Solvent Extraction of Iridium(IV) with the Petroleum Sulfoxide

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The petroleum sulfoxide was used in the extraction of iridium(IV) from hydrochloric acid solution. Iridium(IV) was extracted quantitatively with petroleum sulfoxide in xylene. Sodium hydroxide solution could be used as stripping agent. Extraction parameters of Ir(IV), including petroleum sulfoxide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, hydrochloric acid concentration and sodium hydroxide concentration of aqueous phase, were studied in detail. In order to find an optimum condition to separate iridium and rhodium, solvent extraction experiments were performed from chloride solution by using petroleum sulfoxide as an extractant. A new process for the extraction of iridium by petroleum sulfoxide was developed. Based on this process, Ir(IV) can be extracted from a mixed chloride solution containing a large amount of Rh(III) and less amount of Ir(IV).

Key Words: Iridium, Solvent extraction, Petroleum sulfoxide.

INTRODUCTION

Iridium has been found to be an important rare noble metal and widely used in the making of precise alloys, apparatus, corrosion-resistant chemical wares and plug electrodes owing to its specific physical and chemical properties[1-4]. Since natural resources for iridium metal are limited and the demand for iridium in industry will continue to grow, it is important to find an effective separation process to recover iridium from low-grade ores or secondary resources. Various hydrometallurgical processes such as solvent extraction[5,6], ion exchange[7] and precipitation[8] have been accomplished for the recovery of iridium in chloride media. Solvent extraction has been considered as a most efficient technique for the recovery and separation of iridium from hydrochloric acid solutions[9-12].

Sulfoxide extractants are soft base ligands and are considered to have strong affinity for soft Lewis acid metals such as palladium and platinum. Sulfoxide extractants were first proposed for use in the separation of palladium and platinum from some other platinum-group metals[13-16]. In the present work, The petroleum sulfoxide was used in the extraction of Ir(IV) from hydrochloric acid solution. Extraction parameters of Ir(IV), including petroleum sulfoxide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, hydrochloric acid concentration and sodium hydroxide concentration of aqueous phase, were studied in detail. Based on the independent extraction experiments of Ir(IV) and Rh(III), the desirable separation parameters of Ir(IV) and Rh(III) were selected. We developed a new process for the extraction of Ir(IV) by petroleum sulfoxide from a mixed chloride solution containing a large amount of Rh(III) and little Ir(IV).

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of Ir(IV). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Ir 264 nm.

The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Petroleum sulfoxide was obtained from Yunnan Petrochemical Company. Stock solution of iridium was prepared by diluting H_2IrCl_6 in ultra-pure water. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of petroleum sulfoxide in xylene.

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 10 min, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Ir(IV) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase before and after the extraction.

RESULTS AND DISCUSSION

Influences of the extractant concentration: To investigate the effect of petroleum sulfoxide concentration on the extraction performances of Ir(IV), the experiments were performed at the fixed conditions. The results are shown in Fig. 1. As can be seen from Fig. 1, petroleum sulfoxide dissolved in xylene with the extractant concentration varying from 2 to 10 % (v/v). The percentage extraction of Ir(IV) increased in the range from 73.0 to 95.4 % by increasing petroleum sulfoxide concentration from 2 to 8 % (v/v). Further increasing petroleum sulfoxide concentration from 8 to 10 % (v/v), the percentage extraction of Ir(IV) only had a slight increase (from 95.4 to 95.5 %). 8 % (v/v) petroleum sulfoxide was needed for quantitative extraction of Ir(IV) from a 4 mol L^{-1} HCl aqueous solution containing 100 mg L^{-1} iridium.
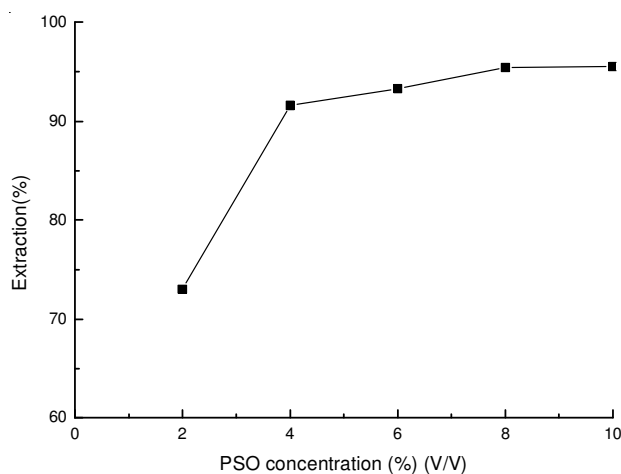
Fig. 2. Effect of HCl concentration on the extraction of Ir(IV); $C_{Ir(IV)}$: 100 mg L^{-1}, C_{PSO} : 8 % (v/v), O/A : 1.0, contact time : 10 min

Fig. 1. Effect of extractant concentration on the extraction of Ir(IV); $C_{Ir(IV)}$: 100 mg L^{-1}, C_{HCl} : 4.0 mol L^{-1}, O/A : 1.0, contact time : 10 min

Influences of hydrochloric acid concentration: In industrial application for extraction of Ir(IV), the acidity of stock solution usually influences significantly. The effect of hydrochloric acid concentration on the extraction of Ir(IV) is shown in Fig. 2. The extraction curve indicated extraction percentage of Ir(IV) increased with increasing HCl concentration from 0.1 mol L^{-1} to 4.0 mol L^{-1}. When HCl concentration was 4 mol L^{-1}, more than 95 % extraction of Ir(IV) was obtained. Further increase of HCl concentration from 4 to 6 mol L^{-1}, the percentage extraction of Ir(IV) kept constant. Therefore, 4 mol L^{-1} HCl was adopted in all subsequent experiments.

Influences of contact time: To extract Ir(IV) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 3. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 1 to 25 min. Extraction percentage of Ir(IV) increased with increasing contact time from 1 to 10 min. Further increase of contact time from 10 to 25 min, the percentage extraction of Ir(IV) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of Ir(IV) was found to be about 10 min.
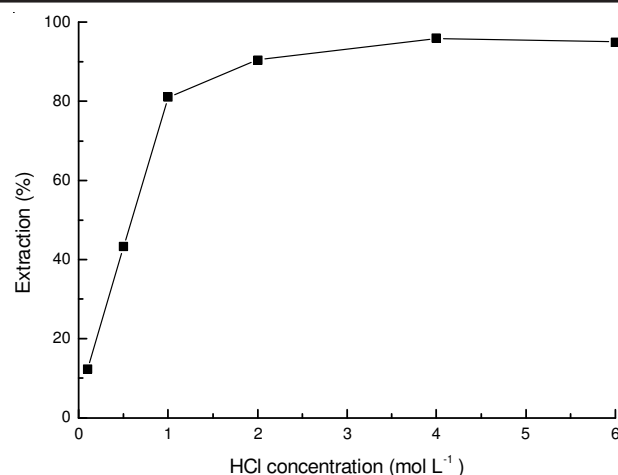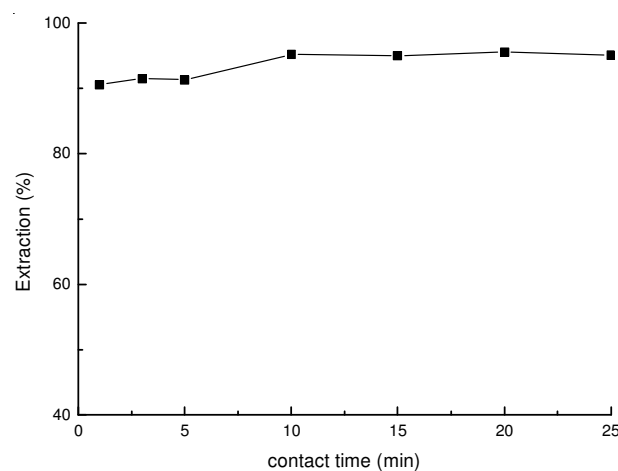
Fig. 3. Effect of contact time on the extraction of Ir(IV); $C_{Ir(IV)}$: 100 mg L^{-1}, C_{PSO} : 8 % (v/v), O/A : 1.0, C_{HCl} : 4.0 mol L^{-1}

Influences of organic/aqueous (O/A) phase ratio: To obtain optimal organic/aqueous phase ratio for extraction of Ir(IV), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig. 4. As can be seen from Fig. 4, extraction percentage of Ir(IV) increased with increasing organic/aqueous phase ratio from 0.6 to 1.0. By further increasing organic/aqueous phase ratio from 1.0 to 3.0, the percentage extraction of Ir(IV) kept constant. Therefore, Ir(IV) can be extracted efficiently by controlling organic/aqueous phase ratio, 1.0.

Stripping properties of iridium: Iridium loaded in the organic phase was stripped with various stripping agents, such as sodium hydroxide, thiourea and sodium sulfite as stripping agents. In the following experiments, the organic phase loaded with 100 mg L^{-1} Ir(IV) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 10 min; aqueous/organic phase ratio, 1.0. The results show that Ir(IV) can not be stripped from organic phase with sodium sulfite and thiourea. Sodium hydroxide solution can be used as the effective stripping agent. As can be seen from Fig. 5, by increasing sodium hydroxide concentration from 0.0 to 0.3 wt %, the percentage stripping of Ir(IV) increased from 86.8 to 99.5 %. The stripping was quantitative when 0.3 wt % NaOH solution was used.
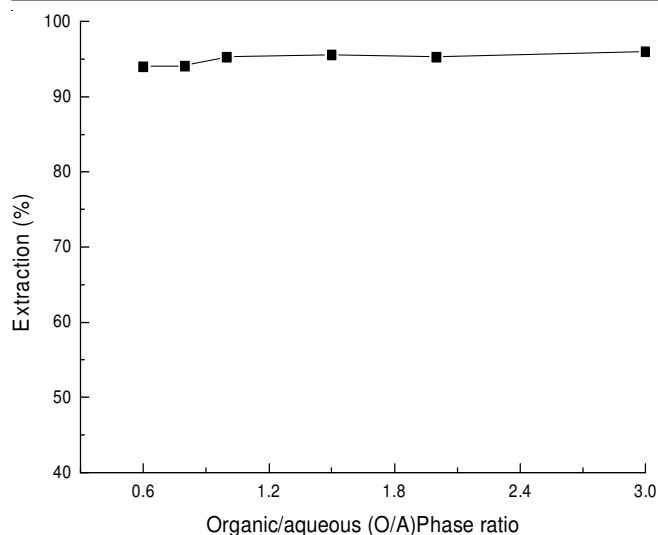
Fig. 4.   Effect of O/A on the extraction of Ir(IV); $C_{Ir(IV)}$: 100 mg L^{-1}, C_{PSO} : 8 % (v/v), contact time: 10 min, C_{HCl} : 4.0 mol L^{-1}
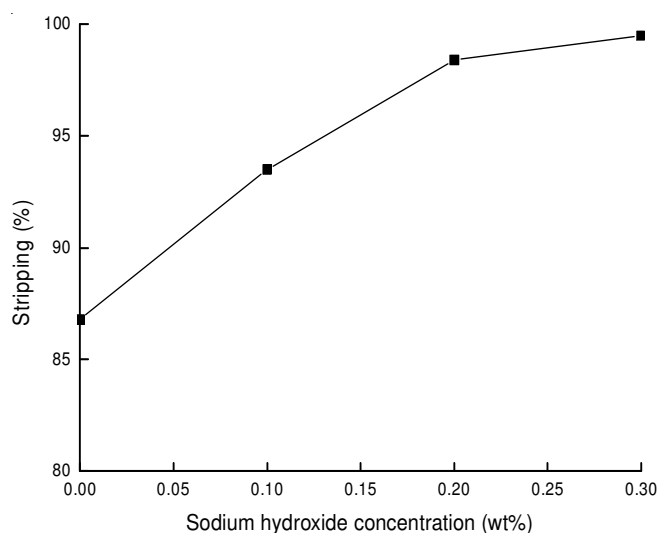

Fig. 5.   Effect of stripping reagent concentration on the stripping of Ir(IV); $C_{Ir(IV)}$: 100 mg L^{-1}, C_{PSO} : 8 % (v/v), O/A: 1.0, contact time : 10 min

Extraction of Rh(III) from chloride solution by petroleum sulfoxide: Extraction experiments of Rh(III) from chloride solution were carried out by using petroleum sulfoxide. The results are shown in Fig. 6. The result shows that extraction percentage of Rh(III) decreased with increasing of Rh(III) concentration. In our experimental range, extraction percentage of Rh(III) was lower than 25 %.

Extraction of Ir(IV) and Rh(III) from the mixed solution by petroleum sulfoxide: Extraction experiments of Ir(IV) and Rh(III) from the mixed chloride solution were carried out by using petroleum sulfoxide. The separation factor was defined as the ratio of distribution coefficient of Ir(IV) to that of Rh(III). Fig. 7 shows the variation in the separation factor between Ir(IV) and Rh(III) obtained from our experiments. Molar ratio (Rh/Ir) had a great effect on the separation factor. The separation factor increased with increasing of Rh/Ir molar ratio. It may be concluded that Ir(IV) can be extracted from a mixed chloride solution containing a large amount of Rh(III) and less amount of Ir(IV).
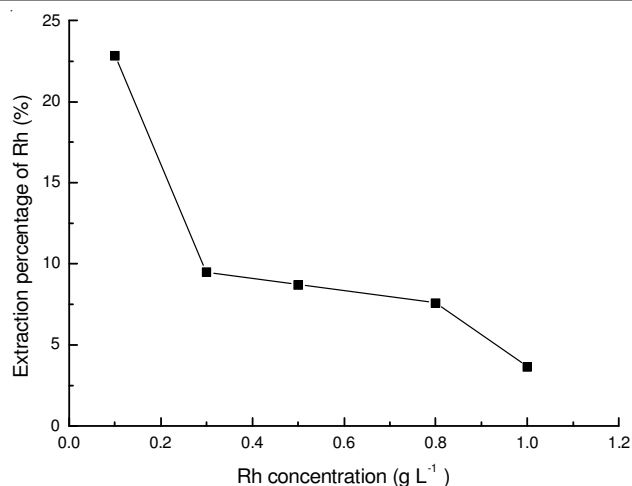

Fig. 6.   Effect of Rh(III) concentration on the extraction of Rh(III). C_{PSO} : 8 %, C_{HCl} : 4.0 mol L^{-1}, O/A : 1.0, contact time : 10 min
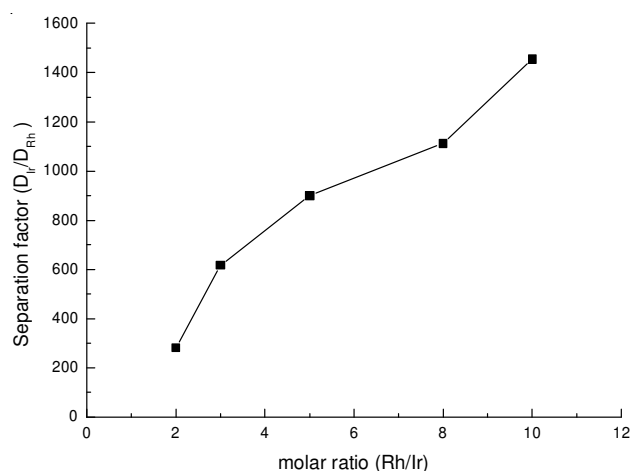

Fig. 7.   Effect of molar ratio(Rh/Ir) on separation factor for Ir(IV) and Rh(III) C_{PSO} : 8 %, CHCl : 4.0 mol L^{-1}, O/A : 1.0, contact time : 10 min

Conclusion

The solvent extraction of Ir(IV) from hydrochloric acid solutions were investigated using the petroleum sulfoxide diluted in xylene. Extraction parameters of Ir(IV) were obtained and summarized as the following: the petroleum sulfoxide concentration, 8 % (v/v); organic/aqueous phase ratio, 1.0; hydrochloric acid concentration of aqueous solution, 4.0 mol L^{-1}; contact time of two phases 10 min. Iridium(IV) loaded in organic phase could be stripped efficiently using an aqueous solution containing sodium hydroxide. Based on the independent extraction experiments of Ir(IV) and Rh(III), the desirable separation parameters of Ir(IV) and Rh(III) were selected. A new process for the extraction of iridium by petroleum sulfoxide was developed. Based on this process, Ir(IV) can be extracted from a mixed chloride solution containing a large amount of Rh(III) and less amount of Ir(IV).

REFERENCES

1. M.A. Taher, S. Puri, R.K. Bansal and B.K. Puri, *Talanta*, **45**, 411 (1997).
2. B. Tang, F. Han and G.Y. Zhang, *Talanta*, **56**, 603 (2002).
3. C. Locatelli, *Talanta*, **85**, 546 (2011).
4. V. Druskovic, V. Vojkovic and S. Miko, *Talanta*, **62**, 489 (2004).
5. A. Mhaske and P. Dhadke, *Hydrometallurgy*, **63**, 207 (2002).
6. P.P. Sun and M.S. Lee, *Hydrometallurgy*, **105**, 334 (2011).
7. D.G. Pearson and S.J. Woodland, *Chem. Geol.*, **165**, 87 (2000).
8. G. Schreier and C. Edtmaier, *Hydrometallurgy*, **68**, 69 (2003).
9. L.H. Zou, J. Chen and Y. Huang, *Hydrometallurgy*, **72**, 31 (2004).
10. C.S. Kedari, M.T. Coll, A. Fortuny, E. Goralska and A.M. Sastre, *Hydrometallurgy*, **82**, 40 (2006).
11. C.S. Kedari, M.T. Coll, A. Fortuny, E. Goralska and A.M. Sastre, *Sep. Sci. Technol.*, **40**, 1927 (2005).
12. M.S. Lee, J.Y. Lee and P.P. Sun, *Korean J. Metal Mater.*, **48**, 430 (2010).
13. Y.W. Li, G.B. Gu, H.Y. Liu, H.H.Y. Sung, I.D. Williams and C.K. Chang, *Molecules*, **10**, 912 (2005).
14. L. Pan and Z.D. Zhang, *Miner. Eng.*, **22**, 1271 (2009).
15. L. Pan, G.B. Gu, F.W. Wang and Y.J. Wei, *Chinese J. Inorg. Chem.*, **24**, 520 (2008).
16. J.S. Preston and A.C. du Preez, *Solvent Extr. Ion Exch.*, **20**, 359 (2002).