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Separation of Rh(III) from the Mixed Chloride Solutions Containing Pt(IV) and Pd(II) by Extraction with Alamine336

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Solvent extraction experiments of Pt(IV), Pd(II) and Rh(III) by Alamine336 were performed from the mixed chloride solutions. In the HCl concentration range from 1 to 5 M, most of Pt and Pd were extracted from the mixed solutions. However, the extraction percentage of Rh was much smaller than that of Pt and Pd. Lower concentration of Alamine336 in strong HCl solution led to higher separation factor of Rh from Pt and Pd. Adding $SnCl_2$ to the mixed solutions increased the extraction percentage of Rh, while the extraction percentage of Pt and Pd was little affected. Our results showed that selective separation of Rh or coextraction of the three platinum group metals from the mixed solution would be possible by adjusting the extraction conditions.

Key Words: Separation, Platinum, Palladium, Rhodium, Alamine336

Introduction

Platinum group metals(PGMs) are extensively used in automobile, chemical and electronics industry owing to their specific physical and chemical properties. Among PGMs, platinum, palladium and rhodium are used in automobile catalysts to reduce the emission level from the exhaust gas and the automobile industry consumes PGMs in a great measure.[1] The high cost of recovery and limited resources of these metals make it necessary to recover the metals from industry waste. Considering the difficulties related with the separation and purification of PGMs, it is important to find an effective separation process to recover these metals with high purity.[1] According to the published literatures, ion exchange and solvent extraction have been widely employed to separate and recover them. Among Pt, Pd and Rh, extraction of Rh is the most difficult owing to its intricate chemical properties in chloride solution.[2] Rhodium has seven existence forms of aqua-chloro complexes from $[Rh(H_2O)_6^{3+}]$ to $[RhCl_6^{3-}]$.[2] The highly charged octanedral complexes are difficult to extract owing to steric effects.[2]

Various neutral and anionic extractants have been used in the extraction of Pt, Pd and Rh from chloride solution.[2-9] In the extraction of PGMs from chloride solution, anionic extractants are better than neutral extractants when HCl concentration is not strong. With the increase of HCl concentration, the fraction of undissociated metal acid complex increases and neutral extractants are better to extract these neutral complexes at high HCl concentration.

Alamine336 (Tertiary amine, R_3N, $R = CH_3(CH_2)_7$) is a sort of anionic extractant and has been widely used in extracting various metal ions[2,10-13] In this study, we chose Alamine336 to separate Rh(III) from the mixed hydrochloride solutions containing Pd and Pt. The optimum conditions for the separation of Rh from Pd and Pt were investigated by varying HCl and Alamine336 concentration. It has been reported that $SnCl_2$ has a positive effect on the extraction of Rh. Effect of adding tin chloride on the separation of Rh from the mixed chloride solution was also investigated.

Experimental

Stock solutions of $PtCl_4$, $PdCl_2$, $RhCl_3$ and $SnCl_2$ were prepared by dissolving the necessary amount of the metal chlorides in doubly distilled water. Reagent grade of $PtCl_4$, $PdCl_2$, $RhCl_3$, and $SnCl_2$ was used in preparing these solutions. The acidity of the solution was adjusted by adding reagent HCl (36%) solution.

Alamine336 (Henkel Corp.) was used without further purification. Equal volume of Alamine336 and HCl were mixed according to reaction (1) to form Alamine336 salt (R_3NHCl) which takes part in the solvent extraction of metals.[3,10,11] Alamine336 salt was diluted with toluene.

$$R_3N_{org} + HCl = R_3NHCl_{org} \qquad (1)$$

In this reaction, subscript org represents organic phase.

Throughout the solvent extraction experiments in our study, freshly prepared aqueous solutions were used. Equal volume (20 mL) of aqueous and organic phase was mixed in a 100 mL screwed cap bottle and shaken for 30 mins with a wrist action shaker. The aqueous phase was separated after settling the mixture. All the extraction experiments were carried out at ambient temperature. The concentration of metal in the aqueous phase was measured by ICP-OES (Spectro arcos). The concentration of metal in the organic phase was obtained from mass balance.

Results and Discussion

Effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solution of Pt (IV) and Pd (II). Fig. 1 shows the effect of Alamine336 and HCl concentration

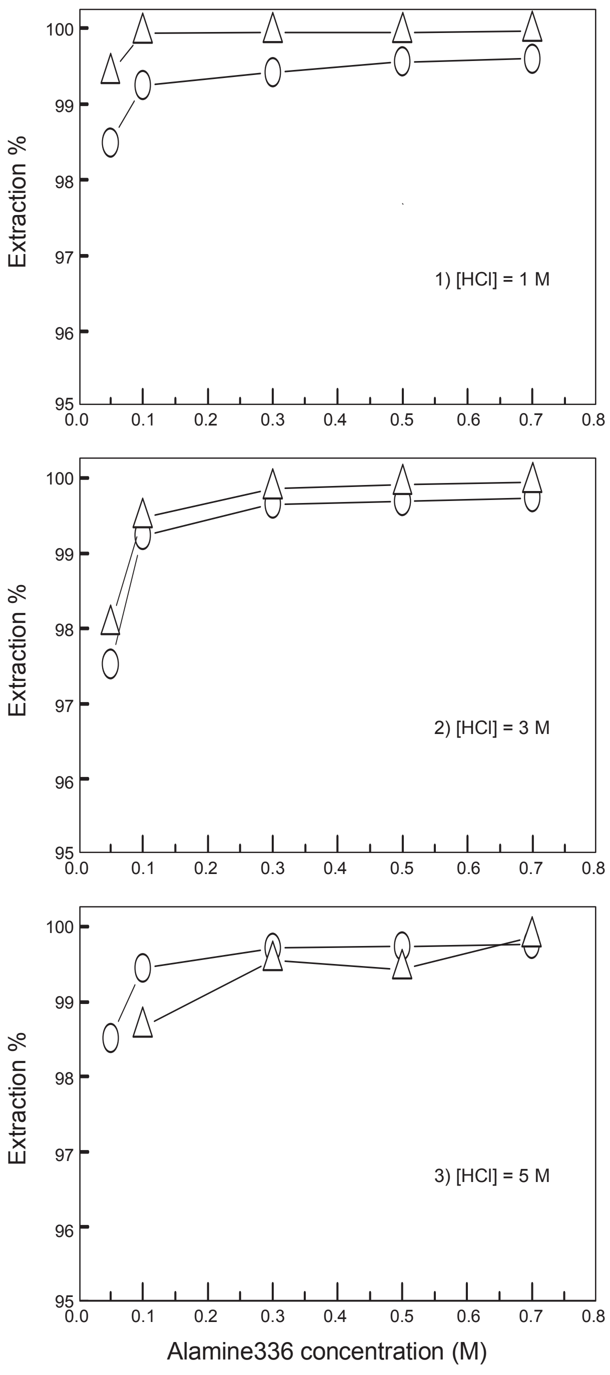

Figure 1. Effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solutions of Pt(IV) and Pd(II). ($[PtCl_4]_{total}$ = 0.001 M, $[PtCl_2]_{total}$ = 0.001 M) (–○–: Pt(IV), –△–: Pt(II)).

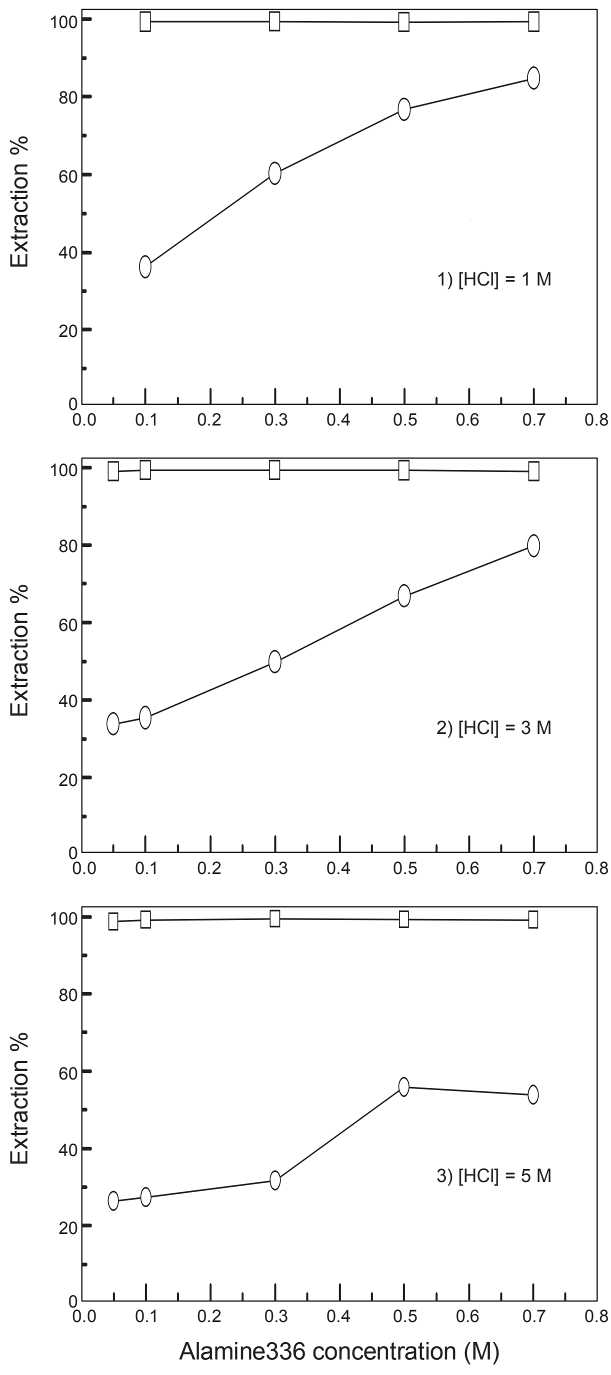

Figure 2. Effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solutions of Pt(IV) and Rh(III). ($[PtCl_4]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M) (–□–: Pt(IV), –○–: Rh(III)).

on the extraction of metals from the mixed solutions of Pt (IV) and Pd (II). In these experiments, the initial concentration of Pt and Pd was kept at 0.001 M. The extraction percentage of both metals increased with the increase of Alamine336 concentration. When Alamine336 concentration was higher than 0.3 M, Pt and Pd were almost completely extracted by Alamine336. When HCl concentration is 1 and 3 M, extraction percentage of Pd was higher than that of Pt, while extraction percentage of Pt was higher than that of Pd at 5 M HCl. In our experimental range, Pt and Pd were well extracted by Alamine336 and it would be difficult to separate these two metals by solvent extraction with Alamine336 alone. The extraction reaction of Pt and Pd by Alamine336 can be represented as:[3,4]

$$PtCl_6^{2-} + 2R_3NHCl_{org} = PtC1_6(R_3NH)_{2,org} + 2Cl^- \quad (2)$$

$$PdCl_4^{2-} + 2R_3NHCl_{org} = PdC1_4(R_3NH)_{2,org} + 2Cl^- \quad (3)$$

According to the published literatures,[5,6] the extraction of platinum will decrease at higher concentration of hydrochloric acid

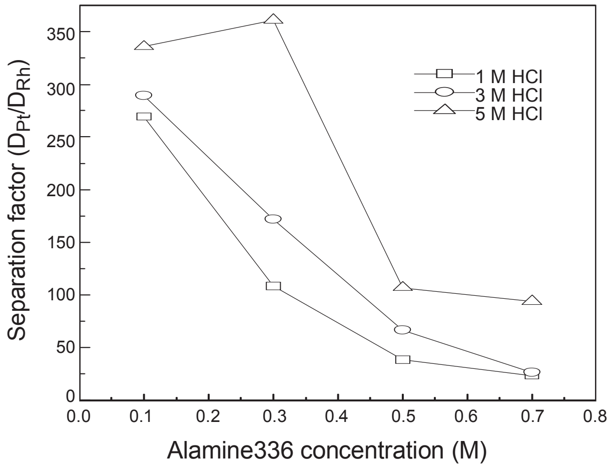

Figure 3. Separation factor for Pt(IV) and Rh(III) at different HCl concentration with respect to Alamine336 concentration. ($[PtCl_4]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M).

owing to the mass action effect of chloride ions. In our study, the concentration of HCl was not very high and the effect of HCl concentration on the extraction of platinum was not obvious. The extraction results in Fig. 1 imply that both Pt and Pd can be simultaneously extracted by Alamine336 by adjusting HCl and Alamine336 concentration.

Fig. 2 shows the effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solutions of Pt(IV) and Rh(III). The initial concentration of Pt and Rh was kept at 0.001M. It is seen in Fig. 2 that most of Pt was extracted by Alamine336 in our experimental ranges. However, the extraction of Rh depended on HCl and Alamine336 concentration. Extraction percentage of Rh decreased with the increase of HCl concentration when Alamine336 concentration was constant. Separation factor between Pt and Rh was defined as

$$\text{separation factor} = \frac{D_{Pt}}{D_{Rh}} \tag{4}$$

Variation of the separation factor with extraction conditions is represented in Fig. 3. According to this figure, the separation factor between Pt and Rh decreased with the increase of Alamine336 concentration and with the decrease of HCl concentration. The variation of separation factor is due to the fact that the extraction percentage of Pt was nearly constant while that of Rh increased with increasing Alamine336 concentration as shown in Fig. 2. Considering that the value of separation factor was relatively large, it may be concluded that separation of Rh from Pt is possible at low concentration of Alamine336 in strong HCl solution.

Fig. 4 shows the effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solutions of Pd(II) and Rh(III). The initial concentration of Pd and Rh was kept at 0.001 M. Extraction percentage of Pd was more than 99% in our experimental range. However, the extraction behavior of Rh was similar to those obtained from the mixed solution with Pt. Extraction percentage of Rh increased with increasing Alamine336 concentration and with decreasing HCl concentration.

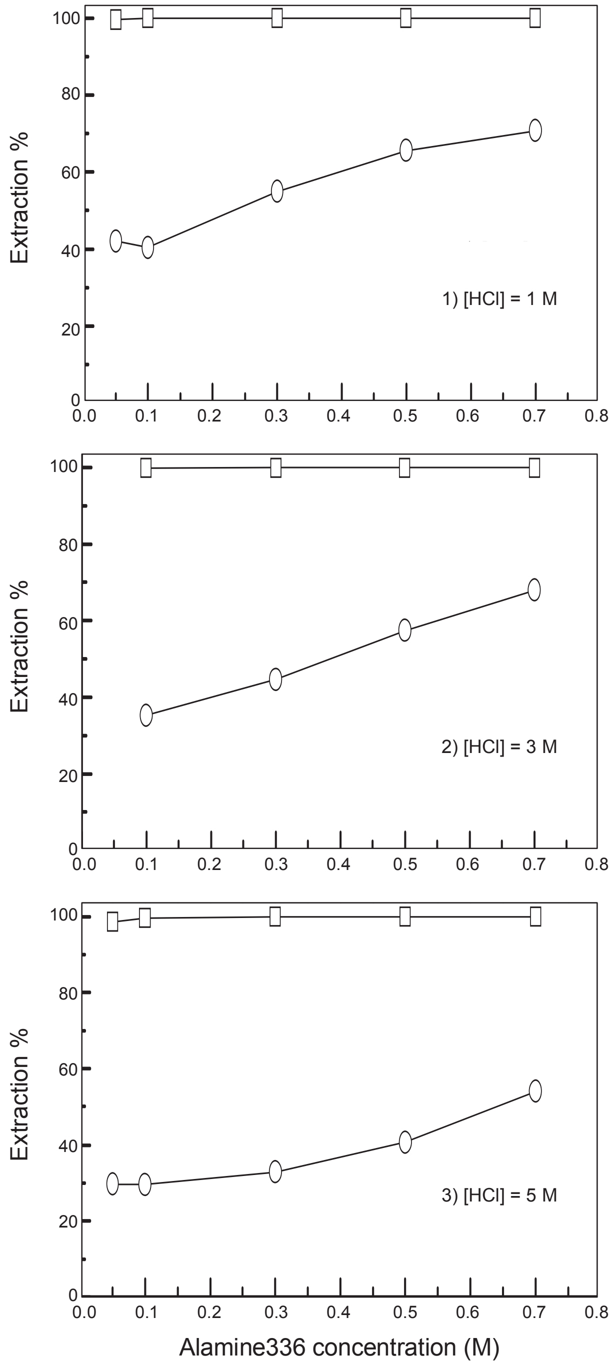

Figure 4. Effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solutions of Pd(II) and Rh(III). ($[PtCl_2]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M) (–□–: Pd(II), –○–: Rh(III)).

Fig. 5 represents the variation of the separation factor between Pd and Rh. In this figure, separation factor was defined as the ratio of the distribution coefficient of Pd to that of Rh, i.e., D_{Pd}/D_{Rh}. Separation factor decreased with increasing Alamine336 concentration. Higher separation factor was obtained with stronger HCl concentration. The drop rate of separation factor with Alamine336 concentration became steeper when HCl concentration became stronger. The maximum value of separation factor between Pd and Rh obtained in this study was around 4000, which is much higher than that between Pt and Rh. Separa-

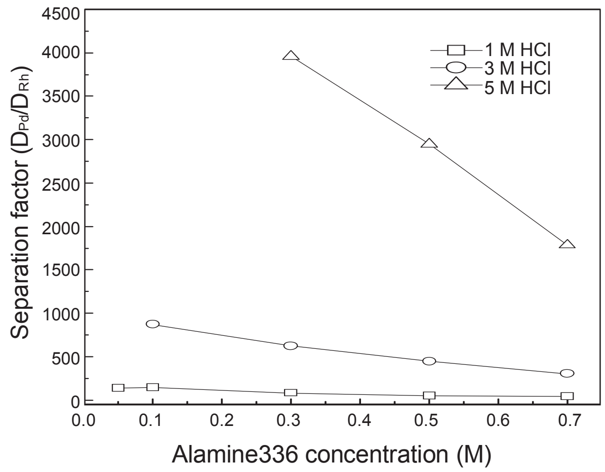

Figure 5. Separation factor for Pd(II) and Rh(III) at different HCl concentration with respect to Alamine336 concentration. ($[PtCl_2]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M).

tion of Rh and Pd would be easier than separation of Rh and Pt.

Effect of Alamine336 and HCl concentration on the extraction of metals from the mixed solution of Rh(III), Pt(IV) and Pd(II). Separation experiments were performed from the mixed solution of Rh(III), Pt(IV) and Pd(II). The concentration of these three metals was kept at 0.001 M and the results are shown in Fig. 6. Most of Pt and Pd were extracted in our experimental range, while the extraction percentage of Rh depended on the extraction conditions. The extraction percentage of Rh increased with the increase of Alamine336 concentration at the same HCl concentration. When Alamine336 concentration was same, the extraction percentage of Rh increased with the decrease of HCl concentration. Rhodium is the most expensive of the platinum group metals. Therefore, it is economical to separate preferentially rhodium from the platinum group metals. According to Fig. 6, it is possible to separate Rh from Pt and Pd by extracting these two metals with Alamine336. For the purpose of isolating rhodium, high concentration of HCl is favorable.

Some studies have reported that adding $SnCl_2$ to the rhodium solution increased the extraction percentage of Rh by Kelex100, Cyanex921 and TBP owing to the reducing action of Sn(II).[4-6] In order to investigate the effect of adding $SnCl_2$ on the separation of Rh from the mixed solution, $SnCl_2$ was added to the mixed solution of Rh, Pt and Pd. In these mixed solution, the concentration of the three platinum group metals was kept at 0.001 M, while $SnCl_2$ concentration was controlled to 0.01 M. The extraction behavior of the platinum group metals together with tin is shown in Fig. 7. In our experimental range, most of Pt, Pd and Sn were extracted by Alamine336. The extraction percentage of Rh was from 40 to 80% depending on the concentration of HCl and Alamine336. When HCl concentration was 1 and 3 M, the extraction percentage of Rh increased with the increase of Alamine336 concentration. However, Alamine336 concentration has negligible effect on the extraction percentage of Rh at 5 M HCl concentration.

Fig. 8 shows the variation of the extraction percentage of Rh with Alamine336 concentration in the absence and presence of $SnCl_2$. It is obvious that adding $SnCl_2$ has a favorable effect

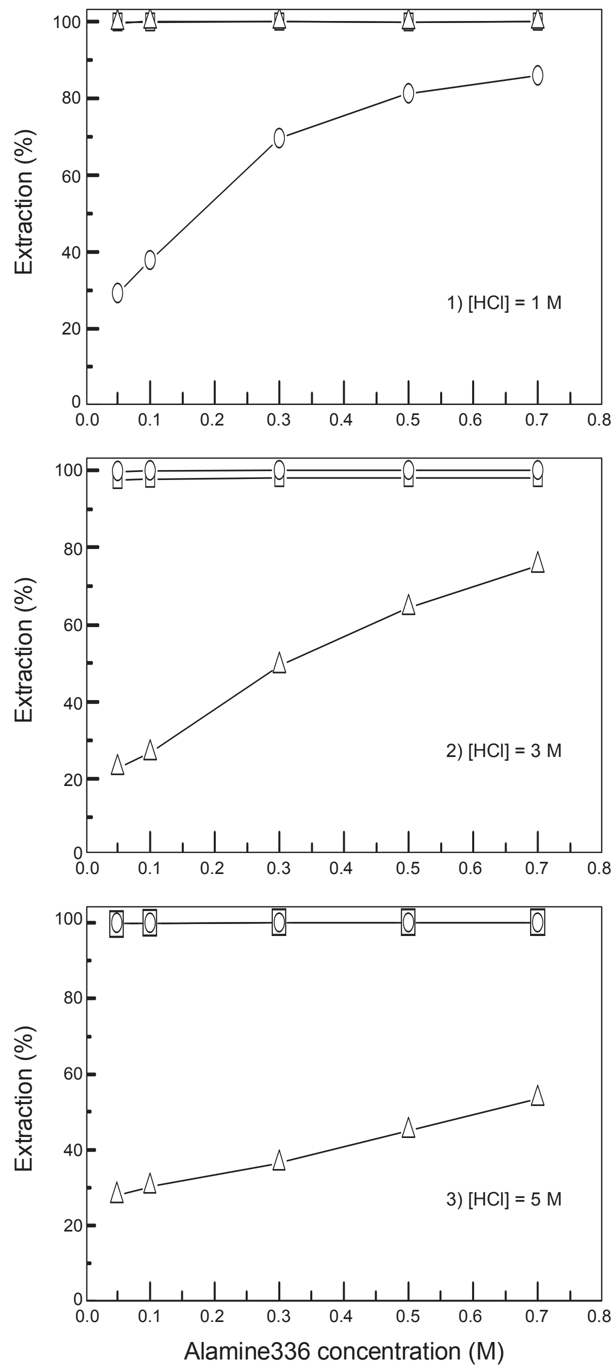

Figure 6. Effect of Alamine336 concentration on the extraction % of metals ad diffierent HCl concentration in the mixed solutions of Pt(IV) Pd(II) and Rh(III). ($[PtCl_4]_{total}$ = 0.001 M, $[PdCl_2]_{total}$ = 0.001 M, $[PdCl_3]_{total}$ = 0.001 M) (–□–: Pt(IV), –○–: Rd(II), –△–: Rh(III)).

on the extraction of Rh. According to the literatures, rhodium is activated after adding $SnCl_2$ and most of trivalent rhodium complexes are reduced to monovalent rhodium complexes by the oxidation of Sn(II) to Sn(IV), which is represented in Eqs. (5) and (6).[5,6,14]

$$RhCl_6^{3-} + 6SnCl_3^- = [Rh(SnCl_3)_5]^{4-} + SnCl_6^{2-} + 3Cl^- \quad (5)$$

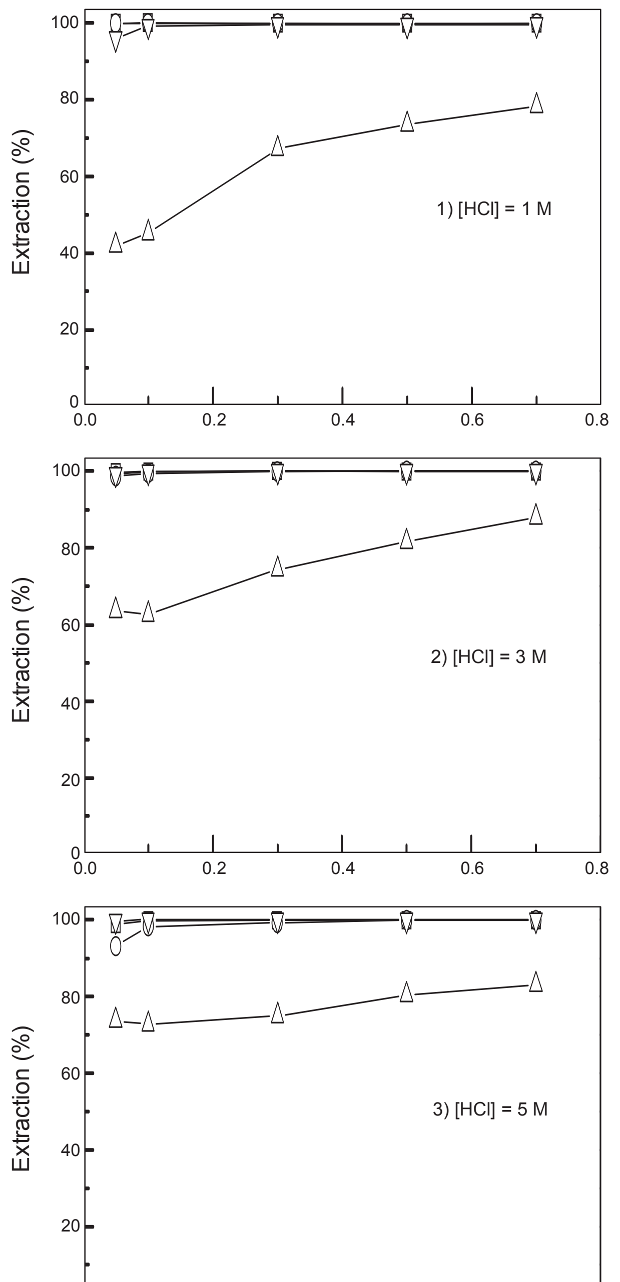

Figure 7. Effect of Alamine336 concentration on the extraction of metals from the mixed solutions of Pt(IV) Pd(II) and Rh(III) at diffierent HCl concentration in the presence of $SnCl_2$. ($[PtCl_4]_{total}$ = 0.001 M, $[PdCl_2]_{total}$ = 0.001 M, $[PdCl_3]_{total}$ = 0.001 M, $[SnCl_2]_{total}$ = 0.01 M) (-□-: Pt(IV), -○-: Rd(II), -△-: Rh(III), -▽-: Sn(II)).

$$RhCl_5(H_2O)^{2-} + 12SnCl_3^- \rightarrow [Rh(SnCl_3)_5]^{4-} + SnCl_6^{2-} + 6SnCl_3^- + 2Cl^- + H_2O \quad (6)$$

In our experiment, the molar ratio of Sn to Rh was more than 10, which value is enough to produce an activated rhodium solution.[1] It is shown in Fig. 8 that the increase in the extraction percentage of Rh in the presence of $SnCl_2$ was pronounced with the increase of HCl concentration.

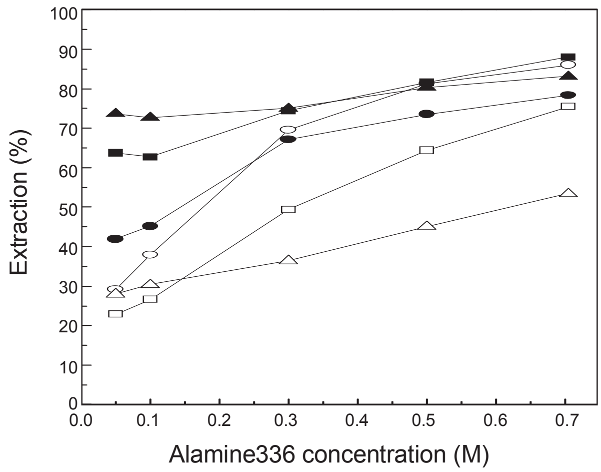

Figure 8. Effect of $SnCl_2$ on the extraction of Rh(III) from the mixed solutions of Pt, Pd and Rh at diffierent HCl concentration with respect to Alamine336 concentration. ($[PtCl_4]_{total}$ = 0.001 M, $[PdCl_2]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M) (-○-: 1M HCl, -□-: 3 M HCl, -△-: 5 M HCl, -●-: 1 M HCl, -■-: 3 M HCl, -▲-: 5 M HCl, open is without $SnCl_2$, solid is with $SnCl_2$).

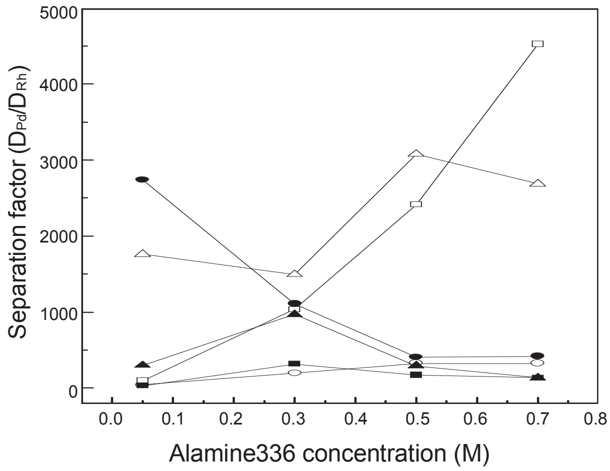

Figure 9. Separation factor for Pt(IV) and Rh(III) at different HCl concentration with respect to Alamine336 concentration. ($[PtCl_4]_{total}$ = 0.001 M, $[PdCl_2]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M) (-○-: 1 M HCl, -△-: 3 M HCl, -□-: 5 M HCl, -●-: 1 M HCl, -▲-: 3 M HCl, -■-: 5 M HCl, open is without $SnCl_2$, solid is with $SnCl_2$).

Figs. 9 and 10 represent the variation in the separation factors of D_{Pt}/D_{Rh} and D_{Pd}/D_{Rh} at different HCl concentration in the presence and absence of $SnCl_2$. When HCl concentration was 1 M, adding $SnCl_2$ to the mixed solution of the three PGMs increased both of the separation factors (D_{Pt}/D_{Rh} and D_{Pd}/D_{Rh}). However, both of the separation factors in the absence of $SnCl_2$ were much higher than those in the presence of tin chloride when HCl concentration was 3 and 5 M. This phenomena is due to the fact that adding $SnCl_2$ to the mixed solution had a positive effect on the extraction of Rh. Our results indicate that there are two routes to obtain Rh from the mixed chloride solutions containing Pt and Pd. One is to extract all the three PGMs at high HCl concentration by adding $SnCl_2$. The other route is to extract both Pt and Pd from the mixed solution at weak HCl concentration in

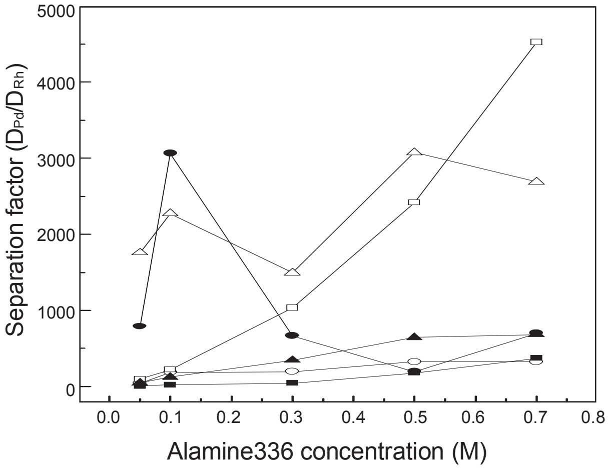

Figure 10. Separation factor for Pd(II) and Rh(III) at different HCl concentration with respect to Alamine336 concentration. ($[PtCl_4]_{total}$ = 0.001 M, $[PdCl_2]_{total}$ = 0.001 M, $[RhCl_3]_{total}$ = 0.001 M) (–○–: 1 M HCl, –△–: 3 M HCl, –□–: 5 M HCl, –●–: 1 M HCl, –▲–: 3 M HCl, –■–: 5 M HCl, open is without $SnCl_2$, solid is with $SnCl_2$).

the absence of $SnCl_2$ and leave the rhodium in the chloride solution. In the former route, the three PGMs which were extracted into Alamine336 could be separated by employing scrubbing and stripping.

Conclusions

Solvent extraction behavior of Pd (II), Pt (IV) and Rh (III) was investigated from the mixed chloride solution with Alamine336 in different concentration of HCl solutions. Most of Pt and Pd could be extracted from the mixed chloride solution by adjusting HCl and Alamine336 concentration. However, the extraction percentage of Rh was found to be dependent on the extraction conditions and decreased with the increase of HCl concentration. Separation of Rh from the mixed solution containing Pt and Pd would be possible by extracting Pt and Pd at high HCl concentration. Adding $SnCl_2$ to the mixed solutions of the three platinum group metals has a favorable effect on the extraction of Rh, while the extraction of Pt and Pd was not affected. Our results could be utilized in developing a strategy to recover rhodium from the mixed solutions of platinum and palladium.

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References

1. Rao, C. R. M.; Reddi, G. S. *Trends in the Analytical Chemistry* **2000**, *19*, 565.
2. Benguerel, E.; Demopoulos, G. P.; Harris, G. B. *Hydrometallurgy* **1996**, *40*, 135.
3. Lee, M. S; Lee, J. Y.; Rajesh Kumar J.; Kim J. S.; Sohn J. S. *Materials Transactions* **2008**, *49*, 2823.
4. Zou, L.; Chen, J.; Pan, X. *Hydrometallurgy* **1998**, *50*, 193.
5. Mhaske, A. A.; Dhadke, P. M. *Hydrometallurgy* **2001**, *61*, 143.
6. Shafiqul, A. M.; Inoue, K. *Hydrometallurgy* **1997**, *46*, 373.
7. Levitin, G.; Schmuckler, G. *Reactive & Functional Polymers* **2003**, *54*, 149.
8. Mhaske, A.; Dhadke, P. *Separation Science and Technology* **2001**, *36*, 3253.
9. Nowottny, C.; Halwachs, W.; Schügerl, K. *Separation and Purification Technology* **1997**, *12*, 135.
10. Lee, M. S.; Lee, K. J.; Oh, Y. J. *Mater. Trans.* **2004**, *45*, 2364.
11. Gai, H. F.; Shen, J. L.; Hughes, M. A. *Hydrometallurgy* **1990**, *25*, 293.
12. Filiz, M. *Hydrometallurgy* **2007**, *87*, 58.
13. Sayar, N.A.; Filiz, M.; Sayar, A. A. *Hydrometallurgy* **2007**, *86*, 27.
14. Iwasaki, S.; Nagai, T.; Miki, E.; Mizumachi, K.; Ishimori, T.; *Chem. Bull. Soc. Jpn* **1984**, *57*, 386.