sulphur containing ligands are highly selective for extraction of Pt(IV), and have been widely used in the extraction of this species[23-26]. 4-(4-methoxybenzylideneamino)-5-methyl-4H-1,2,4-triazole-3-

thiol(MBIMTT) is a sulphur containing ligand and it is highly water repellent. It does not form emulsion at the time of extraction. Because of the determination of small amounts of noble metals in minerals containing large amount of base metals is difficult; the effectiveness of MBIMTT has been evaluated as an extractant for platinum (IV) from variety of palladium bearing materials and process solutions. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru (III) and Au(III) and Pd(II)[27-30]. We report here the use of MBIMTT as an extractant for platinum (IV) from hydrochloric acid medium.

MATERIALS AND METHODS

Equipments and reagents

A Shimadzu UV-Visible spectrophotometer (UV-1601) with 1cm quartz cells was used for measurement. pH measurements were carried out with an Elico digital pH meter model LI-120(± 0.01)

A stock solution of platinum(IV) was prepared by dissolving 1g of platinum(IV) chloride hydrate in dilute AnalaR hydrochloric acid (1M) and diluting to 100ml with distilled water and further standardizing it[31]. A working solution $100 \mu\text{g ml}^{-1}$ was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT synthesized by known literature method[27]. MBIMTT (0.1M) solution was prepared in chloroform.

Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in distilled water. All the chemicals used were of AR grade. Double distilled de-ionized water was invariably used throughout the measurements.

Recommended method

An aqueous solution containing $100 \mu\text{g}$ of platinum(IV) and enough hydrochloric acid and water were added to give final concentration of 1M with respect to hydrochloric acid in a total volume of 25 ml. The resulting solution was transferred to 125 ml separating funnel. The aqueous phase was equilibrated once with 10 ml of 0.1M MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was stripped with two 10 ml portions of water. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Platinum(IV) was estimated spectrophotometrically by stannous chloride method[31]

RESULTS AND DISCUSSION

Extraction of platinum(IV) as a function of acid concentration

The extraction of $100 \mu\text{g}$ platinum(IV) was carried out from different acid medium with 0.1 M MBIMTT in chloroform keeping the aqueous to organic volume ratio 2.5:1. The extraction was found to be quantitative from hydrochloric acid (Fig.1). The extraction was found to be quantitative in very high concentration of nitric acid but was incomplete in sulphuric acid. Hence the use of hydrochloric acid is recommended for further studies.

Effect of reagent concentration

The concentration of MBIMTT in chloroform was varied from the 1×10^{-5} to 0.2M over the acid range 1M to 10M hydrochloric acid. It was found that 0.1M reagent in chloroform was needed for the quantitative extraction of platinum(IV) from 1M hydrochloric acid.

Effect of equilibration time

Variation of the shaking period from 5 seconds to 5 minutes showed that a minimum 10 second equilibration time is adequate for quantitative extraction of platinum(IV) from hydrochloric acid media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of platinum(IV) hydrochloric acid medium. Prolonged shaking up to 5 minutes has no adverse effect on the efficiency of extraction.

Effect of diluents

The extractions were performed from 1M hydrochloric acid medium using 0.1M MBIMTT in various solvents as diluents. It was found that 0.1M MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of platinum(IV). The extraction of platinum(IV) was found to be incomplete in isobutyl methyl ketone, isoamylalcohol, n-butanol and 4-methyl-2-pentanol. Chloroform is recommended for further extraction procedure because it offers better phase separation.

Table: 1 Effect of diverse ions on the extractive determination of platinum(IV)

$Pt(IV) = 100 \mu\text{g}$; aqueous phase = $1 \text{ mol/dm}^3 \text{ HCl}$; Aq/Org = 25:10; extractant = $0.1 \text{ mol/dm}^3 \text{ MBIMTT}$ in Chloroform

Tolerance limit (mg)	Foreign ion added
100	Fluride, Citrate, Oxalate, Acetate, EDTA, Malonate, Bromide, Iodide
20	Ca(II), Ba(II), Be(II), Mg(II), Fe(III)
15	Mn(II), Fe(II), Cr(III), Co(II)
10	Mo(VI), Sr(II), Ti(IV), Ce(IV)
5	U(VI), Mn(VII), Sb(III), Zn(II), Pb(II), Hg(II), Ni(II), Sn(II), Cu(II)

Table: 2 Binary separation of platinum(IV) from iron(III), cobalt(II), nickel(II) and copper(II)

Composition of Metal ions, μg	Recovery* Pd(II) %	Relative Standard Deviation %
Pt(IV) 100; Fe(III); 15000	99.6	0.13
Pt(IV), 100; Co(II); 10000	99.7	0.07
Pt(IV), 100; Ni(II); 5000	99.6	0.11
Pt(IV), 100; Cu(II); 5000	99.8	0.13

*-average of six determinations

Table.3: Analysis of synthetic mixture

Composition (μg)	Palladium found ^a (μg)	Recovery*(%)	R.S.D.(%)
Pt, 100; Pd,500	99.8	99.6	0.07
Pt, 100; Au,500	99.6	99.8	0.05
Pt, 100; Ru,500	99.4	99.7	0.07
Pt, 100; Rh,500	99.6	99.8	0.05
Pt, 100; Pd,500; Ru,500	99.5	99.9	0.06
Pt, 100; Pd,500; Au,500	99.6	99.7	0.06
Pt, 100; Pd,500; Rh,500	99.5	99.8	0.07
Pt, 100; Pd,500; Ru,500; Au, 500	99.4	99.7	0.08
Pt, 100; Pt,500; Rh,500; Au, 500	99.4	99.7	0.07
Pt, 100; Pd,200; Ru,200; Au, 200; Rh(III),200; Fe,2000; Co, 2000; Ni, 2000; Cu, 2000	99.5	99.6	0.06

*- average six determination

Table 4: Analysis of alloys

Alloy	Composition (%)	Platinum taken (μg)	Platinum found* (μg)	Recovery (%)	R.S.D. (%)
Solder alloy	Pt, 10; Pd, 30; Au, 60	100	99.7	99.8	0.05
Oakay alloy	Pt, 20; Pd, 10.5; Ni, 60; V, 9.5	100	99.6	99.5	0.06
Alloy for electrical contacts	Pt, 10; Pd, 35; Ag, 30; Cu, 14; Au, 10; Zn, 1.0	100	99.4	99.5	0.05

*- average six determination

Nature of extracted species

The composition of complex was confirmed by using log D- log C plot. The graph $\log D_{[Pt(IV)]}$ versus $\log C_{[MBIMTT]}$ at 4M hydrochloric acid was found to be linear and having slope of 1.3(Fig.2). Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Pt(IV): MBIMTT].

Loading capacity of MBIMTT

The concentration of platinum(IV) was varied to determine the loading capacity of MBIMTT. The loading capacity of 10 mL of 0.1 M MBIMTT was found to be 6.5 mg of platinum(IV).

Effect of Diverse Ions

Various ions were used in order to assess the tolerance of these ions on the extraction of platinum(IV).

Platinum(IV) was extracted in the presence of different diverse ions (Table 1). The tolerance limit was set as the amount of foreign ions cause $\pm 2\%$ errors in recovery of platinum. The results showed that in the extraction and determination 100 μg of the platinum, these ions did not interfere at the level tested. The reproducibility of platinum extraction investigated from six replicate measurement was found to be $99.00 \pm 0.95\%$.

Binary separation of platinum(IV) from base metals

The method allowed separation and determination of platinum(IV) from a binary mixture containing either iron (III), cobalt(II), nickel(II), and copper(II).

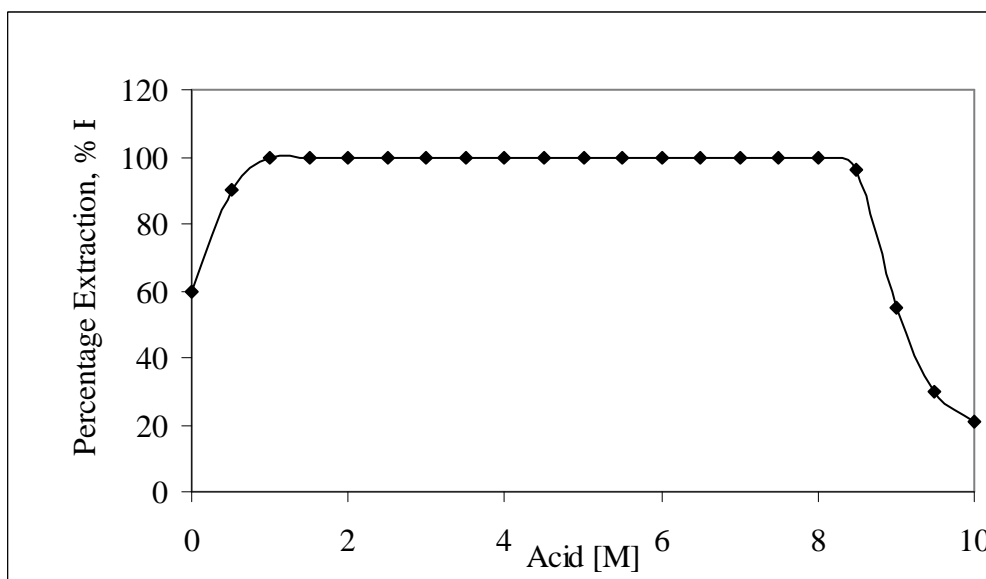


Fig.1. Extraction of Pt(IV) with 0.1M MBIMTT in hydrochloric acid medium

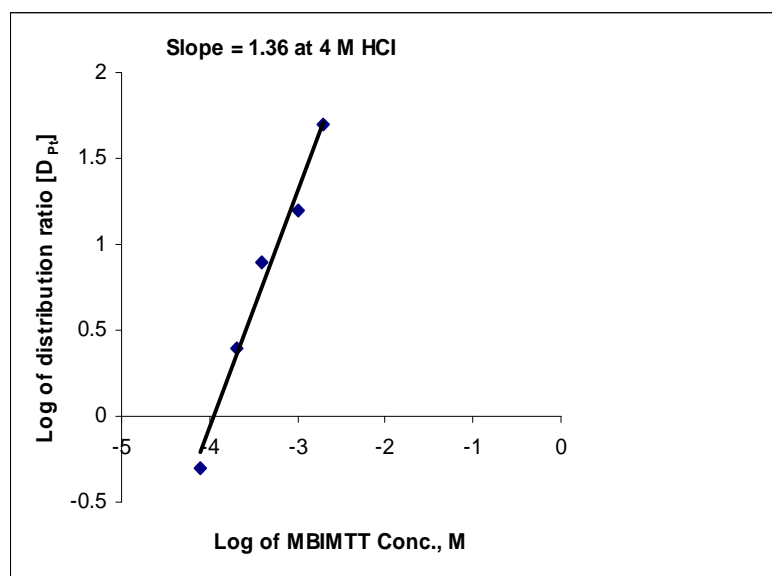


Fig.2. Log-log plot of distribution ratio (D_{Pt}) versus MBIMTT concentration at 4M HCl

The separation of platinum(IV) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1M MBIMTT in chloroform at 1M hydrochloric acid. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate[32], 1-nitroso-2 naphthol[32], DMG[32], and pyrimidine-2-thiol[33] respectively. Platinum is stripped from the organic phase with two 10 ml portion of water. The extract was evaporated to moist dryness and leached with 1M hydrochloric acid to form the solution. Platinum(IV) was estimated spectrophotometrically with stannous chloride[32]. The recovery of platinum(IV) and that added ions was 99.6 % and results are reported in Table 2.

Separation of platinum(IV) from multi-component synthetic mixture

In its natural occurrence platinum is always associated with the noble and base metal, hence its separation from these metals is of great importance. Under the optimum condition for extraction of platinum(IV), there is quantitative extraction of Au(III), Pd(II) and Rh(III). But the co extracted metal ions cannot be back stripped by water. Thus the MBIMTT reagent is made selective towards platinum(IV) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of platinum from many metal ions (Table 3).

Analysis of alloys

To ascertain the selectivity of the reagent the proposed method was successfully used in the determination of platinum(IV) in alloys. The synthetic mixtures were prepared corresponding to the composition of the alloys. The results of the analysis are reported in Table 4. The average recovery of platinum(IV) has been found to be 99.6 %.

CONCLUSION

These results underline the potential of the proposed method for the quantitative, selective extraction of platinum(IV) with MBIMTT containing low concentration of palladium. It is free from interference from the large number of diverse ions which are associated with platinum(IV) in its natural occurrence. The important features of this method are low reagent concentration is required, and the time required for the equilibrium is very short (30 seconds). The method is applicable to the analysis of platinum(IV) in synthetic mixtures and corresponding to alloys. The method is very simple, selective and reproducible.

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