Chemical Equilibria in a Mixed Solution of Nickel and Cobalt Chloride

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Ionic equilibria in the mixed solution of nickel and cobalt chloride were analyzed by considering the complex formation reactions, the mass and charge balance equations. The activity coefficients of solutes and water activity were calculated by using Bromley equation. Cobalt ion has a strong tendency to form various complexes with chloride ion, such as CoCl_3^- and CoCl_4^{2-} , while NiCl^+ was the only complex formed between nickel and chloride ion. Distribution of nickel and cobalt species with the compositions and pH values of the solution was obtained from the analysis of ionic equilibria in the mixed chloride solutions. The predicted pH values for $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system agreed well with those measured at 298 K up to ionic strength of 9.53 mol/kg.

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1. Introduction

Similarity in the chemical nature of nickel and cobalt has made it difficult to separate the two metals. Many studies have been performed on the solvent extraction separation of nickel and cobalt with various extractants.¹⁻³⁾ The optimum condition to separate the two metals with solvent extraction depends on the various factors, such as the nature of the leaching solution and the concentration ratio of the two metals. In chloride solution, cobalt ion has a strong tendency to form complexes with chloride ion, such as CoCl_2° , CoCl_3^- and CoCl_4^{2-} .⁴⁾ However, it was found from the speciation of nickel chloride solution that most of nickel is present as Ni^{2+} and NiCl^+ .^{5,6)}

The difference between nickel and cobalt in the tendency to form chloride complexes was utilized to separate the two metals from chloride solution with an anionic extractant.³⁾ The data on the distribution of nickel and cobalt species with the composition of the mixed chloride solution enable us to analyze the solvent extraction equilibria of nickel and cobalt from chloride solution. We have already reported the ionic equilibria of nickel chloride in HCl solution.⁵⁾ We applied Bromley equation to estimate the equilibrium constants for the formation of cobalt chloride complexes and the interaction parameter.⁴⁾

In this study, we analyzed the ionic equilibria in the mixed solution of nickel and cobalt chloride at high ionic strength. For this purpose, the complex formation reactions, the mass and charge balance equation were considered. The activity coefficients of solutes and water activity were calculated by using Bromley equation.⁷⁾ Distribution of nickel and cobalt species with the composition of the mixed solution was obtained. The measured pH values for the $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system at 298 K were compared with the calculated values in this study.

2. Experimental

Mixed solutions of nickel and cobalt chloride were prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, HCl and

NaOH in distilled water. All chemicals were of reagent grade. First, known amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, HCl and NaOH were added to 100 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 the solution was controlled to 298 K by using a water bath. Once the temperature of the solution was stable, solution pH was measured with a pH meter (Orion 920A).

3. Results and Discussion

3.1 Chemical model

Table 1 shows the formation reactions of various nickel complexes considered in this study and the corresponding equilibrium constants at zero ionic strength.^{8,9)} Unlike nickel complexes, the equilibrium constants for the formation of cobalt chloride complexes were reported at different ionic strength of HClO_4 medium and are shown in Table 2.⁸⁾ The formation reaction of CoCl^+ can be represented by

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

$$K^0 = K^I \frac{\gamma_{\text{CoCl}^+}}{\gamma_{\text{Co}^{2+}} \gamma_{\text{Cl}^-}} \quad (2)$$

Taking logarithm on both sides of the above equation and rearrangement of the resulting equation leads to

Table 1 Thermodynamic equilibrium constants for the formation of nickel complexes at 298 K.

Reaction	Log K	Reference
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	-1.29	8
$\text{Ni}^{2+} + \text{OH}^- = \text{NiOH}^+$	4.10	9
$\text{Ni}^{2+} + 2\text{OH}^- = \text{Ni(OH)}_2^\circ$	8.00	9
$2\text{Ni}^{2+} + \text{OH}^- = \text{Ni}_2\text{OH}^{3+}$	3.30	9
$4\text{Ni}^{2+} + 4\text{OH}^- = \text{Ni}_4(\text{OH})_4^{4+}$	28.30	9

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Table 2 Reported values for the equilibrium constant of cobalt chloride complexes at different ionic strength in the HClO₄ medium at 298 K.

Reaction	$\log K^1$ ($I = 5$)	$\log K^1$ ($I = 7$)	$\log K^1$ ($I = 8$)	$\log K^1$ ($I = 9$)	$\log K^1$ ($I = 10$)
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.04	0.23	0.40	0.64	0.82
$\text{Co}^{2+} + 2\text{Cl}^- = \text{CoCl}_2^\circ$	-0.62	-0.15	0.30	0.78	1.26
$\text{Co}^{2+} + 3\text{Cl}^- = \text{CoCl}_3^-$	-1.40	-0.70	0.02	0.80	1.60
$\text{Co}^{2+} + 4\text{Cl}^- = \text{CoCl}_4^{2-}$	—	—	-0.9	0.2	1.4

$$\log K^1 = \log K^0 + \log \gamma_{\text{Co}^{2+}} + \log \gamma_{\text{Cl}^-} - \log \gamma_{\text{CoCl}^+} \quad (3)$$

The activity coefficient of solute was calculated by using Bromley equation. The Bromley equation for the activity coefficient of the cation at 298 K, γ_M , is represented by the following equations.⁷⁾

$$\log \gamma_M = -\frac{0.5108(z_M)^2 I^{0.5}}{1 + I^{0.5}} + F_M = -A(z_M)^2 + F_M \quad (4)$$

$$F_M = \sum_X \left[\frac{(0.06 + 0.6B_{MX}) \times |z_M z_X|}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} \right] \times \frac{(|z_M| + |z_X|)^2}{4} [X] \quad (5)$$

In the above equations, z is ionic charge and I ionic strength of a 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

$$\log K^1 = \log K^0 - 4A + F_{\text{Co}^{2+}} + F_{\text{Cl}^-} - F_{\text{CoCl}^+} \quad (6)$$

In the HClO₄ medium, the concentrations of Co^{2+} , Cl^- and CoCl^+ are negligible compared to the HClO₄ concentration.^{10,11)} Hence, F term for the activity coefficient of the anion is related only to the cation H^+ , while F term for the activity coefficient of cation is related to the anion ClO_4^- of the medium.^{10,11)} Substitution of the F terms for Co^{2+} , Cl^- and CoCl^+ into the above equation results in

$$\begin{aligned} \log K^1 = & \log K^0 - 4A \\ & + \left[\frac{2(0.06 + 0.6B_{\text{Co}^{2+}, \text{ClO}_4^-})}{\left(1 + \frac{1.5}{2} I\right)^2} + B_{\text{Co}^{2+}, \text{ClO}_4^-} \right] \\ & \times \frac{9}{4} [\text{ClO}_4^-] + \left[\frac{(0.06 + 0.6B_{\text{H}^+, \text{Cl}^-})}{(1 + 1.5I)^2} + B_{\text{H}^+, \text{Cl}^-} \right] \\ & \times [\text{H}^+] - \left[\frac{(0.06 + 0.6B_{\text{CoCl}^+, \text{ClO}_4^-})}{(1 + 1.5I)^2} + B_{\text{CoCl}^+, \text{ClO}_4^-} \right] \\ & \times [\text{ClO}_4^-] \end{aligned} \quad (7)$$

Bromley reported the value of $B_{\text{Co}^{2+}, \text{ClO}_4^-}$ and $B_{\text{H}^+, \text{Cl}^-}$.⁷⁾ Inserting these values together with the concentrations of H^+ and ClO_4^- into eq. (7) resulted in the equations with two unknowns, K^0 and $B_{\text{CoCl}^+, \text{ClO}_4^-}$. The value of K^0 and $B_{\text{CoCl}^+, \text{ClO}_4^-}$ were estimated by the least square method of these equations. Table 3 represents the equilibrium constants

Table 3 Estimated equilibrium constant and interaction parameter at 298 K.

Reaction	$\log K^0$	Interaction parameter
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.22	$B_{\text{CoCl}^+, \text{ClO}_4^-}$ 0.43
$\text{Co}^{2+} + 3\text{Cl}^- = \text{CoCl}_3^-$	-3.02	$B_{\text{H}^+, \text{CoCl}_3^-}$ 0.25
$\text{Co}^{2+} + 4\text{Cl}^- = \text{CoCl}_4^{2-}$	-9.06	$B_{\text{H}^+, \text{CoCl}_4^{2-}}$ -0.05

Table 4 Thermodynamic equilibrium constants for the formation of cobalt complexes at 298 K.

Reaction	Log K	Reference
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	14.0	8
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.22	4
$\text{Co}^{2+} + 2\text{Cl}^- = \text{CoCl}_2^\circ$	-3.95	4
$\text{Co}^{2+} + 3\text{Cl}^- = \text{CoCl}_3^-$	-3.02	4
$\text{Co}^{2+} + 4\text{Cl}^- = \text{CoCl}_4^{2-}$	-9.06	4
$\text{Co}^{2+} + \text{OH}^- = \text{CoOH}^+$	4.30	8
$\text{Co}^{2+} + 2\text{OH}^- = \text{Co(OH)}_2^\circ$	8.40	8
$2\text{Co}^{2+} + \text{OH}^- = \text{Co}_2\text{OH}^{3+}$	2.70	8
$4\text{Co}^{2+} + 4\text{OH}^- = \text{Co}_4(\text{OH})_4^{4+}$	25.60	8

and interaction parameters obtained by this procedure.⁴⁾ Table 4 lists the equilibrium constants for the formation of cobalt complexes.

Since activity coefficients of electrically neutral species could not be calculated with Bromley equation, the activity coefficients of CoCl_2° , Co(OH)_2° and Ni(OH)_2° were assumed to be unity.

The water activity for a single electrolyte ij , $a_{\text{W},ij}^\circ$, was calculated using the following Bromley equation for the osmotic coefficient, ϕ_{ij} .¹²⁾

$$\begin{aligned} \phi_{ij} = & 1 - 2.303 \left[\frac{0.5108|z_i z_j|}{I} \left\{ 1 + \sqrt{I} - \frac{1}{1 + \sqrt{I}} \right. \right. \\ & \left. \left. - 2 \ln(1 + \sqrt{I}) \right\} - \frac{(0.06 + 0.6B_{ij}) \times |z_i z_j|}{\frac{1.5}{|z_i z_j|}} \right. \\ & \left. \times \left\{ \frac{1 + 2\frac{1.5}{|z_i z_j|} I}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} - \frac{\ln\left(1 + \frac{1.5}{|z_i z_j|} I\right)}{\frac{1.5}{|z_i z_j|} I} \right\} - 0.5B_{ij} I \right] \end{aligned} \quad (8)$$

$$\ln a_{\text{W},ij}^\circ = -\frac{18.02vm}{1000} \phi_{ij} \quad (9)$$

where v represents the number of moles of ions and m , the molality of the electrolyte.

The water activity of the mixed electrolyte solutions was calculated from the water activity of a single electrolyte with the following equation suggested by Meissner.¹²⁾

$$\ln a_{\text{W},\text{mix}} = \sum \sum \frac{I_i I_j}{I^2} \left[\frac{(|z_i| + |z_j|)^2}{|z_i z_j|} \right] \times \ln a_{\text{W},ij}^\circ \quad (10)$$

where I_i represents the ionic strength of the individual ions, which equals $0.5m_i(z_i)^2$.

For the $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system, the following mass and charge balance equations were obtained from the complex formation reactions shown in Tables 1 and 4.

$$[\text{Co}]_t = [\text{Co}^{2+}] + [\text{CoCl}^+] + [\text{CoCl}_2^\circ] + [\text{CoCl}_3^-] + [\text{CoCl}_4^{2-}] + [\text{CoOH}^+] + [\text{Co}(\text{OH})_2^\circ] + 2[\text{Co}_2\text{OH}^{3+}] + 4[\text{Co}_4(\text{OH})_4^{4+}] \quad (11)$$

$$[\text{Ni}]_t = [\text{Ni}^{2+}] + [\text{NiCl}^+] + [\text{NiOH}^+] + [\text{Ni}(\text{OH})_2^\circ] + 2[\text{Ni}_2\text{OH}^{3+}] + 4[\text{Ni}_4(\text{OH})_4^{4+}] \quad (12)$$

$$[\text{Cl}]_t = [\text{Cl}^-] + [\text{CoCl}^+] + 2[\text{CoCl}_2^\circ] + 3[\text{CoCl}_3^-] + 4[\text{CoCl}_4^{2-}] + [\text{NiCl}^+] \quad (13)$$

$$[\text{Na}]_t = [\text{Na}^+] \quad (14)$$

In the above equations, subscript t represents the total concentration.

$$[\text{H}^+] + 2[\text{Co}^{2+}] + [\text{CoCl}^+] + [\text{CoOH}^+] + 3[\text{Co}_2\text{OH}^{3+}] + 4[\text{Co}_4(\text{OH})_4^{4+}] + [\text{Na}^+] + 2[\text{Ni}^{2+}] + [\text{NiCl}^+] + [\text{NiOH}^+] + 3[\text{Ni}_2\text{OH}^{3+}] + 4[\text{Ni}_4(\text{OH})_4^{4+}] = [\text{Cl}^-] + [\text{CoCl}_3^-] + 2[\text{CoCl}_4^{2-}] + [\text{OH}^-] \quad (15)$$

In the $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system, there were 19 solutes in the equilibrium state, *i.e.*, $[\text{Co}^{2+}]$, $[\text{CoCl}^+]$, $[\text{CoCl}_2^\circ]$, $[\text{CoCl}_3^-]$, $[\text{CoCl}_4^{2-}]$, $[\text{CoOH}^+]$, $[\text{Co}(\text{OH})_2^\circ]$, $[\text{Co}_2\text{OH}^{3+}]$, $[\text{Co}_4(\text{OH})_4^{4+}]$, $[\text{Ni}^{2+}]$, $[\text{NiCl}^+]$, $[\text{NiOH}^+]$, $[\text{Ni}(\text{OH})_2^\circ]$, $[\text{Ni}_2\text{OH}^{3+}]$, $[\text{Ni}_4(\text{OH})_4^{4+}]$, $[\text{H}^+]$, $[\text{Na}^+]$, $[\text{Cl}^-]$ and $[\text{OH}^-]$. In order to calculate the equilibrium concentrations and activity coefficients of these 19 solutes and water activity, 39 independent equations were needed. These independent equations were obtained from 14 complex formation reactions shown in Tables 1 and 4, 4 mass balance equations, a charge balance equation, 19 activity coefficient equations of solute and the activity equation of water. These equations were solved by Newton-Raphson method.

Table 5 shows the experimental compositions of the $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system together with the pH values measured at 298 K, in which the unit of concentration is molality. Also the pH values and ionic strength calculated in this study are shown in this table. 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 up to ionic strength of 9.53 mol/kg.

3.2 Distribution of chemical species

Figure 2 shows the distribution of cobalt chloride complexes with HCl concentration in the absence and presence of 1.0 mol/kg NiCl_2 , when CoCl_2 concentration was 1.0 mol/kg. It is seen in Fig. 2 that most of cobalt exists as cobalt ion and the mole fraction of the cobalt ion is nearly constant up to 3.0 mol/kg HCl. The mole fraction of CoCl^+ decreased with increasing HCl concentration, while that of CoCl_2° , CoCl_3^- and CoCl_4^{2-} increased with increasing HCl concentration. The mole fraction of cobalt chloride complexes decreased in the following order, $\text{Co}^{2+} > \text{CoCl}^+ > \text{CoCl}_3^- > \text{CoCl}_2^\circ > \text{CoCl}_4^{2-}$. The presence of NiCl_2 enhanced the

Table 5 Compositions of synthetic mixed chloride solution of nickel and cobalt and calculated results.

N	$[\text{CoCl}_2]_t$	$[\text{NiCl}_2]_t$	$[\text{HCl}]_t$	$[\text{NaOH}]_t$	pH	pH _C	I_C
1	0.1	0.1	0.1	0	1.22	1.14	0.67
2	0.1	0.1	0.5	0.4	1.17	1.11	1.06
3	0.1	0.1	1.0	0.9	1.15	1.07	1.54
4	0.1	0.1	1.5	0.9	0.36	0.24	2.02
5	0.1	0.1	2.0	2.1	6.44	6.48	2.57
6	1.0	1.0	1.0	0.5	0.03	0.03	5.53
7	1.0	1.0	1.0	0.8	0.23	0.43	5.56
8	1.0	1.0	1.0	1.3	5.67	5.78	5.84
9	1.0	1.0	1.5	0.8	-0.18	-0.17	5.90
10	1.0	1.0	2.0	2.2	5.43	5.48	6.54
11	1.5	1.5	0.1	0	0.47	0.66	6.59
12	1.5	1.5	1.0	0.5	-0.17	-0.14	7.15
13	1.5	1.5	1.0	1.3	5.30	5.23	7.54
14	1.5	1.5	1.5	0.8	-0.43	-0.34	7.47
15	1.5	1.5	2.0	1.0	-0.48	-0.55	7.76
16	2.0	2.0	0.1	0	0.34	0.50	7.95
17	2.0	2.0	1.0	0.5	-0.31	-0.29	8.42
18	2.0	2.0	1.5	0.8	-0.51	-0.48	8.67
19	2.0	2.0	2.0	1.9	0.08	0.30	9.07
20	2.0	2.0	2.0	2.3	4.88	4.66	9.53

(N: number,
pH: measured values of pH,
pH_C: calculated values of pH,
 I_C : calculated values of ionic strength)

Fig. 1 Comparison of pH values between measured and calculated in this study.

complex formation of CoCl_2° , CoCl_3^- and CoCl_4^{2-} , while the mole fraction of CoCl^+ decreased in the presence of NiCl_2 .

Figure 3 shows the variation in the mole fraction of Ni^{2+} and NiCl^+ with HCl concentration in the absence and presence of 1.0 mol/kg CoCl_2 , when NiCl_2 concentration was 1.0 mol/kg. Most of nickel existed as nickel ion in the concentration range of up to 3.0 mol/kg HCl. The mole fraction of nickel ion decreased slightly with increasing HCl

Fig. 2 Effect of HCl and NiCl_2 concentration on the distribution of cobalt chloride complexes at 1.0 mol/kg CoCl_2 concentration. (Open: without NiCl_2 , Closed: in the presence of 1.0 mol/kg NiCl_2)

Fig. 4 Distribution of cobalt species with the pH of mixed chloride solution. ($[\text{CoCl}_2]_t = 1.0 \text{ mol/kg}$, $[\text{NiCl}_2]_t = 1.0 \text{ mol/kg}$)

Fig. 3 Effect of HCl and CoCl_2 concentration on the distribution of nickel species at 1.0 mol/kg NiCl_2 concentration. (Open: without CoCl_2 , Closed: in the presence of 1.0 mol/kg CoCl_2)

Fig. 5 Distribution of nickel species with the pH of mixed chloride solution. ($[\text{CoCl}_2]_t = 1.0 \text{ mol/kg}$, $[\text{NiCl}_2]_t = 1.0 \text{ mol/kg}$)

concentration, while that of NiCl^+ increased greatly with increasing HCl concentration. The presence of CoCl_2 increased the mole fraction of NiCl^+ but decreased slightly the mole fraction of nickel ion.

Figure 4 shows the distribution of cobalt species with solution pH in the mixed solution of 1.0 mol/kg CoCl_2 and 1.0 mol/kg NiCl_2 . In the pH range of 0 to 6, most of cobalt existed as cobalt ion and the mole fraction of cobalt chloride complexes decreased with solution pH in the following order,

$\text{CoCl}^+ > \text{CoCl}_3^- > \text{CoCl}_2^0 > \text{CoCl}_4^{2-}$. The mole fraction of cobalt hydroxide complexes increased greatly with solution pH in the following order, $\text{Co}_2\text{OH}^{3+} > \text{CoOH}^+ > \text{Co}_4(\text{OH})_4^{4+} > \text{Co}_2(\text{OH})_2^0$, when solution pH was higher than 3.2.

Figure 5 shows the distribution of nickel species with solution pH in the mixed solution of 1.0 mol/kg CoCl_2 and 1.0 mol/kg NiCl_2 . Most of nickel existed as nickel ion in the pH range of 0 to 6. The mole fraction of nickel hydroxide

complexes increased greatly with increasing solution pH in the following order, $\text{Ni}_2\text{OH}^{3+} > \text{NiOH}^+ > \text{Ni}_4(\text{OH})_4^{4+} > \text{Ni}(\text{OH})_2^\circ$, when the value of solution pH was between 2.0 and 4.5. Among the nickel hydroxide complexes, the mole fraction of $\text{Ni}_4(\text{OH})_4^{4+}$ increased greatly with solution pH and was higher than that of NiCl^+ , when solution pH was higher than 6.0.

4. Conclusions

Ionic equilibria in the mixed solution of nickel and cobalt chloride were analyzed by considering the complex formation reaction, the mass balance equations and a charge balance equation. The activity coefficients of solutes and water activity were calculated by using Bromley equation. In the pH range of -0.5 to 6.4 , the measured pH values for the $\text{NiCl}_2\text{-CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ system at 298 K agreed well with the calculated values up to ionic strength of 9.53 mol/kg . Distribution of nickel and cobalt species with the composition and solution pH was obtained by analyzing the ionic equilibria.

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