

Articles

Chemical Equilibria of Nickel Chloride in HCl Solution at 25 °C

Man Seung Lee and Sang-Ho Nam^{†,*}

Department of Advanced Materials Science & Engineering, Mokpo National University, Chonnam 534-729, Korea

[†]Department of Chemistry, Mokpo National University, Chonnam 534-729, Korea. *E-mail: shnam@mokpo.ac.kr

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Chemical equilibria of nickel chloride in HCl solution at 25 °C were analyzed by considering chemical equilibria, mass and charge balance equations. The activity coefficients of solutes were calculated by using Bromley equation. The necessary thermodynamic properties, such as the equilibrium constant for the formation of NiCl⁻ at zero ionic strength and interaction parameter, were evaluated by applying Bromley equation to the stability constant data reported in the literature. It was found that most nickel exists as Ni²⁺ in HCl solution up to 5 molality HCl. The pH values of NiCl₂-HCl-H₂O system at 25 °C calculated in this study agreed well with the pH values measured by employing pH meter.

Key Words: NiCl₂, HCl, Ionic equilibria, pH

Introduction

Nickel is a silver white metal and is essential to the iron and steel industry. Nickel increases other metal's strength, toughness, and corrosion resistance when alloyed with other metals.¹ Nickel containing alloys have played a key role in the development of materials for the aerospace industry. Since nickel ores of commercial significance are relatively few, nickel should be recovered not only from its natural ores but also from the industrial wastes. Separation and purification of nickel from cobalt is one of the most difficult processes of metal separation, because of the similarity in their chemical behavior. However, the tendency to form complexes with chloride ion is different between cobalt and nickel and this difference can be utilized in developing a separation process for nickel.²

Information on the distribution of nickel containing species with the composition of a solution is valuable in choosing a process to recover nickel from the industrial wastes. Osmotic coefficients, water activities, and activity coefficients of NiCl₂ solution at 25 °C were reported.³ It has been reported from the speciation of nickel chloride solution that most nickel is present as Ni²⁺ and NiCl⁺.^{4,6} Libuś and Tialowska suggested that NiCl⁻ complex exists as an outer-sphere ion pair [Ni(H₂O)₆]²⁺Cl⁻ in nickel chloride solution.⁷ The thermodynamic compilations of the National Bureau of Standard and Russian Academy of Science disagree as to possible ion pairing. While the NBS presents no data for any complexes of nickel and chloride ions, the Russian Academy of Science reported data for NiCl⁻ as well as NiCl_{2(aq)}.⁸

In this study, ionic equilibria for nickel chloride in HCl solution were analyzed by considering chemical equilibria, mass and charge balance equations. Thermodynamic properties, such as equilibrium constants for the formation of NiCl⁻ at zero ionic strength and interaction parameter, were

estimated by applying Bromley equation to the reported equilibrium constant for the formation of NiCl⁻ at different ionic strength. The activity coefficient of chemical species was calculated by using Bromley equation. The validity of the ionic equilibria for the NiCl₂-HCl-H₂O system at 25 °C was verified by comparing the measured values of solution pH with those calculated in this study.

Experimental

Nickel chloride solutions with different composition were prepared by dissolving NiCl₂·6H₂O and HCl in distilled water. All chemicals were of reagent grade. First, known amounts of NiCl₂·6H₂O and HCl 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 the solution was controlled to 25 °C by using a water bath. Once the temperature of the solution was stable, solution pH was measured with a pH meter (Orion 920A).

Results and Discussion

Ionic equilibria of nickel chloride in HCl solution. In HCl solution, nickel ion forms complexes with chloride and hydroxide ion. It has been reported that NiCl⁻ and NiCl_{2(aq)} are formed in the chloride solution.⁸ Nickel ion reacts with hydroxide ion to form complexes such as NiOH⁺, Ni(OH)_{2(aq)}, Ni(OH)₃⁻, Ni₂OH³⁺, and Ni₄(OH)₄⁴⁺.⁶ In strong HCl solution, the concentration of hydroxide ion is so low that the formation of nickel hydroxide complexes can be ignored. The following mass and charge balance equations were obtained for strong HCl solution.

$$[\text{Ni}]_{\text{total}} = [\text{NiCl}_2]_{\text{total}} = [\text{Ni}^{2+}] + [\text{NiCl}^-] + [\text{NiCl}_{2(aq)}] \quad (1)$$

$$[\text{Cl}]_{\text{total}} = 2[\text{NiCl}_2]_{\text{total}} + [\text{HCl}]_{\text{total}} \quad (2)$$

$$= [\text{Cl}^-] + [\text{NiCl}^+] + 2[\text{NiCl}_{2\text{aq}}]$$

$$[\text{H}^+] + 2[\text{Ni}^{2+}] + [\text{NiCl}^+] = [\text{Cl}^-] + [\text{OH}^-] \quad (3)$$

In strong HCl concentration range where the concentration of hydroxide ion is negligible. Equation (3) reduces to

$$[\text{H}^+] = [\text{HCl}]_{\text{total}} \quad (4)$$

The activity coefficient of solutes was calculated by Bromley equation. The following equation represents Bromley equation for the activity coefficient of the cation, γ_M , at 25 °C.⁹

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

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

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

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 .

In order to calculate the activity coefficients of chemical species, the interaction parameter between M and X , B_{MX} , is required. However, Bromley reported only the interaction parameter between Ni^{2+} and Cl^- . Table 1 lists the equilibrium constants for the formation of NiCl^+ at different $\text{Ni}(\text{ClO}_4)_2$ molality.^{7,8} Thermodynamic properties, such as the interaction parameter between NiCl^+ and Cl^- and equilibrium constant for the formation of NiCl^+ at zero ionic strength, were evaluated from these data shown in Table 1. The equilibrium constant for the formation of NiCl^+ at a given ionic strength, K^1 , is related to the equilibrium constant at zero ionic strength, K^0 , and to the activity coefficient as follows

$$K^0 = K^1 \frac{\gamma_{\text{NiCl}^+}}{\gamma_{\text{Ni}^{2+}} \gamma_{\text{Cl}^-}} \quad (7)$$

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

$$\log K^1 = \log K^0 + \log \gamma_{\text{Ni}^{2+}} + \log \gamma_{\text{Cl}^-} - \log \gamma_{\text{NiCl}^+} \quad (8)$$

Substitution of the expression for the activity coefficient of

Table 1. Variation of the equilibrium constant for the formation of NiCl^+ with $\text{Ni}(\text{ClO}_4)_2$ concentration.

	molality of $\text{Ni}(\text{ClO}_4)_2$				
	1.0	1.5	2.0	2.5	3.0
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+, K^1$	0.08	0.08	0.10	0.12	0.16

each species into Eq. (8) gives

$$\log K^1 = \log K^0 - 4A + F_{\text{Ni}^{2+}} + F_{\text{Cl}^-} - F_{\text{NiCl}^+} \quad (9)$$

The stability constants shown in Table 1 were determined by potentiometric method in the medium of 0.01 molality HCl concentration.⁷ Since $\text{Ni}(\text{ClO}_4)_2$ concentration was much higher than that of HCl in these measurements, the concentration of Cl^- and NiCl^+ are negligible compared to Ni^{2+} and ClO_4^- concentration. Hence, F term for the activity coefficient of the anion is related only to Ni^{2+} concentration, while F term for the activity coefficient of cation is related to the anion ClO_4^- . In this case, F terms for Ni^{2+} , Cl^- and NiCl^+ could be represented by

$$F_{\text{Ni}^{2+}} = \left[\frac{2(0.06 + 0.6B_{\text{Ni}^{2+}, \text{ClO}_4^-})}{\left(1 + \frac{1.5}{2} I\right)^2} + B_{\text{Ni}^{2+}, \text{ClO}_4^-} \right] \times \frac{3^2}{4} [\text{ClO}_4^-] \quad (10)$$

$$F_{\text{Cl}^-} = \left[\frac{2(0.06 + 0.6B_{\text{Ni}^{2+}, \text{Cl}^-})}{\left(1 + \frac{1.5}{2} I\right)^2} + B_{\text{Ni}^{2+}, \text{Cl}^-} \right] \times \frac{3^2}{4} [\text{Ni}^{2+}] \quad (11)$$

$$F_{\text{NiCl}^+} = \left[\frac{(0.06 + 0.6B_{\text{NiCl}^+, \text{ClO}_4^-})}{(1 + 1.5I)^2} + B_{\text{NiCl}^+, \text{ClO}_4^-} \right] \times [\text{ClO}_4^-] \quad (12)$$

Substitution of the above three equations into Eq. (9) results in

$$\log K^1 + 4A - 2 \times \left[\frac{2(0.06 + 0.6B_{\text{Ni}^{2+}, \text{ClO}_4^-})}{\left(1 + \frac{1.5}{2} I\right)^2} + B_{\text{Ni}^{2+}, \text{ClO}_4^-} \right]$$

$$\times \frac{9}{4} [\text{Ni}(\text{ClO}_4)_2] - \left[\frac{2(0.06 + 0.6B_{\text{Ni}^{2+}, \text{Cl}^-})}{\left(1 + \frac{1.5}{2} I\right)^2} + B_{\text{Ni}^{2+}, \text{Cl}^-} \right]$$

$$\times \frac{9}{4} [\text{Ni}(\text{ClO}_4)_2] = \log K^0 - 2$$

$$\times \left[\frac{(0.06 + 0.6B_{\text{NiCl}^+, \text{ClO}_4^-})}{(1 + 1.5I)^2} + B_{\text{NiCl}^+, \text{ClO}_4^-} \right] \times [\text{Ni}(\text{ClO}_4)_2] \quad (13)$$

The left-hand side of the above equation at each $\text{Ni}(\text{ClO}_4)_2$ concentration can be calculated by using the data shown in Table 1 and by using Bromley equation. Figure 1 shows a plot of $\text{Ni}(\text{ClO}_4)_2$ concentration vs y -value of Eq. (13). The inter

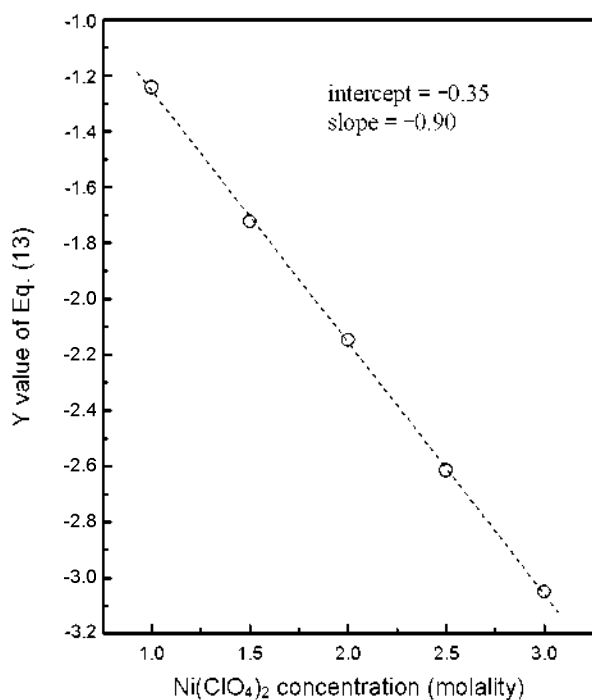


Figure 1. Evaluation of the equilibrium constant for the formation of NiCl^- and interaction parameter from the reported in the literature by using Eq. (13).

cept of this straight line is the equilibrium constant at zero ionic strength and the slope of this straight line is related to the interaction parameter. The following thermodynamic values were obtained from the slope and intercept of this plot in Fig. 1.

$$\log K^0 = -0.35 \quad (14)$$

$$B_{\text{NiCl}^+, \text{ClO}_4^-} = 0.44 \quad (15)$$

Chemical equilibria analysis. Table 2 lists the stability constant for the formation of NiCl^- and $\text{NiCl}_2^{\text{aq}}$ reported by the Russian Academy of Science.⁸ It is seen in Eq. (14) and Table 2 that there is some difference in the value of the equilibrium constant for the formation of NiCl^- between reported by the Russian Academy of Science and evaluated in this study.

Table 3 shows the experimental compositions of $\text{NiCl}_2\text{-HCl-H}_2\text{O}$ system together with pH values measured at 25 °C. The unit of concentration in Table 3 is molality. The pH of a nickel chloride solution was calculated by using both the equilibrium constant for the formation of NiCl^- evaluated in this study and the data reported by the Russian Academy of Science. The values of pH and the ionic strength calculated for each case are shown in Table 3. In order to compare the precision of the pH values calculated for each case, both measured and calculated pH values are shown together in Fig. 2. It is seen in Fig. 2 and Table 3 that the experimental pH values are in good agreement with the calculated values by using the equilibrium constant for the formation of NiCl^- evaluated in this study. When the ionic strength of a solution was low, the calculated pH values by using the data reported by Russian Academy of

Table 2. Equilibrium constant for the formation of nickel chloride complexes reported by the Russian Academy of Science.

Reaction	K
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^-$	2.1265
$\text{Ni}^{2+} + 2\text{Cl}^- = \text{NiCl}_2^{\text{aq}}$	5.9237

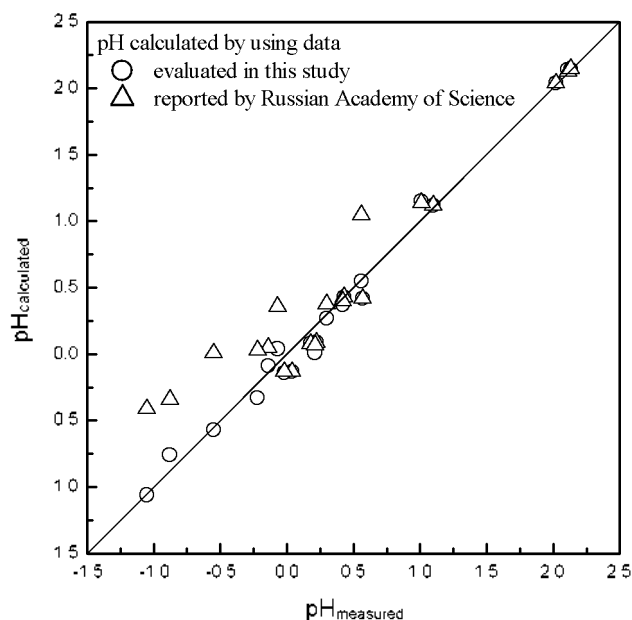


Figure 2. Comparison of pH values between measured and calculated in this study.

Science and evaluated in this study agrees well with the measured values. However, as the ionic strength of a solution increases, neglect of the formation of $\text{NiCl}_2^{\text{aq}}$ improves the precision of the calculated pH values.

The mean activity coefficients of nickel chloride solution at 25 °C were obtained by calculating the activity coefficient of nickel and chloride ion with Bromley equation and then inserting these activity coefficients to the following equation.

$$\gamma_{\pm} = [\gamma_{\text{Ni}^{2+}}(\gamma_{\text{Cl}^-})^2]^{1/3} \quad (16)$$

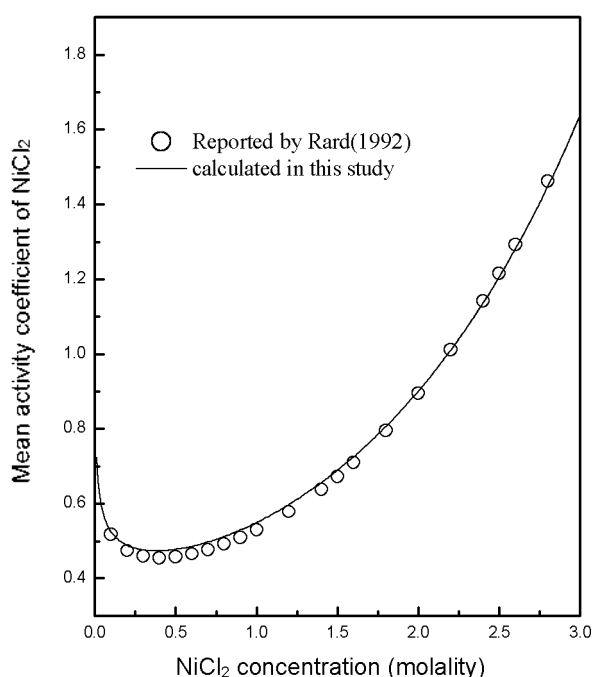
Rard reported the mean activity coefficients of nickel chloride solution at 25 °C as a function of NiCl_2 molality.³ The mean activity coefficients of nickel chloride solution at 25 °C reported by Rard and calculated in this study are shown in Fig. 3. The two mean activity coefficients are in good agreement up to 3.0 molality NiCl_2 .

Figure 4 shows the distribution of nickel containing species with HCl concentration when the concentration of NiCl_2 was fixed at 1.0 molality. It is seen in Fig. 4 that most nickel exists as Ni^{2+} in the concentration range of up to 5 molality HCl. As HCl concentration increased, the mole fraction of NiCl^- gradually increased. Figure 5 shows the distribution of nickel containing species with NiCl_2 concentration when HCl concentration was fixed at 1.0 molality. It is seen in Fig. 5 that most nickel exists as Ni^{2+} up to 1.0 molality NiCl_2 concentration.

Table 3. Experimental conditions and calculated results for the synthetic solution (Unit : molality).

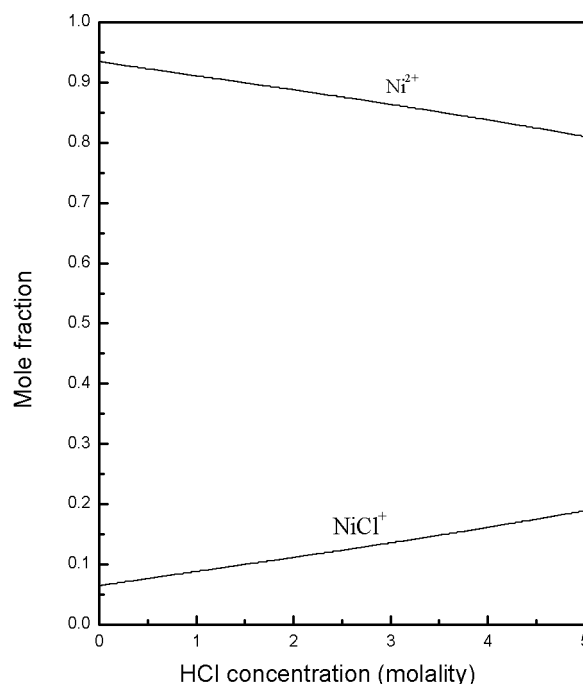
N	[NiCl ₂]	[HCl]	pH _{meas}	pH _{cal} ¹	I _{cal} ¹	pH _{cal} ²	I _{cal} ²
1	0.01	0.011	2.02	2.04	0.04	2.04	0.04
2	0.01	0.097	1.10	1.12	0.13	1.12	0.13
3	0.01	0.49	0.43	0.43	0.52	0.43	0.51
4	0.01	0.99	0.22	0.09	1.02	0.09	1.00
5	0.01	1.49	0.04	-0.13	1.52	-0.13	1.50
6	0.1	0.01	2.11	2.14	0.31	2.13	0.28
7	0.1	0.098	1.01	1.15	0.39	1.14	0.36
8	0.1	0.5	0.57	0.42	0.79	0.42	0.70
9	0.1	1.0	0.18	0.08	1.29	0.08	1.13
10	0.1	1.49	-0.02	-0.14	1.77	-0.13	1.57
11	0.5	0.0097	2.13	2.14	1.46	2.15	1.04
12	0.5	0.5	0.42	0.37	1.94	0.40	1.25
13	0.5	1.0	0.21	0.01	2.42	0.07	1.50
14	1.0	0.5	0.30	0.27	3.35	0.38	1.64
15	1.0	1.0	-0.14	-0.09	3.82	0.05	1.79
16	2.0	0.5	-0.07	0.04	6.09	0.36	2.08
17	2.0	1.0	-0.22	-0.33	6.54	0.03	2.15
18	2.0	1.99	-0.88	-0.76	7.43	-0.34	2.50
19	3.0	0.1	0.56	0.55	8.35	1.05	2.35
20	3.0	1.0	-0.55	-0.57	9.10	0.01	2.38
21	3.0	2.2	-1.05	-1.06	10.07	-0.41	2.74

pH_{meas} : measured pH values. pH_{cal}¹, I_{cal}¹ : calculated values of pH and ionic strength by using the thermodynamic constant evaluated in this study. pH_{cal}², I_{cal}² : calculated values of pH and ionic strength by using the data reported by the Russian Academy of Science.

**Figure 3.** Comparison of the mean activity coefficients of NiCl₂ solution at 25 °C between reported in the literature and calculated in this study.

Conclusions

By considering chemical equilibria, mass and charge balance equations for NiCl₂-HCl-H₂O system at 25 °C, chemical equilibria in the solution were analyzed. The equilibrium constant

**Figure 4.** Distribution of nickel containing species with HCl concentration in 1.0 molality NiCl₂ solution.

for the formation of NiCl⁻ at zero ionic strength and the interaction parameter between NiCl⁻ and Cl⁻ were evaluated by applying Bromley equation to the reported equilibrium constants for the formation of NiCl⁻ at different ionic strength of Ni(ClO₄)₂ solution. Activity coefficients of solutes were calculated by using Bromley equation. In the experimental ranges

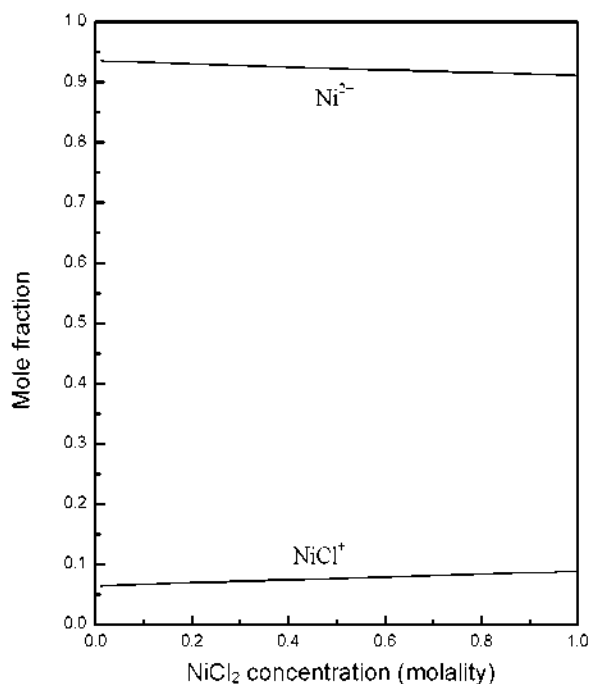


Figure 5. Distribution of nickel containing species with NiCl_2 concentration in 1.0 molality HCl solution.

up to 3 molality NiCl_2 , the measured pH values were in good agreement with the pH values calculated by using the equili-

brium constant and interaction parameter evaluated in this study. When the ionic strength of nickel chloride solution became high, neglect of the formation of undissociated molecule $\text{NiCl}_{2(aq)}$ improves the precision of the calculated pH values. Distribution diagram of nickel containing species with NiCl_2 and HCl concentration indicated that most nickel exists as Ni^{2+} up to 5 molality HCl solution. The results obtained in this study can be applied to the analysis of solvent extraction of nickel from chloride solution.

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