Solvent Extraction and Separation Studies of Platinum Using Bis(2-ethylhexyl) Hydrogen Phosphate

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The extraction of platinum(II) from hydrochloric acid solution using bis(2-ethylhexyl) hydrogen phosphate in toluene was studied as a function of several variables, such as hydrochloric acid concentration, reagent concentration, metal ion concentration, temperature, effect of various diluents, and effect of various diverse ions. The proposed method was further applied for the separation of platinum from palladium, gold, and osmium in different ratios and to estimate the amount of platinum present in commercially available samples.

Various organic reagents have been used for the extraction of Pt(II) in different media. Gentry and Sherrington[1] used 8-quinolinethiol for Pt(II) extraction at pH 2.5—5.0. With sodium *N*,*N*-diethyldithiocarbamate[2] and mesityl oxide,[3] quantitative extraction of Pt(II) was achieved. Khattak and Magee[4] and Shillington and Tait[5] investigated the application of high molecular weight amine for the extraction of platinum in the presence of associated noble and base metals. Difficulties encountered in the platinum metal separation have been reviewed by Beamish and Van Loon.[6] A considerable amount of work has been done on the extraction with chelating extractants coordinating through sulfur. The extraction of platinum(IV) with such extractants is poor;[7,8] it is possible only after reduction of Pt(IV) to Pt(II) by a reductant such as tin(II) chloride.[9] Extraction of platinum(IV) with trioctylamine[10,11] from acid media, use of supported liquid membranes[12] and surfactants[13] and use for recovery of metal has also been studied in detail. As far as work with organophosphorus reagents is concerned, their full potential is yet to be exploited for extraction and separation of noble metals. Tributyl phosphate (TBP) (100%)[14] and trioctylphosphine oxide (TOPO)[15,16] with HCl have been used as extracting reagents for platinum. The platinum(II) and (IV) complexes with diethyl hydrogen dithiophosphate and derivatives of 8-quinolinol respectively were found to be extractable into organic solvents.[17,18] Kan Kimura[19] has reported poor extraction of Pt(IV) by bis(2-ethylhexyl) hydrogen phosphate (HDEHP) from chloride media, but no study of the effect of HDEHP concentration on extraction of Pt(IV) was found. In the present study, Pt(IV) was first reduced to Pt(II) by tin(II) chloride in acidic medium[20] before actual extraction with HDEHP. The method is simple and rapid for quantitative extraction of platinum. This method was further applied for the separation of platinum from palladium, gold, osmium, and other metals.

Experimental

Apparatus and Reagents. GBC 911 A UV/visible Spectrophotometer and Systronic digital pH meter MK (VI) were used. HDEHP was supplied by Dai-hachi Chemical Industries Ltd., Japan, and was used without further purification. A stock solution of platinum was prepared by dissolving an appropriate amount of $K_2[PtCl_6]$ in a minimum quantity of dilute hydrochloric acid and was standardized by known method.[21] The required concentration of this solution was prepared by further dilution with doublly distilled water. All other chemicals used were of analytical grade.

Procedure. An aliquot of solution containing Pt(IV) was taken in the separating funnel and to it hydrochloric acid and tin(II) chloride were added, so that the final concentration of HCl and $SnCl_2$ in 10 ml of aqueous phase was 0.5 M and 0.08 M (1 M = 1 mol dm^{-3}) respectively. 10 ml of 2.5×10^{-3} M HDEHP in toluene was then added and the mixture was equilibrated for 2 min. The two phases were allowed to separate. The metal loaded organic phase was back extracted with 10 ml of 4 M HCl and platinum was determined spectrophotometrically at 405 nm.

Results and Discussion

Extraction as the Function of Hydrochloric Acid Concentration. Pt(II) was extracted in the acidity range of 0.025—4.0 M HCl in the presence of 0.08 M $SnCl_2$ with 2.5×10^{-3} M HDEHP in toluene. Quantitative extraction was observed to take place between 0.25—2.5 M HCl, hence all extractions were carried out at 0.5 M HCl (Fig. 1).

To study the effect of concentration of $SnCl_2$ on % extraction of platinum, varying amounts of $SnCl_2$ were added to the aqueous phase containing 0.5 M HCl. It was observed that 5×10^{-2} to 1.8×10^{-1} M of tin(II) chloride was sufficient to favor quantitative extraction of Pt(II), while with concentrations of $SnCl_2$ less than 5×10^{-2} M the reduction of platinum was incomplete, resulting in lesser % extraction.

Extraction as a Function of HDEHP Concentration. Pt(II) was extracted at varying concentrations of HDEHP (1×10^{-4}—1×10^{-1} M) and it was found to be quantitative

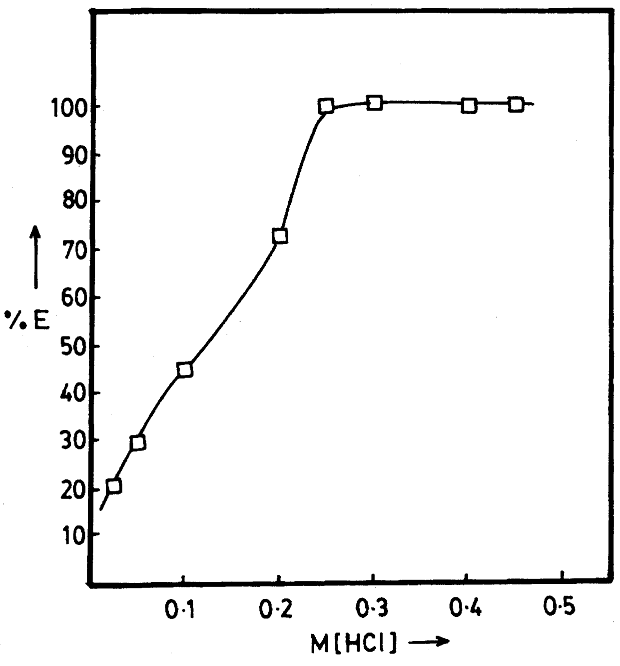

Fig. 1. Effect of concentration of hydrochloric acid on percentage extraction of Pt(II).

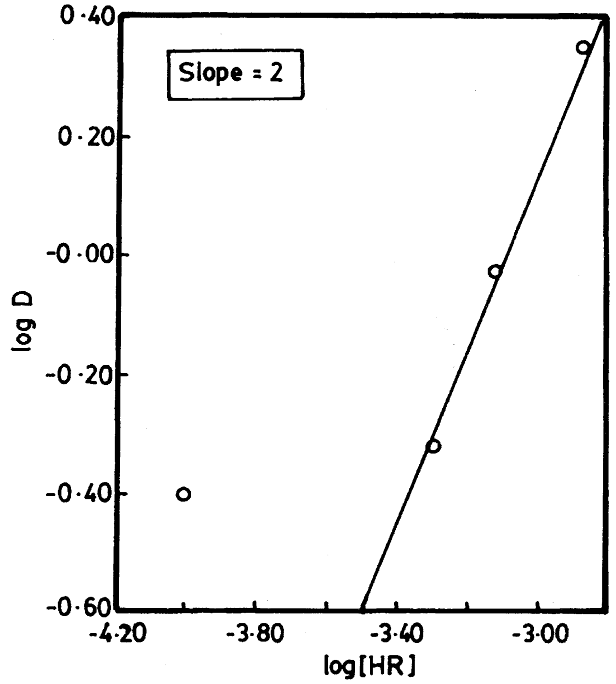

Fig. 2. Dependency of distribution ratio of platinium(II) on HDEHP concentration in toluene.

with 2.5×10^{-3} M of HDEHP. It was observed that, as the concentration of HDEHP decreases below 2.5×10^{-3} M, the % extraction of platinum also decreases.

Nature of the Extracted Species. The nature of the extracted species was ascertained by evaluating the distribution constant (D) while varying extractant concentration. The composition of the extracted species was obtained from the plot of $\log D$ vs. log [HDEHP] at a fixed mixture of 0.5 M HCl and 0.08 M $SnCl_2$ (Fig. 2). From the slope value of 1.87, the composition of the extractable species is supposed to be 1:2 or $Pt(DEHP)_2$.

Extraction with Various Diluents. Pt(II) was extracted with 2.5×10^{-3} M HDEHP in different solvents. The extraction was 100% with toluene and xylene. Both benzene and cyclohexane were found to give 99.7% extraction of Pt(II). Carbon tetrachloride (99.3%), chloroform (94.5%), dichloromethane (98.1%), and hexane (95.1%) do not favor quantitative extraction.

Effect of Temperature. Extraction of Pt(II) was performed at different temperatures using 2.5×10^{-3} M HDEHP in toluene. The concentration of HCl in the aqueous phase was maintained at 5×10^{-1} M. It was observed that the change in temperature over the range from 10 to 50 °C does not affect the percentage extraction of platinum(II).

Effect of Various Stripping Agents. Pt(II) was stripped with various mineral acids of varying molarities after extraction. It was quantitatively stripped with 4 M HCl and 4 M H_2SO_4 while with $HClO_4$ and HNO_3 its recovery was not complete. The solution of 4 M HCl was preferred, since absorbance measurements were carried out in hydrochloric acid media.

Extraction with Varying Metal Ion Concentration and Period of Shaking. Pt(II) was extracted with platinum concentrations ranging from 25—600 μg/10 ml. The extraction was quantitative from 50—500 μg/10 ml. The two immiscible phases were equilibrated for periods ranging from 1—20 min. 100% extraction was observed to take place up to 5 min of shaking, while for more than 5 min the percentage extraction of Pt(II) decreases.

Effect of Various Diverse Ions on Percentage Extraction of Pt(II). Pt(II) was extracted in the presence of a large number of elements. The tolerance limit was set as the amount of foreign ion causing interference of ±1% of extraction of Pt(II). Alkali and alkaline earth metals were tolerated up to the ratio of 1 : 25. Elements of the first transition series and Al^{3+}, Hg^{2+}, Pb^{2+}, Bi^{3+} were tolerated at the ratio of 1 : 10. (Table 1). Anions like chloride, iodide, bromide, nitrate, sulphite, citrate, and oxalate were tolerated up to 20 fold excess of platinum added, but nitrite, sulfate, and tartarate showed lower tolerance limits. Thiocyanate and thiourea were found to be strongly interferring.

Table 1. Effect of Diverse Ions on % Extraction of Pt(II)

Pt(II) : 100 μg, Concentration of HCl : 0.5 M

Tolerance limit (μg)					
1 : 25		1 : 20	1 : 10		1 : 1
Na^+	K^+	Cl^- Br^-	V^{5+}	Cr^{2+}	Ru^{3+}
Cs^+	Rb^+	I^- NO_3^-	Mn^{2+}	Fe^{3+}	
Ca^{2+}	Mg^{2+}	SO_3^{2-}	Co^{2+}	Ni^{2+}	
Sr^{2+}	Ba^{2+}	Citrate	Cu^{2+}	Zn^{2+}	
		Oxalate	Cd^{2+}	Al^{3+}	
			Pd^{2+}	Bi^{3+}	
			Hg^{2+}	Ag^+	

Table 2. Separation of Platinum from Binary Mixtures

Amount (μg)	pH	Extractant HDEHP (M)	Stripping agent	Chromogenic ligand	Avg. %R. 1:1	1:2	1:4
Pd(II)	8.2	0.05 in Toluene	—	α-Nitroso β-Naphthol	99.3	98.8	96.4
+							
Pt(IV)	8.2	0.05 in Toluene	Unextracted	$SnCl_2$	99.9	99.9	95.5
Au(III)	4.0	0.1 HDEHP +0.003 CTAB in $CHCl_3$	—	Direct Spectro-photometric	98.6	98.9	92.6
+							
Pt(IV)	4.0	0.1 HDEHP +0.003 CTAB in $CHCl_3$	Unextracted	$SnCl_2$	98.9	99.3	94.4
Os(VI)	1.5 M HCl	0.01 in Toluene	0.5 M HCl +thiourea	Thiourea	99.3	99.0	90.5
+							
Pt(IV)	1.5 M HCl	0.01 in Toluene	Unextracted	$SnCl_2$	98.9	99.0	94.1

Table 3. Sequential Separation of Palladium, Gold, and Platinum

Mixture	pH	Extractant	Stripping agent	%Recovery 1 : 1 : 1	1 : 4 : 2	1 : 4 : 4	1 : 6 : 2
Pd(II)	8.2	0.05 M HDEHP[a)]	—	99.0	99.2	99.2	98.9
Au(III)	2.5	0.1 M HDEHP+ 0.003 M CTAB[b)]	—	99.6	99.5	99.1	99.4
Pt(IV)	2.5	0.1 M HDEHP+ 0.003 M CTAB	Unextracted	99.3	99.3	99.0	99.2

a) Dissolved in toluene, b) Dissolved in chloroform.

Separation of Platinum from Binary and Ternary Mixtures. Various platinum metals showed different extents of extraction at different pH/acid concentrations and varying concentrations of HDEHP. In some cases, behaviors of metal–HDEHP complex towards various stripping agents were observed to be different. Such differences were fully exploited for the selective separation of Pt–Pd, Pt–Au, and Pt–Os. (Table 2).

Sequential separation of Pd, Au, and Pt was also carried out. It was possible to separate such mixtures in varying ratios of metals by utilizing the differences in their extraction conditions. Pd(II) was extracted at pH 8.2 with 5×10^{-2} M HDEHP in toluene, while Au(III) was extracted at pH 2.5 with mixture of 1×10^{-1} M HDEHP and 3×10^{-3} M hexadecyltrimethylammoniumbromide (CTAB), in chloroform. The non-extractability of Pt(IV) with HDEHP under the extraction conditions developed for Pd(II) and Au(III) was used for its separation (Table 3). The amount in ratios separated were 1 : 1 : 1, 1 : 4 : 2, 1 : 4 : 4, and 1 : 6 : 2. The amount of platinum separated was also determined by employing the proposed reduction–extraction technique. From the overall studies it was observed that the given sequence of extraction of metals was important for achieving quantitative separation, which otherwise results in poor separation.

The proposed method was extended to check the purity of commercially available platinum wire and to estimate the amount of platinum present in pharmaceutical samples (Table 4).

Table 4. Analysis of Real Samples

Sample	%Found	%Content	%RSD
Platinum electrode wire	99.8[a)]	99.9	0.8
Cisplatin injection	65.0[a)]	64.4 — 65.2 (USP method)	1.2
Cytoplatin injection	64.8[a)]	64.4 — 65.2 (USP method)	1.1

a) Average of three determinations.

Conclusion. The proposed method is simple, rapid, and selective for extraction and quantitative estimation of platinum in the presence of a large number of foreign ions. The method also permits clear cut separation of Pd, Au, and Pt. The values obtained for commercial sample analysis are in agreement with the reported values.

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References

1) C. H. R. Gentry and L. G. Sherrington, *Analyst*, **75**, 17

(1950).

2) J. T. Pyle and W. D. Jacobs, *Anal. Chem.*, **36**, 1796 (1964).

3) S. M. Khopkar, *Anal. Chem.*, **38**, 360 (1966).

4) M. Khattak and R. J. Magee, *Anal. Chim. Acta*, **35**, 17 (1966).

5) D. P. Shillington and B. K. Tait, *Solvent Extr. Ion Exch.*, **9**, 749 (1991).

6) F. E. Beamish and J. C. Van Loon, "Recent Advances in the Analytical Chemistry of Noble Metals," Pergamon Press, Oxford (1972), pp. 34—45.

7) K. Inoue, M. Koba, and K. Yoshizuka, *Solvent Extr. Ion Exch.*, **12**, 55 (1994).

8) G. Zuo and M. Muhammed, *Solvent Extr. Ion Exch.*, **13**, 879 (1995).

9) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry," Marcel Dekker Inc., New York and Basel (1977), pp. 604—605.

10) Y. Hasegawa, I. Kobayashi, and S. Yoshimoto, *Solvent Extr. Ion Exch.*, **9**, 759 (1991).

11) J. Fu, S. Nakamura, and K. Akiba, *Sep. Sci. Technol.*, **30**, 609 (1995).

12) T. Nishiki and R. G. Bautista, *AIChE. J.*, **31**, 2093 (1985).

13) A. I. Bulavchenko, E. K. Batischeheva, and V. G. Torgov, *Sep. Sci. Technol.*, **30**, 239 (1995).

14) M. M. Kulkarni and R. M. Sathe, *Indian J. Chem.*, **4**, 258 (1996).

15) K. Inoue, I. Nagamatsu, Y. Baba, and K. Yoshizuka, *Solvent Extr. Ion Exch.*, **7**, 1111 (1989).

16) Y. Surakitbanharn, S. Murlidharan, and H. Freiser, *Solvent Extr. Ion Exch.*, **9**, 45 (1991).

17) H. Bode and W. Arnswald, *Z. Anal. Chem.*, **185**, 99 (1962).

18) B. Cote and G. P. Demopoulus, *Solvent Extr. Ion Exch.*, **12**, 517 (1994).

19) K. Kimura, *Bull. Chem. Soc. Jpn.*, **33**, 1038 (1960).

20) A. Meyers and G. Ayres, *J. Am. Chem. Soc.*, **77**, 2671 (1955).

21) A. I. Vogel, "A Text-Book of Quantitative Inorganic Analysis," 3rd ed, Longman, London (1961), pp. 510—511.