



## Extraction Separation of Gold in *n*-Propyl Alcohol-Ammonium Sulfate Aqueous Two-Phase System

PENGZHI XIANG<sup>1,2,\*</sup> and YUNTAO GAO<sup>3</sup>

<sup>1</sup>Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, P.R. China

<sup>2</sup>School of Chemical Engineering, Yunnan Radio & TV University, No. 113 Xuefu Road, Kunming 650222, P.R. China

<sup>3</sup>School of Chemistry and Biotechnology, Yunnan Nationalities University, Kunming 650031, P.R. China

\*Corresponding author: E-mail: xpz20022002@yahoo.com.cn

(Received: 26 November 2011;

Accepted: 14 September 2012)

AJC-12146

The extraction behaviours of gold(III) in the *n*-propyl alcohol (PrOH)-ammonium sulfate aqueous two-phase extraction system were investigated. The amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> added, the initial volume of *n*-propyl alcohol and the acidity of the system are mainly factors that affect the formation and phase separation of the aqueous two-phase system. Gold(III) is found to be extracted into the *n*-propyl alcohol phase due to the formation of ion pair complex of [Au I<sub>4</sub><sup>-</sup>PrOH<sub>2</sub><sup>+</sup>] in the presence of KI and in hydrochloric acid medium, an extraction rate of 99 % for gold can be achieved under optimized conditions. The proposed method has been applied to the separation of gold from large amount of base metals in synthetic sample and exhibits selectivity to gold(III).

**Key Words:** Extraction, Separation, Gold, *n*-Propyl alcohol, Ammonium sulfate.

### INTRODUCTION

Aqueous two-phase system (ATPS) is one of the promising separation methods that has potential application in the extraction separation and purification of bimolecular<sup>1,3</sup> and has also serves as an extraction technology for metals<sup>4,8</sup>. In general, aqueous two-phase system can be formed by combing two incompatible polymers in water, or one polymer and an inorganic salt<sup>2-9</sup>. An aqueous surfactant two-phase system was also observed with the mixture of cation/anionic surfactant and inorganic salt<sup>10</sup>. Recently, the aqueous ionic liquid two-phase system, consisting of ionic liquid and organic salt is gaining attention for its potential usage as green solvents<sup>11,12</sup>. However, most of phase forming polymers have high viscosity and may form an opaque solution, the subsequent processes are very difficult and the further application of ionic liquid as a separation system is limited due to its instability and much high price.

It has been recently introduced that a mixture of small molecular water-soluble alcohol, such as *n*-propyl alcohol and water can also form aqueous two-phase extraction system by adding inorganic salts<sup>13-15</sup>. Without using high viscosity polymers to form two phases, the subsequent processes of this new aqueous two-phase extraction system can be simplified, for example, direct determination of materials in the extracted phase can be achieved by ICP-AES, HPLC, etc. and the further

purification of extracted materials also become very easy. However, the extraction studies on noble metals with this new aqueous two-phase extraction system<sup>16</sup> were still limited.

The present work was concerned in extraction separation and distribution behaviours of iodide complex of gold(III) in the *n*-propyl alcohol (PrOH)-ammonium sulfate aqueous two-phase extraction system, the formation and phase separation of the aqueous two-phase extraction system in hydrochloric acid medium was also discussed. The method described has also been applied to the separation of gold in the synthetic sample.

### EXPERIMENTAL

Stock solution (1 g/L) of gold(III) was prepared by dissolving analytical reagent grade K<sub>2</sub>AuCl<sub>6</sub>, provided by Kunming Institute of Precious Metals, in 3 mol/L hydrochloric acid, which was diluted with 0.6 mol/L 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 g/L atomic absorption spectrometric solutions respectively. Zn(II) stock solution (2 g/L) was prepared by dissolving 0.501 g of high purity zinc (99.998 %) in 10 mL of concentrated hydrochloric acid and diluted the solution to 250 mL with water. Hydrochloric acid solution (6 mol/L); potassium iodide solution (1 mol/L); ammonium sulfate.

The water used was deionized distilled water and all chemicals used were of analytical reagent grade.

A Hitachi Z-8000 Zeeman flame atomic absorption spectrophotometer was employed for the determination of gold, an ICPQ-1012 inductively coupled plasma-atomic emission spectrometry was used for the determination of metal ions in synthetic sample and spent catalyst samples.

**Procedure:** To obtain aqueous two-phase extraction system, 1 mL of gold(III) working solution, 2 mL of 6 mol/L HCl and 2 mL of 1 mol/L of KI were added to a 50 mL graduated tube. The mixture was diluted to 20 mL with water and left to stand for 5 min to convert gold(III) into iodide-type complex. After addition of 8.0 mL of PrOH and 8 g of  $(\text{NH}_4)_2\text{SO}_4$ , the mixture was shaken for 30 s and then allowed to stand until the mixture was thoroughly separated into two phases. The concentration of gold(III) in upper phase and bottom phase was determined by flame atomic absorption spectrometry (FAAS)<sup>17</sup>. For the separation of the synthetic sample consisted of Au(III) accompanied amount of base metal ions, the upper phase separated is filtrated by a G4 glass sand funnel to remove precipitate of CuI and then washed by a 10 mL aqueous solution containing 0.6 mol/L of HCl, 0.1 mol/L of KI and 3.5 g of  $(\text{NH}_4)_2\text{SO}_4$ . The metal ions that were extracted into upper phase were determined by the method of inductively coupled plasma-atomic emission spectrometry (ICP-AES). The extraction percentage (E %) was calculated.

## RESULTS AND DISCUSSION

**Formation of aqueous two-phase system:**  $(\text{NH}_4)_2\text{SO}_4$  is easy to salt out and has lower temperature coefficient, low price and no side-effect<sup>2,9,18</sup>, so it was considered as the salting out reagent in this study. The experimental results showed that  $(\text{NH}_4)_2\text{SO}_4$  can make the solution separate into two phases, the formation and separation of the *n*-propyl alcohol-ammonium sulfate aqueous two-phase system depends on the amount of  $(\text{NH}_4)_2\text{SO}_4$  added. The effect of the amount of  $(\text{NH}_4)_2\text{SO}_4$  added on the volume variation of upper phase and bottom phase was showed in Fig. 1, where the upper phase volume and the bottom phase volume was designated as  $V_{\text{upper}}$  and  $V_{\text{bottom}}$ , respectively. With more addition of  $(\text{NH}_4)_2\text{SO}_4$ , the upper phase volume increased significantly, on the contrary, the obvious decrease of bottom phase volume could be observed, indicating that PrOH was separated from bottom phase as the result of the hydration of salt. And then,  $V_{\text{bottom}}$  sloped downward to the bottom, whereas,  $V_{\text{upper}}$  attained the top, it is larger than the initial volume of PrOH, this means that almost all of PrOH was separated from bottom phase, but a little water also run into upper phase. After that, water in the upper phase was separated due to the increasing of salting-out effect of  $(\text{NH}_4)_2\text{SO}_4$ , which resulted in the decrease of  $V_{\text{upper}}$  and the increase of  $V_{\text{bottom}}$ . As 6.5 g of  $(\text{NH}_4)_2\text{SO}_4$  was added,  $V_{\text{upper}}$  tended to the initial volume of PrOH, where  $V_{\text{bottom}}$  closed to that of water, the thorough phase separation between PrOH and water was achieved.

Fig. 2 illustrated the relationship between the initial volume of PrOH and the amount of  $(\text{NH}_4)_2\text{SO}_4$  added just as thorough phase separation between PrOH and water. It could be seen that with different initial volumes of PrOH, the amount of  $(\text{NH}_4)_2\text{SO}_4$  needed is different. The larger the initial volume

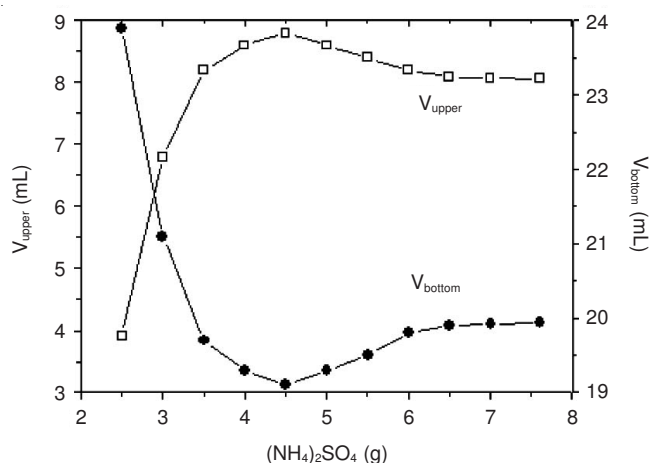


Fig. 1. Effect of the amount of  $(\text{NH}_4)_2\text{SO}_4$  on the volume variation. In 0.6 mol/L HCl, the initial volume: 8 mL for PrOH, 20 mL for water

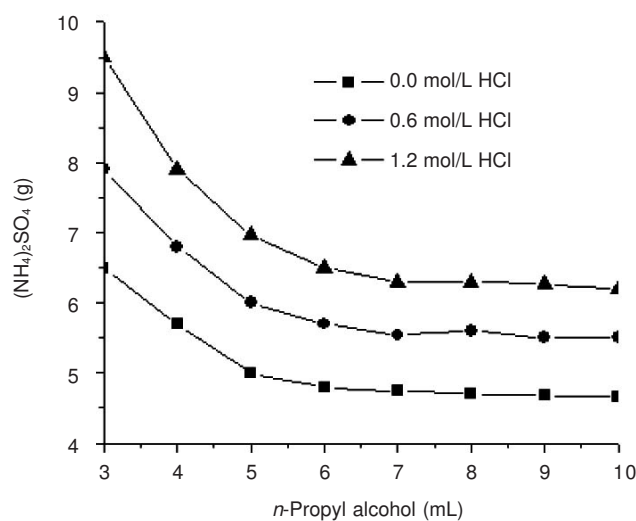


Fig. 2. Relationship between the initial volume of PrOH and the amount of  $(\text{NH}_4)_2\text{SO}_4$  just as thorough phase separation

of PrOH was, the smaller the amount of  $(\text{NH}_4)_2\text{SO}_4$  needed was. In addition, if the acidity of the system was high, more  $(\text{NH}_4)_2\text{SO}_4$  should be added for thorough phase separation, the reason could be ascribed to that the protonation of  $(\text{NH}_4)_2\text{SO}_4$  and PrOH in HCl medium decreased the salting out effect. The amount of  $(\text{NH}_4)_2\text{SO}_4$  required for phase thorough separation was above 5.2 g in the absence of HCl, 6.5 g for 0.6 mol/L HCl medium, 8.1 g for 1.2 mol/L HCl medium, respectively.

**Extraction behaviours of gold(III):** In order to optimize the extraction conditions, the shaking period and the amount of  $(\text{NH}_4)_2\text{SO}_4$  added, the concentration of HCl and KI in the solution on the extraction percentage of gold(III) were investigated. When the shaking period was taken to be 10 s, 20 s, 30 s and 1 min, the corresponding extraction percentages were 94.1, 99.1, 99.2 and 99.2 %, respectively, indicating that the process of extraction was very fast. So 20 s was adequate for quantitative extraction.

The effect of the amount of  $(\text{NH}_4)_2\text{SO}_4$  added on the extraction percentage of gold(III) was illustrated in Fig. 3. The extraction percentage of gold(III) increased with the addition

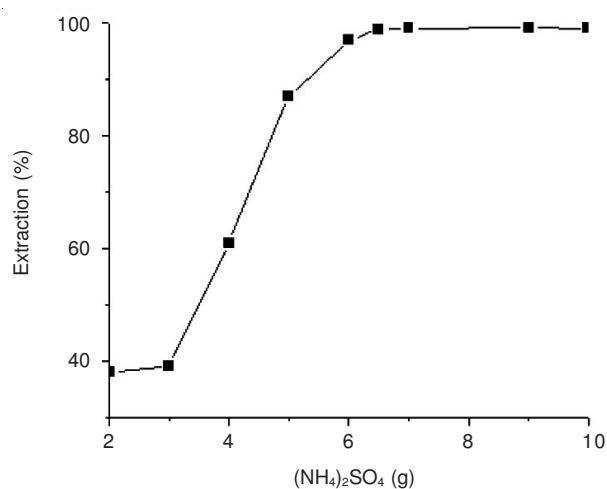


Fig. 3. Effect of the amount of Na<sub>2</sub>SO<sub>4</sub> on extraction percentage. The initial composition was 20 mL water and 8 mL PrOH, 0.6 mol/L of HCl, 0.1 mol/L of KI

of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> required for quantitative extraction of gold(III) was above 6.5 g in the system, in agreement with the amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> added required for thorough phase separation as shown in Fig. 1.

Fig. 4 showed the effect of HCl concentration on the extraction of gold(III). With increase HCl concentration, the extraction percentage of gold(III) increased significantly, when the concentration of HCl was above 0.4 mol/L, the quantitative extraction of gold(III) could be achieved, indicating that increasing of acidity would benefit the extraction. However, if the acidity was too high, the aqueous two-phase system would become unstable, the amount of salting out reagent, therefore, must be increased in order to separate the system into two phases.

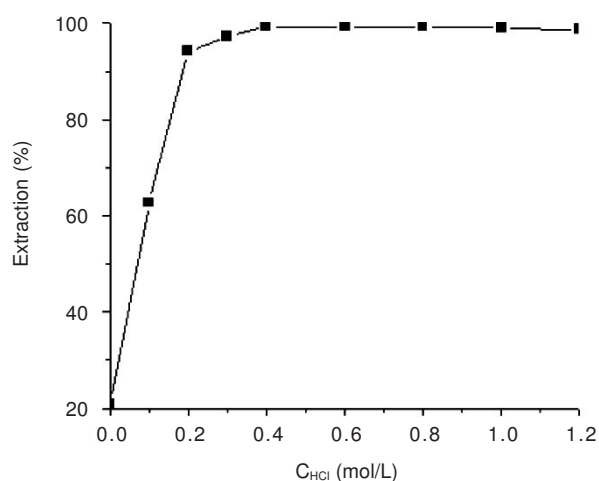


Fig. 4. Effect of the amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> added on extraction percentage. The initial composition was 20 mL water and 8 mL PrOH, 7.0 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1 mol/L of KI

The effect of the potassium iodide concentration on extraction percentage of gold(III) was illustrated in Fig. 5. In absence of KI, only 13.1 % of gold(III) was extracted into the upper phase. The extraction percentage of gold(III) increases obviously with the addition of KI, reaches its maximum at

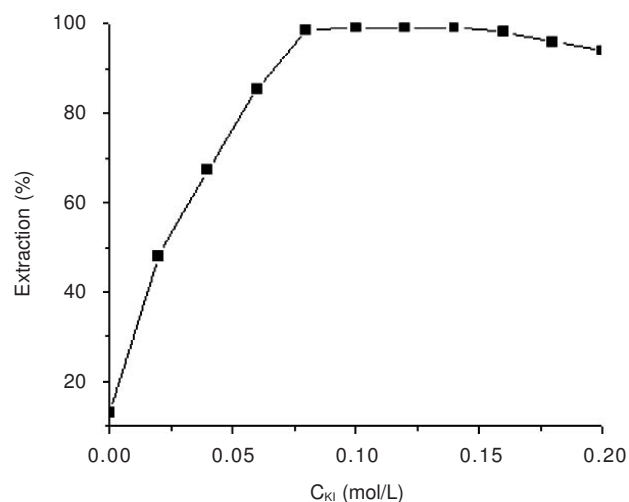
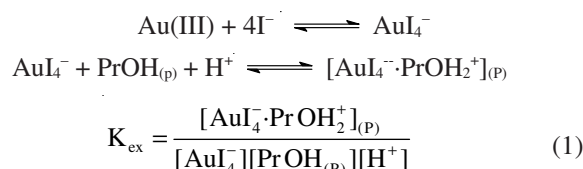


Fig. 5. Effect of the concentration of KI on extraction percentage. The initial composition was 20 mL water and 8 mL PrOH, 0.6 mol/L of HCl, 7 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

0.070 mol/L KI for 0.05 mg of gold(III) and remains constant in the concentration range of 0.070-0.15 mol/L. But the extraction percentage of gold(III) decreased slightly in higher concentration of KI.

To extract gold(III) quantitatively, for the initial composition of 20 mL water and 8 mL of PrOH, 30 s of shaking period, 7 g of Na<sub>2</sub>SO<sub>4</sub> added, 0.6 mol/L of HCl and 0.1 mol/L of KI were considered as the optimal extraction conditions, under such conditions, an extraction percentage of 99.2 % for gold(III) was obtained.

The extraction behaviours of gold(III) in the aqueous two-phase system in presence of KI were much different from that in absence of KI as Fig. 5 shown, indicating that the dominant form of gold(III) is the anion complex of AuI<sub>4</sub><sup>-</sup> in the presence of KI, which can be ascribed by the large stability constant<sup>19,20</sup> of AuI<sub>4</sub><sup>-</sup>, where PrOH is proton-dissociable and easy to form PrOH<sub>2</sub><sup>+</sup> cation in acid medium. The evidences observed in the experiments, such as that the extraction process was very fast and high acidity was favourable for the extraction indicate that ion pair formation of [AuI<sub>4</sub><sup>-</sup>·PrOH<sub>2</sub><sup>+</sup>] is one of the most important mechanisms in this extraction process<sup>21</sup>. Hence, in the presence of KI and HCl medium, the cation of PrOH<sub>2</sub><sup>2+</sup> can associate with the anion of AuI<sub>4</sub><sup>-</sup> to form a neutral ion pair complex of [AuI<sub>4</sub><sup>-</sup>·PrOH<sub>2</sub><sup>+</sup>] which can be extracted into the enriched PrOH upper phase. The extraction process can be expressed as by the follows:



Let

$$D = \frac{[\text{AuI}_4^- \cdot (\text{PrOH}_2^+)]_{(p)}}{[\text{AuI}_4^-]} = K_{\text{ex}} [\text{H}^+][\text{PrOH}]_{(p)} \quad (2)$$

Then

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

where  $K_{ex}$  is the extraction constant,  $D$  is the distribution ratio of Au(III) and  $[PrOH]_{(P)}$  represents the concentration of PrOH in the enriched upper PrOH phase. The subscript "P" denotes enriched PrOH upper phase, while enriched salt-water bottom phase is given without any subscript.

As described in eqn. 3,  $[H^+]$  and  $[PrOH]_{(P)}$  are two main factors that affect distribution ratio ( $D$ ). From Fig. 3, it can be seen that with the increase the addition of  $(NH_4)_2SO_4$ , the phase separation of PrOH and water tends to be thoroughly, this results in the increase of  $[PrOH]_{(P)}$ . Therefore, as shown in eqn. 3, the increasing of acidity and the amount of  $(NH_4)_2SO_4$  will benefit the extraction, which is consistent with the experimental results as illustrated in Figs. 3 and 4.

**Separation of gold(III) and base metal ions:** Gold occurs in practical samples usually associated with large amount of co-existing ions. The extraction of co-existing ions should be taken into account. Different accompanying ions that probably co-exist with gold were respectively added to 10  $\mu$ g of Au(III) and separated according to the proposed separation procedure under the optimal conditions. The influence of co-existing ions is given in Table-1. The results showed that common anions and most of base metal ions used such as  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , Ca(II), Mg(II), Na(I), K(I), Fe(III), Mn(II), Al(III), Pb(II), Co(II), Ni(II), Cr(III), Sn(II) and Zn(II), had no effect on the recovery of gold even at a concentration of 2 mg, but the slight decrease of gold(III) extraction percentage is observed when respectively associated with 2 mg of Cu(II), Cd(II) and Hg(II).

TABLE-1  
EXTRACTION OF CO-EXISTING IONS ON  
THE RECOVERY OF GOLD

Ions	Added (mg)	Extraction of Au(III) (%)	Ions	Added (mg)	Extraction of Au(III) (%)
$Cl^-$	2	98.7	Al(III)	2	99.2
$SO_4^{2-}$	2	99.0	Cu(II)	2	96.2
$NO_3^-$	2	99.0	Zn(II)	2	98.1
$PO_4^{3-}$	2	99.1	Mn(II)	2	98.7
Na(I)	2	99.1	Cd(II)	2	95.2
K(I)	2	99.1	Co(II)	2	98.3
Ca(II)	2	99.3	Ni(II)	2	98.1
Mg(II)	2	99.0	Cr(III)	2	99.1
Fe(III)	2	98.4	Sn(II)	2	99.0
Pb(II)	2	98.7	Hg(II)	2	96.3

The extraction behaviours of base metal ions at 1 mg level under the optimal extraction conditions of gold(III) were then studied. The metal ions that extracted into upper phase were established by ICP-AES. The result was summarized in Table-2. The base metals ions used, except of Cu(II), Hg(II), Cd(II) were scarcely extracted into upper phase. To the extraction separation of Cu(II), red precipitate was observed in the upper phase as the formation of two phases, indicating that with the addition of  $I^-$ , a precipitation reaction of Cu(II) with  $I^-$  occurs and some of the CuI precipitate may run into upper phase. In order to separate gold(III) and Cu(II) thoroughly, the upper phase separated was filtrated by a G4 glass sand funnel to remove precipitate of CuI. As shown in Table-2, Cu(II) was scarcely found in the upper phase filtrated. But the result also supposes that the separation method could not separate Au(III) from Hg(II) and Cd(II).

TABLE-2  
EXTRACTION OF BASE METAL IONS

Ions	Added (mg)	Found in upper phase <sup>a</sup> (%)	Ions	Added (mg)	Found in upper phase <sup>a</sup> (%)
Na(I)	1	0.7	Zn(II)	1	4.5
K(I)	1	0.0	Mn(II)	1	2.2
Ca(II)	1	0.0	Cd(II)	1	86.2
Mg(II)	1	0.1	Co(II)	1	2.7
Fe(III)	1	8.2	Ni(II)	1	4.2
Pb(II)	1	3.1	Cr(III)	1	2.3
Al(III)	1	0.0	Sn(II)	1	4.1
Cu(II)	1	29.3	Hg(II)	1	75.5
Cu(II) <sup>b</sup>	1	2.3	–	–	–

<sup>a</sup>Determined by ICP-AES; <sup>b</sup>Upper phase was filtrated.

The proposed method was applied to the separation of a synthetic sample consisted of Au(III) accompanied with large amount of common base metal ions. The sample solution was prepared in 0.6 mol/L of HCl. The separation was carried out under optimized extraction conditions of Au(III). To separate gold and base metal ions thoroughly, the upper phase filtrated was washed by a 10 mL aqueous solution containing 0.6 mol/L of HCl, 0.1 mol/L of KI and 3.5 g of  $(NH_4)_2SO_4$ . The separation results were determined by ICP-AES and shown in Table-3. The result showed that base metal ions used were scarcely extracted, where the extraction percentage of Au(III) was 98 %. This results indicated that the proposed aqueous two-phase separation method exhibit high selectivity and can be used to separate gold from large amount of base metals.

TABLE-3  
SEPARATION RESULT OF THE SYNTHETIC SAMPLE

Ions	Added (mg)	Found in upper phase <sup>a</sup> , $\times 10^{-3}$ mg	Extraction (%)
Au(III)	0.050	49.0	98.0
Na(I)	1.0	0.0	0.0
K(I)	1.0	0.0	0.0
Fe(III)	1.0	7.0	0.7
Pb(II)	1.0	3.0	0.3
Al(III)	1.0	0.0	0.0
Cu(II)	0.5	0.0	0.0
Zn(II)	1.0	5.0	0.5
Ca(II)	1.0	0.0	0.0
Mg(II)	1.0	0.0	0.0
Mn(II)	1.0	0.0	0.0
Co(II)	1.0	3.0	0.0
Ni(II)	1.0	0.0	0.0

<sup>a</sup>Determined by ICP-AES.

## Conclusion

Experimental results indicate that the initial volume of PrOH and the acidity of the system are mainly factors that affect the formation and phase separation of *n*-propyl alcohol (PrOH)-ammonium sulfate aqueous two-phase extraction system. In presence of KI and in HCl medium, ion pair formation between iodide complex of  $AuI_4^-$  and  $PrOH_2^+$  is a predominant factor govern the extraction of gold in the *n*-propyl alcohol (PrOH)-ammonium sulfate aqueous two-phase extraction system. Increasing of acidity and the amount of  $(NH_4)_2SO_4$  added will favour the extraction.

Results obtained in this work also show that the proposed method exhibits selectivity to gold and can be effectively used

to separate gold from the large amount of base metals. It has the advantages of less poisoning, quicker separation, easier operation and clear phase boundary. Further more subsequent processes of this new aqueous two-phase extraction system are very simple.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support by Yunnan Provincial Scientific Research Funds (Grant No. 2011C163).

#### REFERENCES

1. S.B. Dhoot, J.M. Dalal and V.G. Gaikar, *Sep. Sci. Tech.*, **42**, 1859 (2007).
2. B.Y. Zaslavsky, *Aqueous Two-Phase Partitioning, Physical Chemistry and Bioanalytical Application*, Marcel Dekker: New York, USA (1995).
3. M. Perumalsamy and T. Murugesan, *Sep. Sci. Technol.*, **42**, 2049 (2007).
4. P.A. Aguinaga-Diaz and R.Z. Guzman, *Sep. Sci. Technol.*, **31**, 1483 (1996).
5. R.D. Rogers, A.H. Bond and B.B. Cary, *Sep. Sci. Technol.*, **28**, 1091 (1993).
6. R.D. Rogers, A.H. Bond, 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. J.H. Michael, P.J. Daniel and Y. Hong, *Polymer*, **46**, 2567 (2005).
9. A.J. Tong, Y. Wu, S.D. Tan, L.D. Li, A. Yoshifumi and T. Shigeyuki, *Anal. Chim. Acta*, **369**, 11 (1998).
10. S.H. Li, C.Y. He, H.W. Liu, K. Li and F. Liu, *J. Chromatogr. B*, **826**, 58 (2005).
11. C.Y. He, S.H. Li, H.W. Liu, K. Li and F. Liu, *J. Chromatogr. A*, **1082**, 143 (2005).
12. Z.H. Wang, Y. Zeng, M.H. Ma and C.L. Shu, *J. Microchem.*, **60**, 143 (1998).
13. X.H. Liu, Y.T. Gao, R.S. Tang and W. Wang, *Sep. Purf. Technol.*, **50**, 263 (2006).
14. Y.T. Gao and W. Wang, *Chin. J. Appl. Chem.*, **19**, 578 (2002) (in Chinese).
15. Y.T. Gao, L.S. Wu and W. Wang, *Chin. J. Anal. Chem.*, **29**, 901 (2001) (in Chinese).
16. S.X. Cai and C. Huang, *Analysis of Noble Metals*, Metallurgical Industry Press: Beijing, edn. 2 (1984) (in Chinese).
17. S. Masami, N. Noriko, H. Tadashige, S. Daigo, E. Yukihiro and K. Satoshi, *Anal. Chim. Acta*, **427**, 293 (2001).
18. M. Mojski, *Talanta*, **25**, 163 (1978).
19. E. Hogfeldt, *Stability Constants of Metal-Ion Complexes: Part A: Inorganic Ligands*, Pergamon Press: Oxford, New York, edn. 1 (1982).
20. D.H. Logsdail and M.J. Slater, *Solvent. Extr. Process.*, Elsevier: Oxford, Vol. 3, edn. 1 (1993).
21. M. Zhong, B. Han and H. Yan, *J. Supercrit. Fluids*, **4**, 265 (1991).