Estimation of Thermodynamic Properties and Ionic Equilibria of Cobalt Chloride Solution at 298 K

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We developed a chemical model to analyze ionic equilibria in a cobalt chloride solution at 298 K. The chemical model consisted of chemical equilibria, mass and charge balance equations. The activity coefficients of solutes and water activity were calculated with Bromley equation. Values of the equilibrium constants for the formation of cobalt chloride complexes at zero ionic strength and of the interaction parameters were estimated by applying Bromley equation to the reported equilibrium constants at different ionic strength. The effect of CoCl₂ and HCl concentrations on the distribution of cobalt species was obtained. The predicted pH values for CoCl₂·HCl·NaOH·H₂O system agreed well with those measured at 298 K.

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Keywords: CoCl₂, HCl, equilibrium constant, Bromley, pH

1. Introduction

Cobalt is a strategically important metal as an alloying element in superalloys for aircraft engines, magnetic alloys, hard metal alloys for cutting tool and electrodeposited alloys to provide wear and corrosion-resistant metal coatings. In a hydrometallurgical route for the production of cobalt, separation of cobalt and nickel is one of the most difficult operations owing to the similarities in chemical nature of the two metals. Many studies have been performed on the separation of cobalt and nickel by employing solvent extraction.

Information of the distribution of cobalt and nickel species with the composition of a solution is valuable in choosing an extractant suitable for the separation of cobalt and nickel. In order to analyze the ionic equilibria of the mixed solution of CoCl₂ and NiCl₂, ionic equilibria of the respective solutions need to be developed. We reported the ionic equilibria analysis of NiCl₂ solution. Few studies, however, have been reported on the equilibria of cobalt chloride solution at high ionic strength.

In this study, ionic equilibria for the CoCl₂ in chloride solution were analyzed by considering chemical equilibria, mass and charge balance equations. Thermodynamic properties, such as equilibrium constants for the formation of cobalt chloride complexes at zero ionic strength and interaction parameter, were estimated by applying Bromley equation to the reported equilibrium constant at different ionic strength. The activity coefficient of chemical species was also calculated with Bromley equation. The validity of the ionic equilibria for the CoCl₂·HCl·NaOH·H₂O system at 298 K was verified by comparing the measured values of solution pH with those calculated in this study.

2. Experimental

Cobalt chloride solutions with different composition were prepared by dissolving CoCl₂·6H₂O, HCl and NaOH in distilled water. All chemicals were of reagent grade. First, known amounts of CoCl₂·6H₂O, HCl and NaOH were added to 50 g of distilled water and then the mixture was stirred with a magnetic stirrer until all the chemicals were dissolved. After all the chemicals were dissolved, the temperature of solution was controlled at 298 K by using a water bath. Once the temperature of the solution was stable, a pH of solution was measured with a pH meter (Orion 920A).

3. Results and Discussion

3.1 Estimation of the equilibrium constant

In chloride solution, cobalt ion forms various complexes with chloride and hydroxide ion and the complex formation reaction can be represented by

\[
\text{Co}^{2+} + i\text{Cl}^- \rightleftharpoons \text{CoCl}_{i}^{2-i}
\]

The equilibrium constant for eq. (1) at a given ionic strength, \( K_i^l \), is related to the equilibrium constant at zero ionic strength, \( K_i^0 \), and to the activity coefficient ratio as follows

\[
K_i^l = K_i^0 \frac{\gamma_{\text{CoCl}_{i}^{2-i}}}{\gamma_{\text{Co}^{2+}} \gamma_{\text{Cl}^-}^{i}}
\]

By taking logarithm on both sides of the above equation, it is rearranged as

\[
\log K_i^l = \log K_i^0 + \log \gamma_{\text{CoCl}_{i}^{2-i}} + i \log \gamma_{\text{Cl}^-} - \log \gamma_{\text{Co}^{2+}}
\]

The activity coefficient of solute was calculated by the Bromley equation. The Bromley equation for the activity coefficient of the cation, \( \gamma_M \), is represented by the following equations.

\[
\log \gamma_M = - \frac{0.5108(z_M^2 \gamma_{\text{Cl}^-}^{0.5})}{1 + F_M} + F_M = -A(z_M^2 + F_M)
\]

\[
F_M = \sum_X \left[ \frac{(0.06 + 0.6B_{MX}) \times (\frac{z_M^2 \gamma_X}{[X]})}{(1 + \frac{1.5}{[X]})} \right] + B_{MX}
\]
In the above equations, \( z \) is ionic charge and \( f \) ionic strength of solution and \( B_{MX} \) the interaction parameter between cation \( M \) and anion \( X \).

Substitution of the expression for the activity coefficient of each species into eq. (3) gives

\[
\log K_i^0 = \log K_i^0 + (i^2 - 5i)A + F_{Co^{2+}} + iF_{Cl^{-}} - F_{CoCl^{2-}}
\]

(6)

Table 2 represents the equilibrium constants for the formation of cobalt chloride complexes at different HClO\(_4\) concentration. 6) The concentrations of Co\(^{2+}\), Co\(^{3+}\), Cl\(^-\) and CoCl\(^{2-}\) are negligible compared to the HClO\(_4\) concentration in these studies. 7, 8) Hence, \( F \) term for the activity coefficient of the anion is related only to the cation H\(^+\) of the ionic medium, while \( F \) term for the activity coefficient of cation is related to the anion ClO\(_4\)\(^-\) of the ionic medium. 7, 8) In this case, \( F \) terms for Co\(^{2+}\), Cl\(^-\) and CoCl\(^+\) could be represented by

\[
F_{Co^{2+}} = \left[ \frac{2(0.06 + 0.6B_{Co^{2+},ClO_4}^+)}{(1 + 1.5I)^2} + B_{Co^{2+},ClO_4}^+ \right] \times \frac{3^2}{4} [ClO_4^-]
\]

(7)

\[
F_{Cl^-} = \left[ \frac{0.06 + 0.6B_{H^+},Cl^-}{(1 + 1.5I)^2} + B_{H^+,Cl^-} \right] \times \frac{2^2}{4} [H^+]
\]

(8)

\[
F_{CoCl^-} = \left[ \frac{0.06 + 0.6B_{CoCl^{2-},ClO_4}}{(1 + 1.5I)^2} + B_{CoCl^{2-},ClO_4} \right] \times \frac{2^2}{4} [ClO_4^-]
\]

(9)

Substitution of eqs. (7)–(9) into eq. (6) results in

\[
\log K_i^1 = \log K_i^0 - 4A + \left[ \frac{2(0.06 + 0.6B_{Co^{2+},ClO_4}^+)}{(1 + 1.5I)^2} + B_{Co^{2+},ClO_4}^+ \right] \times \frac{9}{4} [ClO_4^-] + \left[ \frac{0.06 + 0.6B_{H^+},Cl^-}{(1 + 1.5I)^2} + B_{H^+,Cl^-} \right] \times [H^+] - \left[ \frac{0.06 + 0.6B_{CoCl^{2-},ClO_4}}{(1 + 1.5I)^2} + B_{CoCl^{2-},ClO_4} \right] \times [ClO_4^-]
\]

(10)

The logarithm of equilibrium constant thus calculated was 0.401. This indicates that the calculated equilibrium constant agrees well with the value estimated in this study.

The interaction parameter of CoCl\(^+\) was calculated from the \( B_{CoCl^{2-},ClO_4} \) by inserting the interaction parameter of ClO\(_4\)\(^-\) reported by Bromley into the following equation.

\[
B_{CoCl^{2-},ClO_4} = B_{CoCl^-} + B_{ClO_4^-}
\]

(12)

Activity coefficients of electrically neutral species could not be calculated with the Bromley equation. Consequently the activity coefficient of CoCl\(^{2+}\) was assumed to be unity.
3.2 Ionic equilibria analysis

Mass balance equations for chloride and cobalt were obtained from the above chemical equilibria as follows:

\[
[\text{CoCl}_4]^- = 2[\text{CoCl}_2]^- + [\text{HCl}] - [\text{Cl}^-] + [\text{CoCl}^+] \\
+ 2[\text{CoCl}_2^-] + 3[\text{CoCl}_3^-] + 4[\text{CoCl}_2^{2-}] \quad (13)
\]
\[
[\text{Co}]_t = [\text{CoCl}_2]^- = [\text{Co}_3^+] + [\text{CoCl}^+] + [\text{CoCl}_2^-] \\
+ [\text{Cl}^-] + [\text{CoCl}_2^-] + [\text{CoCl}_2^-] + [\text{OH}^+] \\
+ [\text{Co}_2(\text{OH})_2^+] + 2[\text{Co}_2(\text{OH})_2^{3+}] + 2[\text{Co}_2(\text{OH})_2^{4+}] \quad (14)
\]
\[
[\text{Na}]_t = [\text{NaOH}] = [\text{Na}^+] \quad (15)
\]

Where subscript \( t \) represents the total concentration.

The following charge balance equation was obtained from electroneutrality condition.

\[
[\text{H}^+] + 2[\text{Co}_2^+] + [\text{CoCl}^+] + [\text{COOH}^+] + 3[\text{Co}_2(\text{OH})_2^{3+}] + 4[\text{Co}_2(\text{OH})_2^{4+}] + [\text{Na}^+] \\
= [\text{Cl}^-] + [\text{ClCo}_3^-] + 2[\text{CoCl}_2^{2-}] + [\text{OH}^-] \quad (16)
\]

In CoCl₂-HCl-NaOH-H₂O system, there were 13 solutes in the equilibrium state, i.e., [Cl⁻], [Co²⁺], [Co³⁺], [CoCl₂⁻], [CoCl₃⁻], [Co(OH)₂⁻], [Co(OH)₃⁺], [Co₂(OH)₄²⁺], [H⁺], [Na⁺], [OH⁻]. In order to calculate the equilibrium concentrations and activity coefficients of these 13 solutes and the activity of water, 27 independent equations were needed. These equations were obtained from 9 chemical equilibria shown in Table 3, 3 mass balance and charge balance, 13 activity coefficient equations of solutes and activity equation of water. These nonlinear equations were solved by Newton-Raphson method.

Table 5 shows the experimental compositions of CoCl₂-HCl-NaOH-H₂O system together with pH values experimentally measured at 25°C. Also pH values and the ionic strength calculated in this study are shown in Table 5. Both measured and calculated pH values are shown in Fig. 1. From Table 5 and Fig. 1, it is known that the experimental pH values are in good agreement with the calculated values in the experimental ranges considered in this study. This verifies that not only the Bromley equation but also the thermodynamic properties of cobalt chloride obtained in this study were applicable to cobalt chloride solutions.

Figures 2 and 3 show the distribution of cobalt chloride and hydroxide complexes with CoCl₂ concentration in the absence of HCl. It is seen in Fig. 2 that most of cobalt exist as

---

### Table 3 Thermodynamic equilibrium constant for the formation of complexes.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log ( K )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ + \text{OH}^- = \text{H}_2\text{O} )</td>
<td>14.0</td>
<td>6</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + \text{Cl}^- = \text{CoCl}^+ )</td>
<td>0.22</td>
<td>obtained in this study</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + 2\text{Cl}^- = \text{CoCl}_2^- )</td>
<td>-3.95</td>
<td>9</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + 3\text{Cl}^- = \text{CoCl}_3^- )</td>
<td>-3.02</td>
<td>obtained in this study</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + 4\text{Cl}^- = \text{CoCl}_4^- )</td>
<td>-9.06</td>
<td>obtained in this study</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + \text{OH}^- = \text{CoOH}^+ )</td>
<td>4.3</td>
<td>6</td>
</tr>
<tr>
<td>( \text{Co}^{3+} + 2\text{OH}^- = \text{Co(OH)}_2^+ )</td>
<td>8.4</td>
<td>6</td>
</tr>
<tr>
<td>( 2\text{Co}^{3+} + \text{OH}^- = \text{Co}_2(\text{OH})_2^{2+} )</td>
<td>2.7</td>
<td>6</td>
</tr>
<tr>
<td>( 4\text{Co}^{3+} + 4\text{OH}^- = \text{Co}_2(\text{OH})_4^{4+} )</td>
<td>25.6</td>
<td>6</td>
</tr>
</tbody>
</table>

### Table 4 Free energy change for the formation of \( \text{Co}^{3+}, \text{Cl}^- \) and \( \text{CoCl}^+ \) reported by Russian Academy of Science.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^o ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}^{3+} )</td>
<td>-53.64</td>
</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>-131.265</td>
</tr>
<tr>
<td>( \text{CoCl}^+ )</td>
<td>-187.192</td>
</tr>
</tbody>
</table>

### Table 5 Experimental conditions and calculated values of pH and ionic strength. (The unit of concentration was molality)

<table>
<thead>
<tr>
<th>( N )</th>
<th>( [\text{CoCl}_2]_t )</th>
<th>( [\text{HCl}]_t )</th>
<th>( [\text{NaOH}]_t )</th>
<th>pH</th>
<th>pH( _{calc} )</th>
<th>IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
<td>1.20</td>
<td>1.14</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.5</td>
<td>0.4</td>
<td>1.09</td>
<td>1.12</td>
<td>0.78</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0.5</td>
<td>0.4</td>
<td>0.80</td>
<td>0.97</td>
<td>3.29</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.12</td>
<td>0.21</td>
<td>3.80</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.8</td>
<td>0.68</td>
<td>0.61</td>
<td>3.81</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>2.0</td>
<td>0.5</td>
<td>-0.26</td>
<td>-0.40</td>
<td>4.79</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>-0.19</td>
<td>-0.22</td>
<td>4.81</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>2.0</td>
<td>1.7</td>
<td>0.49</td>
<td>0.30</td>
<td>4.84</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>2.0</td>
<td>2.3</td>
<td>5.78</td>
<td>5.32</td>
<td>5.00</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>0.5</td>
<td>0.4</td>
<td>0.68</td>
<td>0.73</td>
<td>6.13</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>-0.20</td>
<td>-0.03</td>
<td>6.57</td>
</tr>
<tr>
<td>12</td>
<td>2.0</td>
<td>1.0</td>
<td>1.1</td>
<td>5.34</td>
<td>5.19</td>
<td>6.67</td>
</tr>
<tr>
<td>13</td>
<td>2.0</td>
<td>2.0</td>
<td>0.5</td>
<td>-0.50</td>
<td>-0.63</td>
<td>7.24</td>
</tr>
<tr>
<td>14</td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
<td>-0.43</td>
<td>-0.45</td>
<td>7.32</td>
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<tr>
<td>15</td>
<td>2.0</td>
<td>2.0</td>
<td>1.7</td>
<td>0.27</td>
<td>0.06</td>
<td>7.43</td>
</tr>
<tr>
<td>16</td>
<td>2.0</td>
<td>2.0</td>
<td>2.3</td>
<td>5.12</td>
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<td>7.63</td>
</tr>
<tr>
<td>17</td>
<td>3.0</td>
<td>1.0</td>
<td>0.5</td>
<td>-0.18</td>
<td>-0.23</td>
<td>8.58</td>
</tr>
<tr>
<td>18</td>
<td>3.0</td>
<td>1.0</td>
<td>0.8</td>
<td>0.11</td>
<td>0.16</td>
<td>8.67</td>
</tr>
<tr>
<td>19</td>
<td>3.0</td>
<td>1.0</td>
<td>1.1</td>
<td>4.90</td>
<td>4.97</td>
<td>8.81</td>
</tr>
</tbody>
</table>

(N: number, pH: measured values of pH, pH\( _{calc} \): values of pH calculated in this study, IC: values of ionic strength calculated in this study)
Co\(^{2+}\) in the concentration range of up to 3 m CoCl\(_2\). As the CoCl\(_2\) concentration increased, the mole fraction of CoCl\(_3^-\), CoCl\(_4^{2-}\) and CoCl\(_{5/2}^{3-}\) greatly increased while that of CoCl\(^{+}\) remained constant. The mole fraction of CoOH\(^+\) and Co(OH)\(_2^{2+}\) decreased with an increase in the CoCl\(_2\) concentration while that of Co\(_3\)OH\(^{3+}\) increased. The mole fraction of Co\(_4\)(OH)\(_4^{4+}\) increased with CoCl\(_2\) concentration and then decreased gradually with a further increase in the CoCl\(_2\) concentration after reached a maximum. By comparing Figs. 2 and 3, it is known that the mole fractions of CoOH\(^+\) and Co\(_3\)OH\(^{3+}\) are higher than that of CoCl\(_4^{2-}\).

Figures 4 and 5 show the distribution of cobalt chloride and hydroxide complexes with HCl concentration when CoCl\(_2\) concentration was 1.0 m. It is seen in Fig. 4 that most of cobalt exists as Co\(^{2+}\) up to 2.0 m HCl concentration. The mole fraction of CoCl\(_2^{+}\), CoCl\(_3^-\) and CoCl\(_4^{2-}\) increased with HCl concentration while that of CoCl\(^{+}\) remained constant. From Fig. 5, it is known that the mole fraction of cobalt hydroxide complexes was very low in the solution containing HCl.
Mean activity coefficients of CoCl$_2$ were calculated by the following equation from the activity coefficient of Co$^{2+}$ and Cl$^-$ calculated with the Bromley equation.

$$\gamma_{\pm,\text{CoCl}_2} = (\gamma_{\text{Co}^{2+}} \cdot \gamma_{\text{Cl}^-})^{1/3}$$

Figure 6 shows mean activity coefficients of CoCl$_2$ calculated and those obtained from literature.$^{11}$

It is seen in Fig. 6 that mean activity coefficients of CoCl$_2$ experimentally measured agreed well with those calculated in this study.

4. Conclusions

By considering chemical equilibria, mass and charge balance equations for CoCl$_2$-HCl-NaOH-H$_2$O system at 298 K, ionic equilibria were analyzed. The equilibrium constants for the formation of cobalt chloride complexes at zero ionic strength and the interaction parameter were estimated by applying the reported equilibrium constants at different ionic strength to the Bromley equation. The distribution of cobalt complexes with CoCl$_2$ and HCl concentrations was obtained by applying ionic equilibria. In the experimental ranges up to ionic strength of 8.8 m, the measured and calculated pH values were in good agreement.

REFERENCES