Solvent Extraction of PtCl$_4$ from Hydrochloric Acid Solution with Alamine336

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We have conducted solvent extraction of Pt(IV) from HCl solution with Alamine336. Solvent extraction reaction in our system was determined from the experimental results by graphical method. The equilibrium constant of the solvent extraction reaction was estimated from our experimental results by considering the activity coefficients of chemical species present in the aqueous phase with Bromley equation. Bromley interaction parameter between hydrogen ion and PtCl$_6^{2-}$ was evaluated from the solvent extraction data reported in the literature. The equilibrium constant for the solvent extraction reaction was estimated from the measured distribution coefficients of Pt(IV) agreed well with those calculated in this study.

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**Keywords:** PtCl$_4$, solvent extraction, Alamine336, HCl

1. Introduction

Platinum group metals are very expensive and their specific physical and chemical properties have made them important materials for the automobile, chemical, and electronics industry. Pt, Pd and Rh are used in automobile catalysts to reduce the emission levels from the exhaust gases and the automobile industry is the major consumer of Pt, Pd and Rh is used in automobile catalysts to reduce the emission levels from the exhaust gases and the automobile industry is the major consumer of platinum group metals. Since platinum has aesthetic qualities and a permanent luster, it is also used in the manufacture of jewelry. Substitution of platinum metal in catalysts by other metals is difficult. Since the resources of the platinum metal are limited, platinum should be recovered not only from its natural ores but also from the industrial wastes. Development of an effective separation process to recover platinum from these resources, especially spent automotive catalysts, is very important.

Separation and purification of platinum group metals is one of the most difficult processes of metal separation, because of the similarity in their chemical behavior in chloride media. The most prominent feature of the aqueous chemistry of platinum group metals in chloride solution is the strong tendency of the metals to form anion complexes with chloride ion. Since the concentration of platinum group metals in industrial wastes is very low, ion exchange and solvent extraction have been widely employed to separate and recover them. Solvent extraction of Pt(IV) with various extractants has been reported.

Alamine336 (Tertiary amine, R$_3$N, R = CH$_3$(CH$_2$)$_7$), a sort of anionic extractants, is also used extensively in extracting various metal ions. In this study, solvent extraction of Pt(IV) from chloride solution by Alamine336 has been performed in the low concentration range of Pt(IV) at moderate HCl concentration. Solvent extraction reaction in our experimental range was identified from the experimental data. Interaction parameter between H$^+$ and PtCl$_6^{2-}$, which is necessary to calculate the activity coefficient of PtCl$_6^{2-}$, was evaluated from the solvent extraction data reported in the literature. The equilibrium constant for the solvent extraction reaction of Pt(IV) by Alamine336 was estimated from our experimental data by considering the activity coefficients of solutes in the aqueous phase.

2. Experimental

Stock solution of platinum(IV) was prepared by dissolving PtCl$_4$ (Aldrich, 98%) and HCl in distilled water. Alamine336 was purchased from Henkel Corporation and used without further purification. Alamine336 was diluted with toluene. Equal volume (30 cm$^3$) of aqueous and organic phase was placed in a 100 cm$^3$ separatory funnel and shaken for 15 min with a mechanical shaker. The aqueous phase was separated after settling the mixture for 1 h. All the experiments were conducted at a temperature of 25 ± 1°C. The concentration of Pt(IV) in the aqueous phase was measured with ICP-OES (Spectroflame EOP). The concentration of Pt in the organic phase was calculated from the mass balance.

3. Results and Discussion

3.1 Solvent extraction of PtCl$_4$ with Alamine336

Figure 1 shows the effect of shaking time on the distribution coefficients of Pt(IV) at the extraction condition of Pt(IV) 5.0 × 10$^{-4}$ and HCl 1 kmol/m$^3$ with 0.002 and 0.005 kmol/m$^3$ Alamine336 (R$_3$N), respectively. In both concentrations of Alamine336, shaking time of 10 min was found to be sufficient to obtain equilibrium state. Therefore, the two phases were shaken for 15 min in further experiments.

It has been reported that Alamine336 reacts with HCl to form Alamine336 salt (R$_3$NHC$I$) in HCl solution and that this Alamine336 salt takes part in the solvent extraction reaction of metals. The following reaction represents the formation of Alamine336 salt in HCl solution.

\[
R_3N\text{org} + HCl = R_3NHCl\text{org}
\] (1)

In the above equation, subscript org represents organic phase.

Many studies have shown that most of the Pt(IV) in HCl solution exists as PtCl$_6^{2-}$. Table 1 lists the stepwise
stability constants for the formation of PtCl$_{5}$$^-$ and PtCl$_{6}^{2-}$.\textsuperscript{12} Distribution of Pt(IV) containing species with HCl concentration was obtained by considering the complex formation reaction shown in Table 1 together with the mass balance equations for Pt and Cl. The calculated mole fractions of Pt(IV) containing species are shown in Fig. 2 as a function of HCl concentration at the Pt(IV) concentration of 1.0 $\times$ 10$^{-3}$ kmol/m$^3$.

Figure 2 reveals that PtCl$_{6}^{2-}$ is the predominant species in our experimental range. Therefore, the following reaction may be responsible for the solvent extraction reaction of Pt(IV) from HCl solution by Alamine336.\textsuperscript{13}

\[
\text{PtCl}_6^{2-} + 2\text{R}_3\text{NH}_{\text{org}} = \text{PtCl}_6(\text{R}_3\text{NH})_{2\text{org}} + 2\text{Cl}^- \quad (2)
\]

Figure 3 shows the effect of HCl concentration on the distribution coefficients of Pt(IV) when the initial concentrations of Pt(IV) and Alamine336 were 4.3 $\times$ 10$^{-4}$ and 0.002 kmol/m$^3$, respectively. The distribution coefficients of Pt(IV) decreased with the increase of HCl concentration.

Figures 4 and 5 show the effect of Alamine336 concentration on the distribution coefficients of Pt(IV) from HCl solution of 1.0 and 3.0 kmol/m$^3$, respectively. In Fig. 4, the initial concentration of Pt(IV) was 4.3 $\times$ 10$^{-4}$ kmol/m$^3$, while the initial concentration of Pt(IV) in Fig. 5 was 9.1 $\times$ 10$^{-4}$ kmol/m$^3$. In both figures, the concentration range of Alamine336 was from 0.002 to 0.007 kmol/m$^3$. Figures 4 and 5 show that log $D$ increases linearly with the increase of log $[\text{R}_3\text{N}]$ in the experimental range and the slope is close to unity.

Figure 6 shows the effect of Pt(IV) concentration when Alamine336 and HCl concentrations were fixed at 0.002 and 1.0 kmol/m$^3$, respectively. The logarithm of Pt(IV) concentration in organic phase is proportional to that of Pt(IV) in the aqueous phase and the slope of this plot is unity, indicating

### Table 1 Stepwise stability constant for the formation of Pt(IV)-chloro complexes at 25°C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl$_4$$^-$$ + $Cl$^- = PtCl$_5$$^-$$</td>
<td>2.016</td>
</tr>
<tr>
<td>PtCl$_5$$^-$$ + $Cl$^- = PtCl$_6$$^{2-}$</td>
<td>2.010</td>
</tr>
</tbody>
</table>

![Fig. 1 Effect of shaking time on the distribution coefficients of Pt(IV) at the initial extraction condition of 5 $\times$ 10$^{-4}$ kmol/m$^3$ Pt(IV) and 1 kmol/m$^3$ HCl.](image1)

![Fig. 2 Distribution of Pt(IV) containing species with HCl concentration at the initial Pt concentration of 1.0 $\times$ 10$^{-3}$ kmol/m$^3$.](image2)

![Fig. 3 Effect of HCl concentration on the extraction of Pt(IV) at the initial Alamine336 concentration of 0.002 kmol/m$^3$. ([PtCl$_4$]$_{\text{total}}$ = 4.3 $\times$ 10$^{-4}$ kmol/m$^3$)](image3)
that the extracted Pt(IV) species exists as a monomer in the organic phase.

Equation (2) suggests that the slope of the straight line in a plot of log D against log \([R_3N]\) should be about two. However, the slope of the straight lines in Fig. 4 was close to unity, indicating that one mole of Alamine336 reacts with one mole of PtCl\(_2\)/C\(_0\) in our experimental range. Some studies have reported that amine extractant can form double salt when the amount of acid is in excess to amine.\(^{14,15}\)

Therefore, Alamine336 can form double salt with excess HCl, which is represented by

\[
R_3NHCl_{org} + HCl = R_3NH_2Cl_{org} \quad (3)
\]

The dependence of log D on log \([R_3N]\) in Figs. 4 and 5 suggests the following reaction to occur in our experimental ranges rather than eq. (2).

\[
PtCl_2^{2-} + R_3NH_2Cl_{org} = PtCl_6^{4-}R_3NH_2_{org} + 2Cl^- \quad (4)
\]

### 3.2 Evaluation of the interaction parameter between H\(^+\) and PtCl\(_2^{2-}\)

We used Bromley equation to calculate the activity coefficients of chemical species present in the aqueous phase. The following equation represents Bromley equation for cation M at 25°C.\(^{16}\)

\[
\log \gamma_M = \frac{-0.5108(z_M)^2I_{0.5}}{1 + I_{0.5}} + F_M = -A(z_M)^2 + F_M \quad (5)
\]

\[
F_M = \sum_X \left[ \frac{(0.06 + 0.6B_{MX}) \times |z_Mz_X|}{1 + \frac{1.5}{|z_Mz_X|}^2} + B_{MX} \right] \times \frac{(|z_M| + |z_X|)^2}{4} \cdot [X] \quad (6)
\]

In the above equations, \(z\) is the ionic charge and I ionic strength of a solution and B\(_{MX}\) the interaction parameter between cation M and anion X.

In calculating the activity coefficients of solutes present in our system by Bromley equation, the activity coefficients of chloride ion and PtCl\(_2^{2-}\) depend on the concentration of H\(^+\) and the interaction parameter between these two ions and hydrogen ion. The value of B\(_{HCl}\) was obtained from the data reported by Bromley,\(^{16}\) while there is no Bromley interac-
tion parameter between PtCl$_4^{2-}$ and H$^+$. Lokhande et al. reported the data on the solvent extraction of Pt(IV) from HCl solution by N-n-octylaniline (RR’NH, $R = C_8H_8$, $R’ = CH_2(CH_2)_2CH_3$). We evaluated Bromley interaction parameter between PtCl$_4^{2-}$ and H$^+$ from these data. They supposed the following reaction to represent the solvent extraction of Pt(IV) from HCl solution by N-n-octylaniline.

\[
\text{RR’NH}_{\text{org}} + \text{HCl} = \text{RR’NH}_2\text{Cl}_{\text{org}} \quad (7)
\]

\[
\text{PtCl}_6^{2-} + 2\text{RR’NH}_2\text{Cl}_{\text{org}} = \text{PtCl}_6(\text{RR’NH})_2_{\text{org}} + 2\text{Cl}^- \quad (8)
\]

The equilibrium constant of the above reaction can be represented as follows:

\[
K_{ex}^o = \frac{[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]^2 \times [\text{Cl}^-]^2}{[\text{PtCl}_6^{2-}] [\text{RR’NH}_2\text{Cl}_{\text{org}}]^2} \quad (9)
\]

In the above equation, $K_{ex}^o$ and $K_{ex}^I$ represent the equilibrium constant of the solvent extraction reaction at ionic strength of zero and I, respectively.

Taking logarithms on both sides of the above equation leads to

\[
\log K_{ex}^o = \log K_{ex}^I + 2 \log \gamma_{\text{Cl}^-} - \log \gamma_{\text{PtCl}_4^{2-}} + \log \frac{[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]}{[\text{PtCl}_6^{2-}] [\text{RR’NH}_2\text{Cl}_{\text{org}}]} \quad (10)
\]

Expression for the activity coefficient of PtCl$_4^{2-}$ by Bromley equation becomes

\[
\log \gamma_{\text{PtCl}_4^{2-}} = -4A + \left[ \frac{2(0.06 + 0.6B_{\text{H}^+,\text{PtCl}_4^{2-}})}{1 + \frac{1.5}{2}} \right] + B_{\text{H}^+,\text{PtCl}_4^{2-}}^2 \times \frac{3^2}{4} [\text{H}^+] \quad (11)
\]

Substitution of the above equation into eq. (10) results in

\[
\log K_{ex}^I + 2 \log \gamma_{\text{Cl}^-} + 4A
= \log K_{ex}^o + \left[ \frac{2(0.06 + 0.6B_{\text{H}^+,\text{PtCl}_4^{2-}})}{1 + \frac{1.5}{2}} \right] + B_{\text{H}^+,\text{PtCl}_4^{2-}}^2 \times \frac{9}{4} [\text{H}^+] - \log \frac{[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]}{[\text{PtCl}_6^{2-}] [\text{RR’NH}_2\text{Cl}_{\text{org}}]} \quad (12)
\]

The value of $K_{ex}^I$ was obtained from the experimental results reported by Lokhande and the activity coefficient of chloride ion was calculated by Bromley equation. In Lokhande’s experimental condition, the volume ratio of aqueous to organic phase was kept at 2.5. Therefore, the following mass balance equations were used in calculating $K_{ex}^I$ from their experimental results.

\[
[\text{PtCl}_6 (\text{RR’NH})_2_{\text{org}}] = \left( \frac{V_{\text{org}}}{V_{\text{aq}}} \right) ([\text{Pt}]_{\text{total}} - [\text{Pt}]_{\text{aq}}) \quad (13)
\]

\[
[\text{RR’NH}_2\text{Cl}_{\text{org}}] = [\text{RR’NH}_2\text{Cl}_{\text{total}}] - 2[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}] \quad (14)
\]

\[
[\text{Cl}^-] = [\text{HCl}_{\text{total}}] + 4[\text{PtCl}_4_{\text{total}}] - 6[\text{PtCl}_6^{2-}] \quad (15)
\]

\[
[V_{\text{org}}/V_{\text{aq}}] = 6[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}] + [\text{RR’NH}_2\text{Cl}_{\text{org}}] \quad (15)
\]

In order to estimate the equilibrium constant of solvent extraction reaction, eq. (4), the equilibrium concentrations and activity coefficients of chemical species present in both phases are required. In calculating the equilibrium concentrations of chemical species present in the aqueous phase of our system, it was assumed that all of the Pt(IV) in the aqueous phase exists as PtCl$_6^{2-}$. The concentration of HCl employed in this study was from 0.1 to 3.0 kmol/m$^3$. The concentration of hydroxide ion can be ignored at this HCl concentration range. On this assumption, the following mass and charge balance equations were obtained when the volume ratio of aqueous to organic was unity.

\[
[\text{PtCl}_6^{2-}]_{\text{total}} = [\text{PtCl}_6^{2-}] + [\text{PtCl}_6(\text{RR’NH})_2] \quad (18)
\]

\[
[R_3N]_{\text{total}} = [R_3\text{NH}_2\text{Cl}_2] + [\text{PtCl}_6(\text{RR’NH})_2] \quad (19)
\]

\[
[\text{Cl}^-]_{\text{total}} = 4[\text{PtCl}_4_{\text{total}}] + [\text{HCl}]_{\text{total}} \quad (20)
\]

\[
[\text{Cl}^-] + 6[\text{PtCl}_6^{2-}] + 2[R_3\text{NH}_2\text{Cl}_2] + 6[\text{PtCl}_6(\text{RR’NH})_2]
\]

\[
= [\text{RR’NH}_2\text{Cl}_{\text{org}}] = [\text{RR’NH}_2\text{Cl}_{\text{total}}] - 2[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]
\]

\[
= [\text{RR’NH}_2\text{Cl}_{\text{org}}] = [\text{RR’NH}_2\text{Cl}_{\text{total}}] - 2[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]
\]

\[
= [\text{RR’NH}_2\text{Cl}_{\text{org}}] = [\text{RR’NH}_2\text{Cl}_{\text{total}}] - 2[\text{PtCl}_6(\text{RR’NH})_2_{\text{org}}]
\]
The number of chemical species present in both phases after extraction is 7 (\(\text{Cl}^-\), \(\text{H}^+\), \(\text{PtCl}_4^{2-}\), \(\text{R}_3\text{NH}_2\text{Cl}_2\), \(\text{PtCl}_4\text{R}_3\text{NH}_2\), \(\text{H}_2\text{O}\), toluene). In order to calculate the concentrations of these 5 species excluding \(\text{H}_2\text{O}\) and toluene, 5 independent equations are required. These 5 equations were obtained from solvent extraction reaction, three mass balance equations, and charge balance. The solution of these 5 nonlinear equations was obtained by using Newton-Raphson method. Since few equations are available to calculate the activity coefficients of chemical species present in the organic phase, the activity coefficients of Alamine336 double salt and the extracted species were assumed to be unity.

In order to estimate the above equilibrium constant from the extraction data, an evaluation function was defined as follows:

\[
\begin{align*}
\log D_{\text{calc}} &= \text{logD}_{\text{expt}} \\
\text{Err} &= \frac{1}{N} \sum (D_{\text{calc}} - D_{\text{meas}})^2
\end{align*}
\]

where \(N\) denotes the number of experimental data and \(D_{\text{calc}}\) and \(D_{\text{meas}}\) represent the distribution coefficient of Pt(IV) calculated in this study and measured, respectively. The following equilibrium constant was obtained by minimizing the Err function.

\[
K_{ex} = \frac{[\text{PtCl}_4\text{R}_3\text{NH}_2][\text{Cl}]^2}{[\text{PtCl}_6^{2-}][\text{R}_3\text{NH}_2\text{Cl}_2][\text{PtCl}_4^{2-}]} = 1.9 \times 10^3
\]

Table 2 gives the experimental conditions along with the results of extraction experiment. Figure 8 shows the measured distribution coefficients of Pt(IV) and the calculated values. The distribution coefficients of Pt(IV) calculated from the initial extraction conditions by using the above equilibrium constant are also shown in Table 2. It is seen in Table 2 and Fig. 8 that the difference between measured and calculated distribution coefficients of Pt(IV) is wide when HCl concentration is lower than 0.5 kmol/m³. When HCl concentration is low, Alamine336 may exist as an Alamine336 salt (\(\text{R}_3\text{NHCl}\)) instead of a double salt (\(\text{R}_3\text{NH}_2\text{Cl}_2\)). This difference in the form of Alamine336 salt at low and high HCl concentration may be the reason of the wide difference between the measured and calculated distribution coefficients of Pt(IV). Standard deviation between the measured and calculated distribution coefficients of Pt(IV) was 0.06. Therefore, it can be safely said that the proposed solvent extraction reaction and equilibrium constant estimated in this study might well represent the reaction occurring in the experimental ranges where HCl concentration is larger than 0.5 kmol/m³.

4. Conclusions

Chemical speciation of \(\text{PtCl}_4\text{HCl}-\text{H}_2\text{O}\) system indicates that most of the Pt(IV) in the solution exists as \(\text{PtCl}_4^{2-}\) in our experimental range. Applying slope analysis method to the

![Fig. 8 Comparison of the distribution coefficients of Pt(IV) between measured and calculated in this study.](image-url)
Experimental results revealed that one mole of Alamine336 reacts with one mole of $\text{PtCl}_6^{2-}$. Solvent extraction reaction was supposed to explain this dependence of Pt(IV) extraction on Alamine336 concentration. The equilibrium constant for this reaction was estimated from the experimental results by considering the activity coefficients of chemical species present in the aqueous phase with Bromley equation. The interaction parameter between $\text{H}^+$ and $\text{PtCl}_6^{2-}$ was evaluated from the data reported in the literature by using Bromley equation. The followings represent solvent extraction reaction supposed by us and the corresponding equilibrium constant estimated in this study.

$$\text{PtCl}_6^{2-} + \text{R}_3\text{NH}_2\text{Cl}_{2,\text{org}} = \text{PtCl}_6\text{R}_3\text{NH}_2,\text{org} + 2\text{Cl}^-, \quad K_{\text{ex}} = 1.9 \times 10^3$$

The measured distribution coefficients of Pt(IV) agreed well with those predicted by using the above equilibrium constant from the initial extraction conditions.

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