

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 CoCl_2 and HCl concentrations on the distribution of cobalt species was obtained. The predicted pH values for CoCl_2 -HCl-NaOH- H_2O system agreed well with those measured at 298 K.

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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.¹⁾ 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.^{2,3)}

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 CoCl_2 and NiCl_2 , ionic equilibria of the respective solutions need to be developed. We reported the ionic equilibria analysis of NiCl_2 solution.⁴⁾ Few studies, however, have been reported on the equilibria of cobalt chloride solution at high ionic strength.

In this study, ionic equilibria for the CoCl_2 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.⁵⁾ The validity of the ionic equilibria for the CoCl_2 -HCl-NaOH- H_2O system at 298 K was verified by comparing the measured values of solution pH with those calculated in this study.

2. Experimental

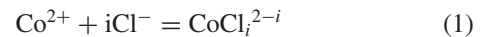
Cobalt chloride solutions with different composition were prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, HCl and NaOH in distilled water. All chemicals were of reagent grade. First, known amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, HCl and NaOH were added

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



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

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

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

$$\log K_i^I = \log K_i^0 + \log \gamma_{\text{Co}^{2+}} + i \log \gamma_{\text{Cl}^-} - \log \gamma_{\text{CoCl}_i^{2-i}} \quad (3)$$

The activity coefficient of solute was calculated by the Bromley equation. The Bromley equation for the activity coefficient of the cation, γ_M , is represented by the following equations.⁵⁾

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

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

$$\times \frac{(|z_M| + |z_X|)^2}{4} [X] \quad (5)$$

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

$$\log K_i^1 = \log K_i^0 + (i^2 - 5i)A + F_{Co^{2+}} + iF_{Cl^-} - F_{CoCl^{2-i}} \quad (6)$$

Table 1 represents the equilibrium constants for the formation of cobalt chloride complexes at different $HClO_4$ concentration.⁶⁾ The concentrations of Co^{2+} , Cl^- and $CoCl_i^{2-i}$ are negligible compared to the $HClO_4$ concentration in these studies.^{7,8)} Hence, F term for the activity coefficient

Table 1 Reported values for the logarithm of equilibrium constant at a series of ionic strength with $HClO_4$ as the inert salt at 298 K.

Reaction	$\log K^1$ ($I = 5$)	$\log K^1$ ($I = 7$)	$\log K^1$ ($I = 8$)	$\log K^1$ ($I = 9$)	$\log K^1$ ($I = 10$)
$Co^{2+} + Cl^- = CoCl^+$	0.04	0.23	0.40	0.64	0.82
$Co^{2+} + 2Cl^- = CoCl_2^\circ$	-0.62	-0.15	0.30	0.78	1.26
$Co^{2+} + 3Cl^- = CoCl_3^-$	-1.40	-0.70	0.02	0.80	1.60
$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	—	—	-0.9	0.2	1.4

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

$$F_{Co^{2+}} = \left[\frac{2(0.06 + 0.6B_{Co^{2+},ClO_4^-})}{\left(1 + \frac{1.5I}{2}\right)^2} + B_{Co^{2+},ClO_4^-} \right] \times \frac{3^2}{4} [ClO_4^-] \quad (7)$$

$$F_{Cl^-} = \left[\frac{(0.06 + 0.6B_{H^+,Cl^-})}{(1 + 1.5I)^2} + B_{H^+,Cl^-} \right] \times \frac{2^2}{4} [H^+] \quad (8)$$

$$F_{CoCl^+} = \left[\frac{(0.06 + 0.6B_{CoCl^+,ClO_4^-})}{(1 + 1.5I)^2} + B_{CoCl^+,ClO_4^-} \right] \times \frac{2^2}{4} [ClO_4^-] \quad (9)$$

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

$$\log K_i^1 = \log K_i^0 - 4A + \left[\frac{2(0.06 + 0.6B_{Co^{2+},ClO_4^-})}{\left(1 + \frac{1.5I}{2}\right)^2} + B_{Co^{2+},ClO_4^-} \right] \times \frac{9}{4} [ClO_4^-] + \left[\frac{(0.06 + 0.6B_{H^+,Cl^-})}{(1 + 1.5I)^2} + B_{H^+,Cl^-} \right] \times [H^+] - \left[\frac{(0.06 + 0.6B_{CoCl^+,ClO_4^-})}{(1 + 1.5I)^2} + B_{CoCl^+,ClO_4^-} \right] \times [ClO_4^-] \quad (10)$$

Bromley reported interaction parameters between Co^{2+} and ClO_4^- and between H^+ and ClO_4^- . The values reported by Bromley and the concentrations of H^+ and ClO_4^- were inserted into eq. (10). This operation led to equations with two unknowns, K_i^0 and B_{CoCl^+,ClO_4^-} . The equilibrium constant for the formation of $CoCl^+$ at zero ionic strength and the interaction parameter between $CoCl^+$ and ClO_4^- were estimated by least square of these equations. Table 2 represents the equilibrium constants and interaction parameters thus obtained in this study. Since this method could not be applied to $CoCl_2^\circ$ of zero charge, the equilibrium constant for the formation of $CoCl_2^\circ$ was obtained from literature.⁹⁾

Table 2 Estimated equilibrium constant and interaction parameter at 298 K.

Reaction	$\log K^\circ$	Interaction parameter	R^2
$Co^{2+} + Cl^- = CoCl^+$	0.22	B_{CoCl^+,ClO_4^-}	0.43 0.99
$Co^{2+} + 3Cl^- = CoCl_3^-$	-3.02	$B_{H^+,CoCl_3^-}$	0.25 0.84
$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	-9.06	$B_{H^+,CoCl_4^{2-}}$	-0.05 0.95

Table 3 represents the equilibrium constants used in this study for the formation of various complexes together with the references. Free energy changes for the formation of Co^{2+} , Cl^- and $CoCl^+$ reported by Russian Academy of Science are listed in Table 4.¹⁰⁾ The equilibrium constant for the formation of $CoCl^+$ was calculated by inserting the thermodynamic data in Table 4 into the following equation.

$$\Delta G^\circ = -RT \ln K. \quad (11)$$

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^+,ClO_4^-} by inserting the interaction parameter of ClO_4^- reported by Bromley into the following equation.

$$B_{CoCl^+,ClO_4^-} = B_{CoCl^+} + B_{ClO_4^-} \quad (12)$$

Activity coefficients of electrically neutral species could not be calculated with the Bromley equation. Consequently the activity coefficient of $CoCl_2^\circ$ was assumed to be unity.

Table 3 Thermodynamic equilibrium constant for the formation of complexes.

Reaction	log K	Reference
$H^+ + OH^- = H_2O$	14.0	6
$Co^{2+} + Cl^- = CoCl^+$	0.22	obtained in this study
$Co^{2+} + 2Cl^- = CoCl_2^\circ$	-3.95	9
$Co^{2+} + 3Cl^- = CoCl_3^-$	-3.02	obtained in this study
$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	-9.06	obtained in this study
$Co^{2+} + OH^- = CoOH^+$	4.3	6
$Co^{2+} + 2OH^- = Co(OH)_2^\circ$	8.4	6
$2Co^{2+} + OH^- = Co_2OH^{3+}$	2.7	6
$4Co^{2+} + 4OH^- = Co_4(OH)_4^{4+}$	25.6	6

 Table 4 Free energy change for the formation of Co^{2+} , Cl^- and $CoCl^+$ reported by Russian Academy of Science.

	ΔG_f° (kJ/mol)
Co^{2+}	-53.64
Cl^-	-131.265
$CoCl^+$	-187.192

3.2 Ionic equilibria analysis

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

$$[Cl]_t = 2[CoCl_2]_t + [HCl]_t = [Cl^-] + [CoCl^+] + 2[CoCl_2^\circ] + 3[CoCl_3^-] + 4[CoCl_4^{2-}] \quad (13)$$

$$[Co]_t = [CoCl_2]_t = [Co^{2+}] + [CoCl^+] + [CoCl_2^\circ] + [CoCl_3^-] + [CoCl_4^{2-}] + [CoOH^+] + [Co(OH)_2^\circ] + 2[Co_2OH^{3+}] + 4[Co_4(OH)_4^{4+}] \quad (14)$$

$$[Na]_t = [NaOH]_t = [Na^+] \quad (15)$$

Where subscript t represents the total concentration.

The following charge balance equation was obtained from electroneutrality condition.

$$[H^+] + 2[Co^{2+}] + [CoCl^+] + [CoOH^+] + 3[Co_2OH^{3+}] + 4[Co_4(OH)_4^{4+}] + [Na^+] = [Cl^-] + [CoCl_3^-] + 2[CoCl_4^{2-}] + [OH^-] \quad (16)$$

In $CoCl_2$ -HCl-NaOH- H_2O system, there were 13 solutes in the equilibrium state, *i.e.*, $[Cl^-]$, $[Co^{2+}]$, $[CoCl^+]$, $[CoCl_2^\circ]$, $[CoCl_3^-]$, $[CoCl_4^{2-}]$, $[CoOH^+]$, $[Co(OH)_2^\circ]$, $[Co_2OH^{3+}]$, $[Co_4(OH)_4^{4+}]$, $[H^+]$, $[Na^+]$, $[OH^-]$. 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 $CoCl_2$ -HCl-NaOH- H_2O 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

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

N	$[CoCl_2]_t$	$[HCl]_t$	$[NaOH]_t$	pH	pH _C	I _C
1	0.1	0.1	0	1.20	1.14	0.38
2	0.1	0.5	0.4	1.09	1.12	0.78
3	1.0	0.5	0.4	0.80	0.97	3.29
4	1.0	1.0	0.5	0.12	0.21	3.80
5	1.0	1.0	0.8	0.68	0.61	3.81
6	1.0	2.0	0.5	-0.26	-0.40	4.79
7	1.0	2.0	1.0	-0.19	-0.22	4.81
8	1.0	2.0	1.7	0.49	0.30	4.84
9	1.0	2.0	2.3	5.78	5.32	5.00
10	2.0	0.5	0.4	0.68	0.73	6.13
11	2.0	1.0	0.5	-0.20	-0.03	6.57
12	2.0	1.0	1.1	5.34	5.19	6.67
13	2.0	2.0	0.5	-0.50	-0.63	7.24
14	2.0	2.0	1.0	-0.43	-0.45	7.32
15	2.0	2.0	1.7	0.27	0.06	7.43
16	2.0	2.0	2.3	5.12	5.09	7.63
17	3.0	1.0	0.5	-0.18	-0.23	8.58
18	3.0	1.0	0.8	0.11	0.16	8.67
19	3.0	1.0	1.1	4.90	4.97	8.81

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

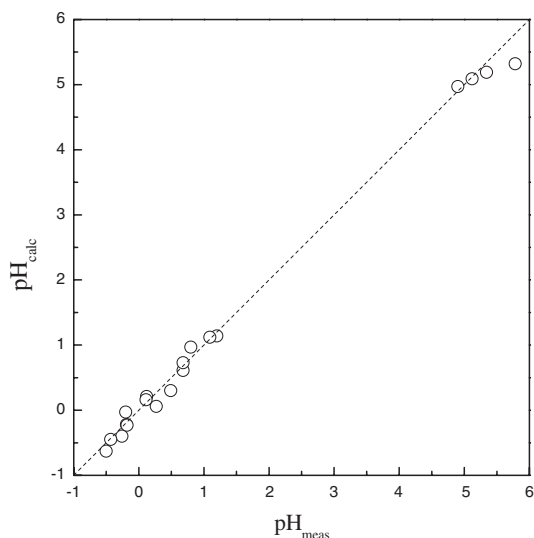


Fig. 1 Comparison of pH values between measured and calculated in this study.

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 $CoCl_2$ concentration in the absence of HCl. It is seen in Fig. 2 that most of cobalt exist as

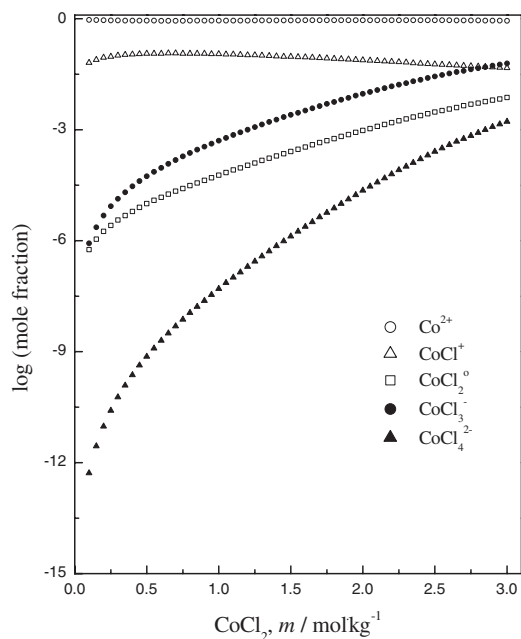


Fig. 2 Distribution of cobalt chloride complexes with the concentration of CoCl_2 in the absence of HCl.

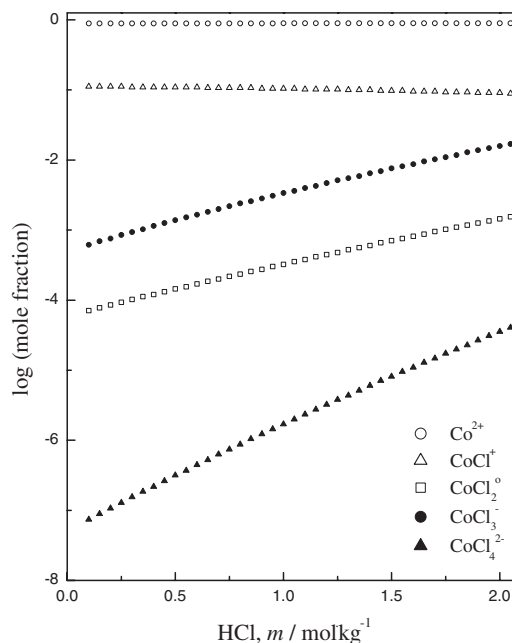


Fig. 4 Distribution of cobalt chloride complexes with HCl concentration. ($[\text{CoCl}_2]_t = 1.0 \text{ m}$).

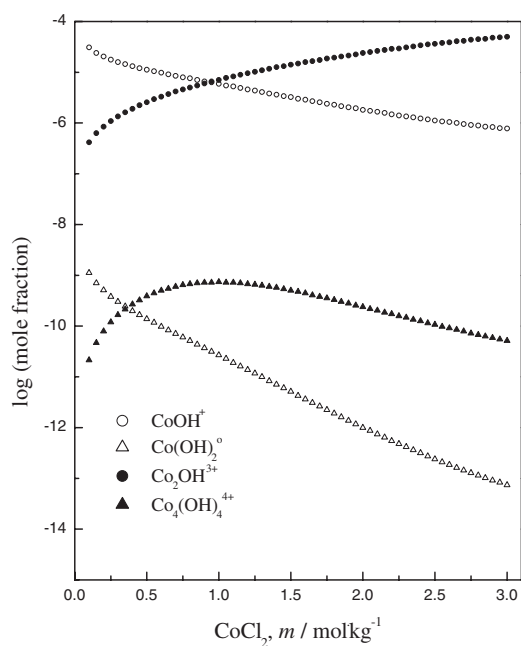


Fig. 3 Distribution of cobalt hydroxide complexes with the concentration of CoCl_2 in the absence of HCl.

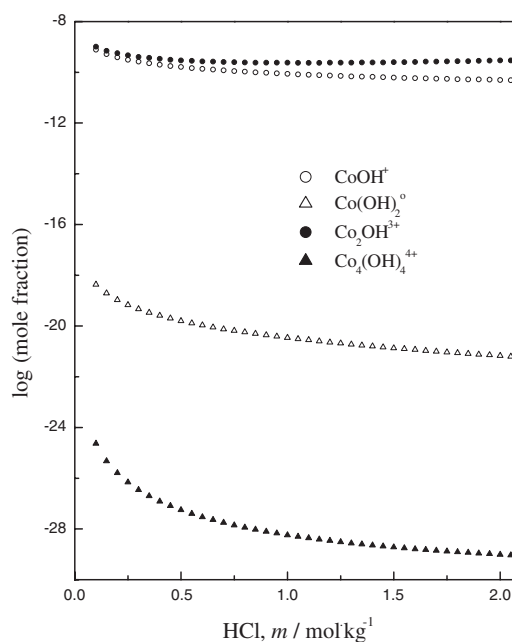


Fig. 5 Distribution of cobalt hydroxide complexes with HCl concentration. ($[\text{CoCl}_2]_t = 1.0 \text{ m}$).

Co^{2+} in the concentration range of up to 3 m CoCl_2 . As the CoCl_2 concentration increased, the mole fraction of CoCl_2° , CoCl_3^- and CoCl_4^{2-} greatly increased while that of CoCl^+ remained constant. The mole fraction of CoOH^+ and Co(OH)_2° decreased with an increase in the CoCl_2 concentration while that of $\text{Co}_3\text{OH}^{3+}$ increased. The mole fraction of $\text{Co}_4(\text{OH})_4^{4+}$ 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 $\text{Co}_3\text{OH}^{3+}$ 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.

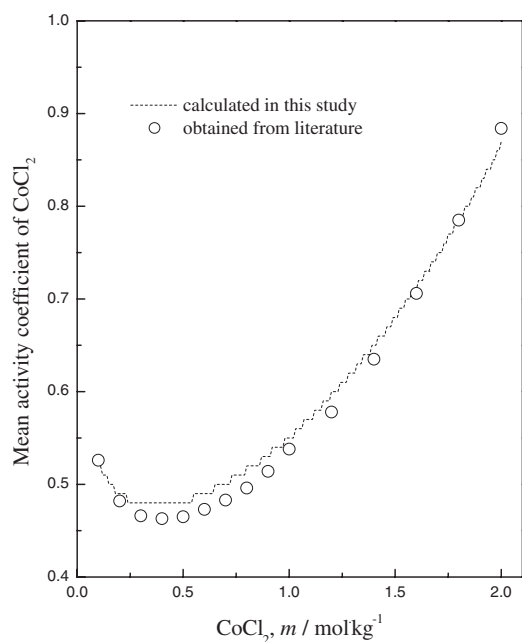


Fig. 6 Variation of the mean activity coefficient of CoCl_2 with the concentration of CoCl_2 .

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.

$$\gamma_{\pm, \text{CoCl}_2} = \{\gamma_{\text{Co}^{2+}}(\gamma_{\text{Cl}^-})^2\}^{1/3} \quad (17)$$

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 $\text{CoCl}_2\text{-HCl-NaOH-H}_2\text{O}$ 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

- 1) F. Habashi: *Handbook of Extractive Metallurgy*, vol. 2 Wiley-VCH, Weinheim (1997) pp. 923–924.
- 2) K. Sarangi, B. R. Reddy and R. P. Das: *Hydrometallurgy* **52** (1999) 253–265.
- 3) N. B. Devi, K. C. Nathasarma and V. Chakravorty: *Hydrometallurgy* **49** (1998) 47–61.
- 4) M. S. Lee and G. S. Lee: *J. of Korean Inst. of Resources Recycling* **12** (2003) 38–45.
- 5) L. A. Bromley: *AIChE Journal* **19** (1973) 313–320.
- 6) E. Högfeldt: *Stability constants of Metal-Ion Complexes: Part A. Inorganic ligands*, Pergamon, Oxford (1982) p. 209.
- 7) J. C. Raposo, J. Sanz, G. Borge, M. A. Olazabal and J. M. Madariaga: *Fluid Phase Equilibria* **155** (1999) 1–19.
- 8) Y. Belaustegi, M. A. Olazabal and J. M. Madariaga: *Fluid Phase Equilibria* **155** (1999) 21–31.
- 9) J. Bjerrum, G. Schwarzenbach and L.G. Sillén: *Stability Constants of Metal-ion Complexes, Part II: Inorganic ligands*, The Chemical Society, London (1957) p. 97.
- 10) J. F. Zemaitis, D. M. Clark, M. Rafal and N. C. Scrivner: *Handbook of aqueous electrolyte thermodynamics*, A publication of the Design Institute for Physical Property Data, NY (1986) p. 602.
- 11) H. S. Harned and B. B. Owen: *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corp., NY (1950) p. 567.