

Selective Separation of Platinum in the Propyl-alcohol-Sodium Sulfate Two-phase Aqueous Extraction System

YUNTAO GAO[†], XIAOHAI LIU^{*}, YE TAO[‡], JIAQIANG WANG[§],
WEI WANG[§], LISHANG WU[§] and XIUEMEI WANG
*Yunnan Institute of Environmental Science, No.23 Wang Jiaba,
Qixiang Road, Kunming 650034, People's Republic of China
Fax: (86)(871)4150483; Tel: (86)(871)4171932
E-mail: lxx@yies.org.cn*

The extraction separation and phase distribution behaviours of iodide complexes of platinum(IV) in propyl-alcohol-sodium sulfate two-phase aqueous extraction system have been investigated. The amount of Na₂SO₄ added, the initial volume of propyl alcohol and the acidity of the system are mainly factors affecting the formation and phase separation of the aqueous two-phase system. Platinum(IV) is found to be extracted into the propyl alcohol phase due to ion pair formation of platinum(IV) as [Pt I₆²⁻·2(PrOH₂⁺)₂] in the presence of KI and HCl medium. The experimental results indicate that platinum can be quantitatively and highly selectively extracted by the optimized method, using which > 99.0 % extraction efficiency can be achieved. The proposed method has been successfully applied to the selective separation of platinum from samples containing large amount of base metals including Fe²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Al³⁺, Pb²⁺ and Zn²⁺ in synthetic sample and exhibits high selectivity to platinum.

Key Words: Aqueous biphasic extraction system, Aqueous two-phase extraction, Platinum, Propyl alcohol, Potassium iodide, Sodium sulfate.

INTRODUCTION

Among its numerous applications, platinum finds extensive use as catalyst, in electronic devices, in aeronautical instruments and increasingly in manufacture of auto exhaust catalysts. The high cost and increasing demand for platinum have stimulated investigations for novel procedures allowing its separation and purification from low-grade ores and spent catalysts. Since platinum occurring in practical samples is usually contaminated by large amount of base metals, its separation and

[†]School of Chemistry and Bio-Science, Yunnan Nationalities University, Kunming 650031, People's Republic of China; E-mail: yuntaogao@kohnu.com

[‡]Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge MA, 02138, USA.

[§]School of Chemistry and Material Science, Yunnan University, Kunming 650031, People's Republic of China.

purification are difficult¹. Therefore, the development of a more efficient, more selective and greener separation methodology is highly desirable. Existing procedures, such as solvent extraction, ion exchange, etc, described in the literature do not meet all of these criteria².

Aqueous biphasic systems or aqueous two-phase systems have been used to separate and purify biomolecules^{3,4} and can also serve as an extraction technology for metal ions⁵⁻⁸. In contrast to conventional organic solvent extraction systems, aqueous biphasic systems hold many advantages. They are environmental friendly due to the elimination of volatile and toxic organic solvents, easier and safer to operate and the lack of emulsification leads to clearer phase boundary and faster separation. Normally, aqueous biphasic systems consist of water, water-soluble polymers or two dissimilar water-soluble polymers and certain inorganic salts. However, most of phase forming polymers have high viscosity and may form an opaque solution. The viscosity and opaqueness make the subsequent operations and analysis difficult, limiting its potential for further application.

An alternative consisting of a mixture of water and small-molecule water-soluble alcohol, such as propyl-alcohol, can also form aqueous biphasic extraction system upon the addition of inorganic salts⁸⁻¹⁰. Compared to high-viscosity polymers, the subsequent manipulation of this new aqueous biphasic systems is greatly simplified. For example, direct determination of materials in the extracted phase can be achieved by ICP, HPLC, *etc.* and further purification of extracted materials also becomes very easy. The application of this improvement to aqueous biphasic systems extraction studies on platinum group metals is only in its incipient stage^{10,11}.

The present work presents an optimized aqueous biphasic systems for platinum(IV) based on propyl-alcohol, water, sodium sulfate and potassium iodide. Extraction separation and phase distribution behaviours of iodide complex of platinum(IV) are described. The formation and phase separation of the aqueous two-phase extraction system in HCl media are also discussed. The optimized system has been applied to the selective separation of platinum in a synthetic sample.

EXPERIMENTAL

Platinum(IV) stock solution (1.00 g/L) was prepared by dissolving analytical reagent grade PtCl₆, provided by Kunming Institute of Precious Metals, in 3.0 M hydrochloric acid and diluting with 0.60 M hydrochloric acid to give a working solution (0.10 g/L). Standard solutions of Mn(II), Fe(III), Pb(II), Al(III), Cu(II), Ca(II) and Mg(II) were prepared by appropriate dilution of commercially available 1.00 mg/mL atomic absorption spectrometric solutions. Zn(II) stock solution (2.0 g/L) was prepared by dissolving 0.501 g of high-purity zinc (99.998 %) in 10. mL of concentrated hydrochloric acid and diluting the solution to 250.0 mL with water. Hydrochloric acid solution (6.0 M), potassium iodide solution (1.0 M) and sodium sulfate were used. The water used was deionized by distillation and all chemicals used were of analytical reagent grade.

A Perkin-Elmer 983 spectrophotometer, with a 1 cm glass cell, was employed for absorbance measurements. An ICPQ-1012 inductively-coupled plasma-atomic emission spectrometry was used for the determination of metal ions used in synthetic sample.

Procedure: To obtain the aqueous biphasic extraction system, 1.0 mL of platinum(IV) working solution, 2.0 mL of 6 M HCl and 2 mL of 1.0 M KI were added to a 50.0 mL graduated tube. The mixture was diluted to 20.0 mL with water and left to stand for 10 min. After the addition of 8.0 mL of propyl alcohol and 8.0 g of Na_2SO_4 , the mixture was shaken for 1 min and allowed to stand until it thoroughly separated into two phases. The volumes of two phases were recorded by reading from the graduation on the tube and these values were used later to calculate the distribution ratio of platinum(IV) in propyl alcohol phase. The concentration of platinum(IV) in the upper propyl alcohol phase and the bottom salt-water phase was determined by N,N-didodecylthio-bioxamide (DDBO) absorption spectrophotometry¹². The metal ions in the synthetic sample were determined by the method of inductively coupled plasma-atomic emission spectrometry(ICP-AES). The distribution ratio (D) and extraction percentage (E %) were calculated.

RESULTS AND DISCUSSION

Phase separation behaviours of the system: One measure of the effectiveness of an extraction solvent is the volume required for clean phase separation. Smaller volumes are clearly advantageous. For this reason, Na_2SO_4 was adopted for its strong salting-out effect on PrOH/ H_2O mixtures. Fig. 1 illustrates the relationship between the amounts Na_2SO_4 needed to barely induce phase separation for given amounts of PrOH and water. The same trend was observed for three concentrations of HCl in the aqueous phase. For a given volume of aqueous phase, the larger the added volume of PrOH, the smaller the amount of Na_2SO_4 was needed.

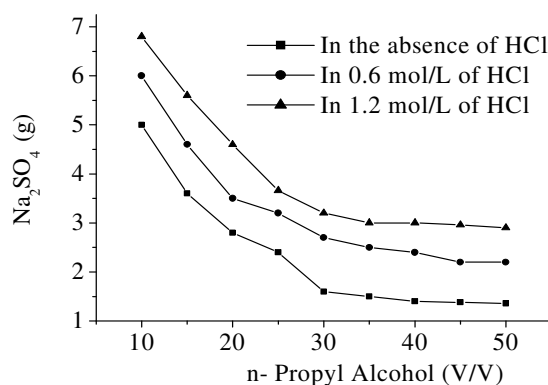


Fig. 1. Relationship between the amounts of PrOH and salts just as the system separates into two phases

Phase separation can be partial or complete, with the latter scenario being desirable. The effect of the amount of Na_2SO_4 on the extent of phase separation in different HCl media is shown in Fig. 2. ΔV represents the difference between the volumes of the PrOH phase after phase separation and before mixing. The initial volume of added PrOH is designated as V_{in} and the volume of the organic phase after the phase separation, V_{end} , *i.e.*, $\Delta V = V_{\text{end}} - V_{\text{in}}$. $\Delta V < 0$, as observed when phase separation barely occurs, indicates that PrOH remained partially mixed in the heavier aqueous phase. Initial increase of the amount of Na_2SO_4 led to an increase in V_{end} , eventually resulting in $\Delta V > 0$. Increasing the concentration of Na_2SO_4 further caused ΔV to reach a maximum, suggesting not only that almost all the PrOH was separated from the bottom phase, but some water also mixed into the upper organic phase. Finally, increasing the amount of Na_2SO_4 beyond the maximum ΔV point, caused it to decrease and asymptotically approach 0, suggesting that in this regime the phase separation between PrOH and water can be considered.

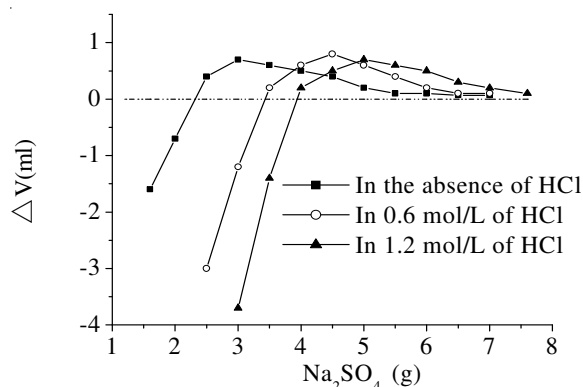


Fig. 2. Effect of Na_2SO_4 amount on phase separation (20 mL water, 8 mL PrOH)

Together, data in Figs. 1 and 2 indicate that more Na_2SO_4 should be added for phase separation in more acidic aqueous solutions. The reason may be that the protonation of SO_4^{2-} decreases the ionic strength of the mixture and hence the salting out effect. In conclusion, the phase separation behaviours of the PrOH sodium sulfate aqueous two-phase system mainly depends on the amount of Na_2SO_4 added, the initial volume of PrOH and the acidity of the system. For a system comprised of 20.0 mL water, 8.0 mL PrOH and 0.6 M of HCl, 3.1 g of Na_2SO_4 was required to induce phase separation and 6.5 g for thorough phase separation. In the absence of HCl and in the more acidic 1.2 M HCl media, 5.5 g and 8.1 g of the salt was required for thorough separation, respectively.

Extraction separation and distribution behaviour of platinum(IV): To optimize the extraction conditions, parameters including the length of mixing time by shaking and the effects of the concentrations of Na_2SO_4 , HCl and KI on the percentage extraction of platinum(IV) were studied.

A mixing/shaking period of 30 s was found to be sufficient for quantitative extraction, indicating that the equilibria relevant to the extraction process are fast. Extending the shaking period up to 2 min had no adverse effect on the efficiency of extraction.

Platinum occurring in practical samples is usually associated with large amounts of base metals, such as Cu, Fe, Zn, Pb, Ca, Mg, Al, *etc.* Therefore, aside from the percentage extraction efficiency for the desired metal ion, the selectivity of the separation method is another important gauging parameter. Fig. 4 illustrates the effect of the concentration of KI on the extraction percentage of platinum(IV) and several base metals ions. Platinum(IV) can be quantitatively extracted for concentrations of KI above 0.08 M and the base metals, with the exception of Cu(II), were present in negligible concentrations in the organic phase. It was apparent that platinum(IV) and Cu(II) were not separated from each other (Fig. 3).

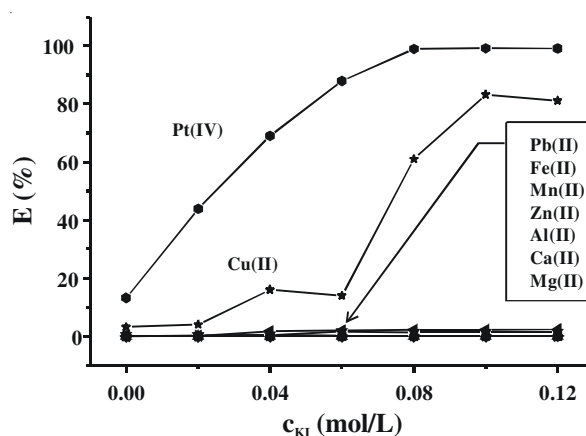


Fig. 3. Effect of KI concentration on extraction

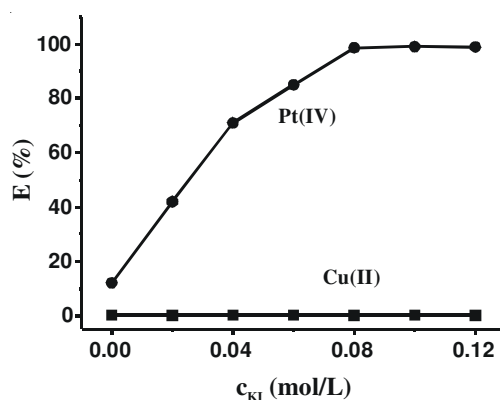


Fig. 4. Effect of KI concentration on extraction in the PrOH-rich phase filtrated

It was observed during the phase separation process that a red precipitate formed and mixed into the upper organic phase. We hypothesized that the precipitate was CuI, formed by the reduction of Cu(II) in the presence of excess iodide. To test this hypothesis, the organic phase was filtered through a G4 glass sand funnel to remove the precipitate and the filtrate was analyzed to determine its platinum and copper contents. When mixtures of 1.0 mg Cu(II) and 0.05 mg platinum(IV) were subjected to both extraction and the additional filtration steps, completely selective isolation of platinum was achieved (Fig. 4). The data show that 0.08 M KI copper is scarcely extracted into upper phase as a homogeneous species, whereas platinum(IV) was quantitatively extracted (> 99.0 %).

The optimized method was applied to the separation of platinum(IV) from a synthetic sample containing platinum(IV) and large amounts of base metals [Fe(III), Pb(II), Mn(II), Al(III), Ca(II), Mg(II), Cu(II) and Zn(II)]. The sample solution was prepared in 0.6 M of HCl and the separation was carried out under optimized extraction conditions. The separation result was determined by ICP-AES and listed in Table-1. Base metals were hardly extracted, whereas the percentage extraction of platinum(IV) was 99.1 %. The proposed aqueous two-phase separation method exhibits high selectivity and can be used to separate platinum from large amount of base metals.

TABLE-1
SEPARATION RESULT OF THE SYNTHETIC SAMPLE

Ions	Added (mg)	Found in propyl alcohol-rich phase* (mg)	Extraction (%)
Pt(IV)	0.05	0.0496	99.1
Fe(III)	1.00	0.0023	2.3
Pb(II)	1.00	0.0013	1.3
Al(III)	1.00	0.0000	0.0
Cu(II)	500.00	0.0000	0.0
Zn(II)	1.00	0.0014	1.4
Ca(II)	1.00	0.0000	0.0
Mg(II)	1.00	0.0000	0.0
Mn(II)	1.00	0.0000	0.0

*ICP-AES determination.

It was found that the extraction behaviours of platinum(IV) in the two-phase aqueous system in the presence and in the absence of KI were quite different, as shown in Fig. 5. Much lower percentage extraction of platinum(IV) was observed in the absence of KI. It is proposed the iodide complex of platinum(IV) has much higher stability and propanol-solubility than that of base metals ions.

Platinum(IV) is known to form stable complexes with I^- . Complexes with the general formula $PtI_m^{(m-4)-}$ have large stability constants^{13,14}. Therefore, $PtI_m^{(m-4)-}$ formed in the presence of platinum(IV) and KI can be extraction into propanol. In comparison, the iodide complexes of base metal ions have small stability constants¹³. This difference imparts the selectivity to present extraction system.

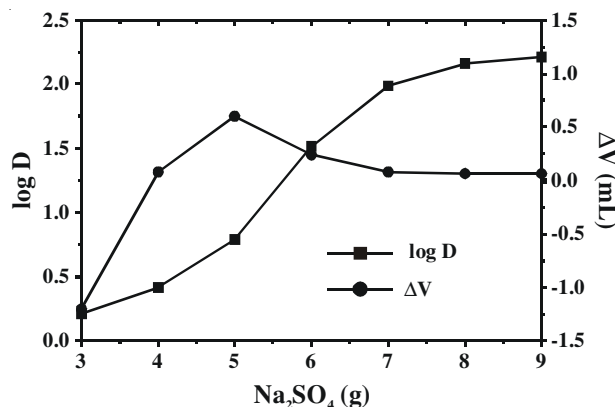
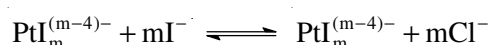
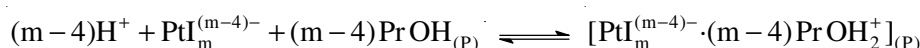


Fig. 5. Effect of Na₂SO₄ amount on distribution ratio of Pt(IV) and variation of upper phase volume (ΔV) (20 mL water, 8 mL PrOH, 0.6 mol/L of HCl and 0.1 mol/L of KI)

The formation of $\text{PtI}_m^{(m-4)-}$ can be expressed as follows:



In addition, PrOH is proton-dissociable and easily forms the PrOH_2^+ cation in acidic media. These cations can associate with the $\text{PtI}_m^{(m-4)-}$ anion to form neutral ion pair complexes $[\text{PtI}_m^{(m-4)-} \cdot (m-4)\text{PrOH}_2^+]$. Such complexes are more hydrophobic and can be extracted into the PrOH phase. If higher-order ($m > 4$) iodide complexes are dominant, this mechanism implies that higher acidity is favourable for the extraction due to increased $[\text{PrOH}_2^+]$. Therefore, it is reasonable to assume that the extraction mechanism of platinum(IV) in the two phase aqueous is based on the ion pair complex formation^{1,14,15}, expressed as follows:



$$K_{\text{ex}} = \frac{[\text{PtI}_m^{(m-4)-} \cdot (m-4)\text{PrOH}_2^+]_{(P)}}{[\text{PtI}_m^{(m-4)-}] [\text{PrOH}_2^+]^{m-4} [\text{H}^+]^{m-4}} \quad (1)$$

Let

$$D = \frac{[\text{PtI}_m^{(m-4)-} \cdot (m-4)\text{PrOH}_2^+]_{(P)}}{[\text{PtI}_m^{(m-4)-}]} = K_{\text{ex}} [\text{PrOH}_2^+]^{m-4} [\text{H}^+]^{(m-4)} \quad (2)$$

Then

$$\log D = \log K_{\text{ex}} + (m-4) \log [\text{H}^+] + (m-4) \log [\text{PrOH}]_{(P)} \quad (3)$$

where K_{ex} is the extraction equilibrium constant and D is the distribution ratio of platinum(IV). $[\text{PrOH}]_{(P)}$ represents the concentration of PrOH in PrOH-rich phase. The subscript 'P' denotes PrOH-rich phase, whereas species in the salt-rich (bottom) phase are given without subscript.

To test the validity of the proposed model of the platinum extraction mechanism, we investigated the dependence of D on $[\text{PrOH}]_{(P)}$ and on $[\text{H}^+]$. Fig. 5 shows the dependence of $\log D$ and ΔV on the amount of added Na_2SO_4 . ΔV is the same parameter as that in Fig. 2 and provides an indirect measure of $[\text{PrOH}]_{(P)}$ (*vide supra*). As the degree of phase separation between PrOH and water increases, the solvent purity of each phase increases, *i.e.*, $[\text{PrOH}]_{(P)}$ increases in the propanol-rich phase. Since logarithm is a monotonically increasing function, an increase in $[\text{PrOH}]_{(P)}$ should, according to eqn. 3, lead to an increase in D . Indeed, the experimental result that the value of $\log D$ is positively correlated to the increase in phase separation efficiency due to the salting out effect of Na_2SO_4 supports the model of extraction presented above. Moreover, as thorough phase separation was achieved upon the addition *ca.* 8 g of Na_2SO_4 , the value of $\log D$ also asymptotically approaches its maximum.

The effect of $[\text{H}^+]$ on D was also investigated. For the experiment to be quantitative, the other parameter of eqn. 3, $[\text{PrOH}]_{(P)}$ must be kept constant through proper setup. Therefore, excess Na_2SO_4 was used in this set of experiments to keep phase separation thorough. In this regime, $\log [\text{PrOH}]_{(P)}$ in eqn. 3 can be considered constant, so that a plot of $\log D$ versus $\log [\text{H}^+]$ should yield a straight line with a slope of $(m-4)$. The experimental result presented in Fig. 6 is in agreement with the prediction of the model. The slope of the line of best fit through the data points was 1.88 ($R = 0.99885$, $SD = 0.02956$), near 2.0. This result lends additional support for the proposed model of extraction and suggests that platinum(IV) occurs in the PrOH phase predominantly as the neutral ion pair complex $[\text{PtI}_6^{2-} \cdot 2\text{PrOH}_2^+]$.

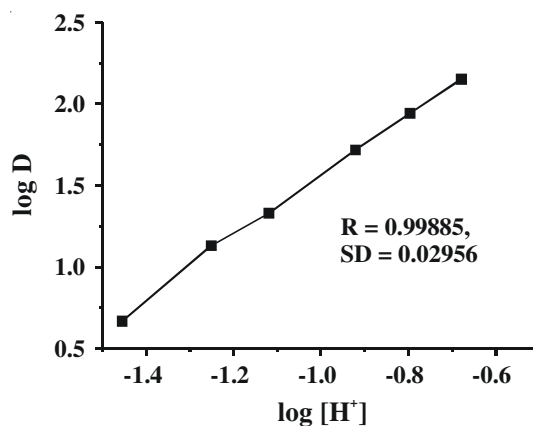


Fig. 6. $\log D$ versus $\log [\text{H}^+]$

Conclusion

The experimental results presented indicate that the initial volume of PrOH , concentration of Na_2SO_4 and the acidity of the system are the main factors that affect the formation and phase separation of the aqueous biphasic system. In the

presence of KI and HCl, ion pair formation between the iodide complex PtI_6^{2-} and PrOH_2^+ appears to be a major pathway leading to the extraction of platinum(IV) in the propyl-alcohol sodium sulfate aqueous biphasic extraction system. Increased acidity and better phase separation using excess Na_2SO_4 are two basic strategies to favour the efficiency of extraction.

Results obtained in this work also show that the proposed method is greener, easier to implement using readily available materials and faster than conventional methods. Most importantly, it exhibits high selectivity for platinum and can be effectively used to separate platinum from samples containing large amounts of base metal contaminants.

REFERENCES

1. D.H. Logsdail and M. Slater, *J. Solvent. Extr. Process. Ind.* Vol. 3. Elsevier: Oxford (1993).
2. S.J. Al-Bazi and A. Chow, *Talanta*, **31**, 815 (1984).
3. T.I. Zvarova, V.M. Shkinev, G.A. Vorobeva, B.Ya. Spivokov and Yu.A. Zolotov, *Mikrochim. Acta, Part III*, 449 (1984).
4. P.A. Aguinaga-Diaz and R.Z. Guzman, *Sep. Sci. Technol.*, **31**, 1483 (1996).
5. R.D. Rogers and J.H. Zhang, *Solvent Extr. Ion. Exch.*, **13**, 141 (1997).
6. R.D. Rogers, A.H. Bondl, C.B. Bauer, J.H. Zhang and S.T. Griffin, *J. Chromatogr. B*, **680**, 221 (1996).
7. A. Yoshifumi, I. Mario and T. Shigeyuki, *Talanta*, **53**, 645 (2000).
8. Z.H. Wang, Y. Zeng, M.H. Ma and C.L. Shu, *J. Microchem.*, **60**, 143 (1998).
9. X.H. Liu, Y.T. Gao, R.S. Tang and W. Wang, *Sep. Purif. Tech.*, **50**, 263 (2006).
10. Y.T. Gao and W. Wang, *Chin. J. Appl. Chem.*, **19**, 578 (2002) (in Chinese).
11. Y.T. Gao, L.S. Wu and W. Wang, *Chin. J. Anal. Chem.*, **29**, 901 (2001) (in Chinese).
12. S.X. Cai and C. Huang, *Analysis of Noble Metals*, Metallurgical Industry Press: Beijing (1984) (in Chinese).
13. E. Hogfeldt, *Stability Constants of Metal-Ion Complexes, Inorganic Ligands*, Pergamon Press: Oxford, New York, edn. 1, Part-A (1982).
14. M. Mojski, *Talanta*, **25**, 163 (1978).
15. S. Masami, N. Noriko, H. Tadashige, S. Daigo, E. Yukihiro and K. Satoshi, *Anal. Chim. Acta*, **427**, 293 (2001).

(Received: 4 February 2009;

Accepted: 11 September 2009)

AJC-7861