

Solvent Extraction of Ni(II) from Strong Hydrochloric Acid Solution by Alamine336

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Slope analysis method was applied to determine the stoichiometry of the solvent extraction reaction of Ni(II) by Alamine336 from strong HCl solution range from 1 to 10 M. Solvent extraction data was obtained from the literature. The effective equilibrium constant for the solvent extraction reaction was estimated by considering the ionic equilibria of NiCl₂ in the HCl solution. The measured distribution coefficients of Ni(II) agreed well with those calculated in this study. Our results suggest that further study on the measurement of the activities of nickel complexes at high HCl solution need to be done.

Key Words: Ni(II), HCl, Alamine336, Solvent extraction

Introduction

Nickel is an essential element in steel and aerospace industry.¹ The major sources for the production of nickel metal are certain raw materials, such as copper converter slag, nickel laterite ore and manganese nodules.² Leaching of these materials with sulfuric or chloride solution results in mixed solution containing nickel and cobalt along with some impurities.³ Separation of nickel from cobalt from sulphate solution is one of the most difficult processes in hydrometallurgy, because of the similarity in their chemical behavior.² In chloride solution, cobalt has a strong tendency to form anionic complexes, such as CoCl₃⁻ and CoCl₄²⁻, at high HCl concentration.⁴ However, most nickel is present as Ni²⁺ and NiCl⁺.⁵⁻⁷ This difference in the complex formation tendency can be utilized in developing a separation process for the two metals by solvent extraction.

Many studies have been reported on the extraction of nickel and separation of Ni(II) and Co(II) from weak HCl solution.^{2,3,8-10} However, very few studies have been performed on the extraction of Ni(II) by anionic extractants from strong HCl solution. Recently, a paper on the solvent extraction of Ni(II) by anionic extractant from strong HCl solution has been published.¹¹ According to this data, nickel was well extracted by Alamine336 (Tertiary amine, R₃N, R = CH₃(CH₂)₇), a sort of anionic extractant, from strong HCl solution. Their data motivated us to analyze the solvent extraction of Ni(II) from strong HCl solution by Alamine336. In this study, their data was analyzed to identify the solvent extraction reaction and the effective equilibrium constant for the solvent extraction reaction was obtained from their experimental data. The equilibrium constant obtained in this study was verified by comparing the measured distribution coefficients of Ni with those calculated in this study.

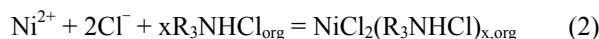
Results and Discussion

Solvent Extraction Reaction of Ni(II) by Alamine336. Some studies have reported that Alamine336 (R₃N) reacts with inorganic acid to form Alamine336 salt and that this Alamine336 salt participates in the solvent extraction of metal ions.¹² The

following equation represents the formation of Alamine336 salt (R₃NHCl) in HCl solution.



Solvent extraction reaction of metal ion by amine may be viewed as either anion exchange or association reaction.¹³ It has been reported that in HCl solution nickel exists as Ni²⁺ and NiCl⁺. Therefore, it is reasonable that association reaction is responsible for the extraction of nickel from HCl solution by amine, which can be represented as



where x represents stoichiometric coefficient for Alamine336 salt.

In solvent extraction, distribution coefficient (D) of a metal is defined as the ratio of metal concentration in the organic to that in the aqueous after extraction. In order to measure the distribution coefficient of nickel at specific extraction condition, equal volume (10 mL) of aqueous and organic phase was hand-shaken for 7 min and was allowed to settle for 60 min before separation.¹¹ The organic phase was prepared by diluting Alamine336 with m-xylene.¹¹ The concentration of nickel in the aqueous phase after extraction was measured by using atomic absorption spectrometer¹¹ and the concentration of nickel extracted into organic phase was obtained by mass balance.

Slope analysis method was employed to determine the stoichiometric coefficient of Alamine336, x, from the experimental results. First, the definition of distribution coefficient was inserted into the equilibrium constant for eq. (2) and then the following equation was obtained by taking logarithm on both sides of the resulting equation.

$$\log D \cong \log K_{ex} + 2 \log [Cl^-] + x \log [R_3NHCl] \quad (3)$$

Equation (3) indicates that a plot of log[R₃NHCl] against log D would give a straight line with a slope of x. Figs. 1 to 3 show the plots for the solvent extraction results at the initial

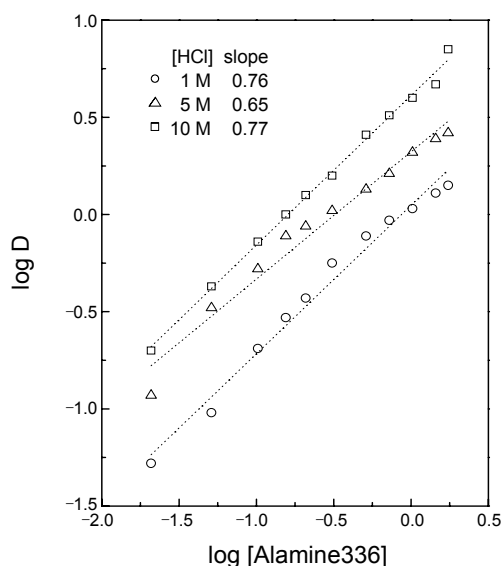


Figure 1. Variation in the distribution coefficient of Ni(II) with Alamine 336 at several HCl concentration (initial concentration of Ni(II) = 0.051 M).

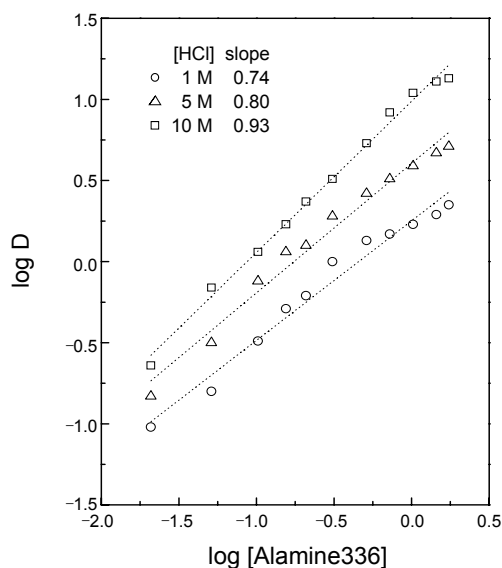
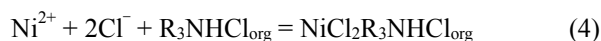


Figure 2. Variation in the distribution coefficient of Ni(II) with Alamine 336 at several HCl concentration (initial concentration of Ni(II) = 0.12 M).

nickel concentration of 0.051, 0.12 and 0.26 M, respectively. In Figs. 1 to 3, the logarithm of the distribution coefficient of nickel increased linearly with the logarithm of Alamine336 concentration, which is consistent with eq. (3). The slope of the plots in Fig. 1 to 3 is between 0.57 and 0.93 and the value of x in eq. (3) might be regarded as unity. Therefore, in the HCl concentration range of 1 to 10 M, solvent extraction reaction of Ni(II) by Alamine336 could be represented as follows



The above equation suggests that the concentration of chloride ion has a positive effect on the distribution coefficient of

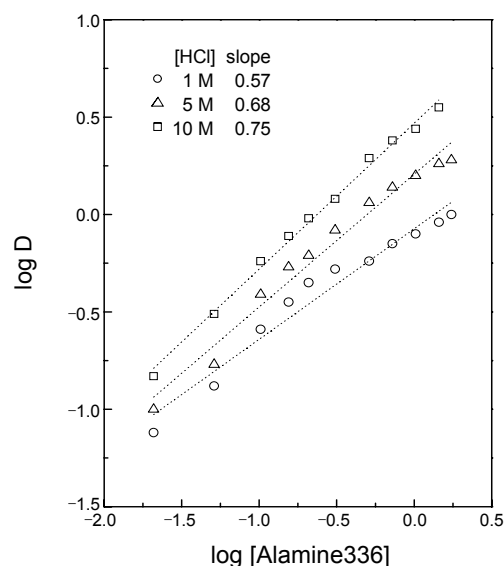


Figure 3. Variation in the distribution coefficient of Ni(II) with Alamine 336 at several HCl concentration. (initial concentration of Ni(II) = 0.26 M).

Ni(II). Experimental results on the extraction of nickel by Alamine336 indicated that the distribution coefficients of Ni increased with the increase of HCl concentration.

Determination of the Equilibrium Constant. The equilibrium constant of solvent extraction of Ni(II) from HCl solution by Alamine336 can be represented as

$$\begin{aligned} K_{\text{ex}} &= \frac{[\text{NiCl}_2\text{R}_3\text{NHCl}]}{[\text{Ni}^{2+}][\text{Cl}^-]^2[\text{R}_3\text{NHCl}]} \times \frac{\gamma_{\text{NiCl}_2\text{R}_3\text{NHCl}}}{\gamma_{\text{Ni}^{2+}}(\gamma_{\text{Cl}^-})^2\gamma_{\text{R}_3\text{NHCl}}} \\ &= K_{\text{ex,eff}} \times \frac{\gamma_{\text{NiCl}_2\text{R}_3\text{NHCl}}}{\gamma_{\text{Ni}^{2+}}(\gamma_{\text{Cl}^-})^2\gamma_{\text{R}_3\text{NHCl}}} \end{aligned} \quad (5)$$

In the above equation, K_{ex} and $K_{\text{ex,eff}}$ represent the equilibrium constant and the effective equilibrium constant, respectively. Effective equilibrium constant is a function of concentration, while equilibrium constant is a function of activity.

In order to estimate effective equilibrium constant, equilibrium concentration of the chemical species which take part in the reaction should be obtained from the experimental data. Normally the solvent extraction data are the overall concentration of the metals in aqueous and organic phases after extraction. In solvent extraction of Ni(II) from HCl solution, Ni^{2+} and NiCl^+ exist in the aqueous phase. Therefore, the equilibrium concentration of Ni^{2+} is different from the overall concentration of nickel in the aqueous phase. The equilibrium concentration of free Ni^{2+} after extraction was obtained from the experimental data by using the chemical equilibria together with mass balance equations. When the volume ratio of aqueous to organic was unity, mass balance equations for nickel, cobalt and Alamine336 reduced to

$$[\text{NiCl}_2\text{R}_3\text{NHCl}] = [\text{Ni}]_{\text{organic,total}} = [\text{Ni}]_{\text{total}} - [\text{Ni}]_{\text{aqueous,total}} \quad (6)$$

$$[\text{R}_3\text{NHCl}] = [\text{R}_3\text{N}]_{\text{total}} - [\text{Ni}]_{\text{organic,total}} \quad (7)$$

$$[\text{Ni}]_{\text{aqueous, total}} = [\text{Ni}^{2+}] + [\text{NiCl}^+] \quad (8)$$

$$[\text{Cl}]_{\text{aqueous, total}} = [\text{Cl}^-] + [\text{NiCl}^+] \quad (9)$$

The effective equilibrium constants thus obtained are 2.81 at 1 M HCl, 0.64 at 5 M HCl, and 0.55 at 10 M HCl solution. The value of effective equilibrium constant decreased with the increase of HCl concentration.

It is possible to predict the distribution coefficient of Ni from the initial extraction conditions by solving nonlinear equations which consists of chemical equilibria, solvent extraction reaction, and mass balance equations. The following equations represent the mass balance equations for Ni, Cl and Alamine336.

$$[\text{Ni}]_{\text{total}} = [\text{NiCl}_2]_{\text{total}} = [\text{Ni}^{2+}] + [\text{NiCl}^+] + [\text{NiCl}_2\text{R}_3\text{NHCl}] \quad (10)$$

$$[\text{Cl}]_{\text{total}} = [\text{HCl}]_{\text{total}} + 2[\text{NiCl}_2]_{\text{total}} + [\text{R}_3\text{N}]_{\text{total}} \\ = [\text{Cl}^-] + [\text{NiCl}^+] + 3[\text{NiCl}_2\text{R}_3\text{NHCl}] + [\text{R}_3\text{NHCl}] \quad (11)$$

$$[\text{R}_3\text{N}]_{\text{total}} = [\text{R}_3\text{NHCl}] + [\text{NiCl}_2\text{R}_3\text{NHCl}] \quad (12)$$

Tables 1, 2, and 3 give the experimental conditions along with the extraction results. The distribution coefficients of Ni(II)

Table 1. Initial extraction conditions and measured and calculated distribution coefficients of Ni(II) from 1 M HCl solution

N	$[\text{NiCl}_2]_{\text{t}}$	$[\text{R}_3\text{N}]_{\text{t}}$	Log D_{expt}	Log D_{calc}
1	0.051	0.021	-1.288	-1.378
2	0.051	0.052	-1.014	-0.984
3	0.051	0.103	-0.693	-0.688
4	0.051	0.155	-0.536	-0.511
5	0.051	0.207	-0.431	-0.386
6	0.051	0.310	-0.248	-0.212
7	0.051	0.517	-0.110	0.009
8	0.051	0.723	-0.031	0.153
9	0.051	1.033	0.031	0.307
10	0.051	1.446	0.110	0.452
11	0.051	1.756	0.148	0.535
12	0.12	0.021	-0.975	-1.378
13	0.12	0.052	-0.773	-0.983
14	0.12	0.103	-0.477	-0.686
15	0.12	0.155	-0.275	-0.508
16	0.12	0.207	-0.196	-0.382
17	0.12	0.310	0.010	-0.207
18	0.12	0.517	0.136	0.014
19	0.12	0.723	0.181	0.159
20	0.12	1.033	0.233	0.312
21	0.12	1.446	0.299	0.457
22	0.12	1.756	0.356	0.540
23	0.26	0.207	0.153	-0.398
24	0.26	0.310	0.222	-0.216
25	0.26	0.517	0.261	0.012
26	0.26	0.723	0.352	0.160
27	0.26	1.033	0.398	0.316
28	0.26	1.446	0.457	0.462
29	0.26	1.756	0.498	0.545

(N: number, Subscript expt: experimentally measured values, calc: calculated values). standard deviation between measured and predicted distribution coefficient = 0.05.

Table 2. Initial extraction conditions and measured and calculated distribution coefficients of Ni(II) from 5 M HCl solution

N	$[\text{NiCl}_2]_{\text{t}}$	$[\text{R}_3\text{N}]_{\text{t}}$	Log D_{expt}	Log D_{calc}
1	0.051	0.021	-0.926	-1.070
2	0.051	0.052	-0.479	-0.668
3	0.051	0.103	-0.286	-0.360
4	0.051	0.155	-0.113	-0.174
5	0.051	0.207	-0.065	-0.042
6	0.051	0.310	0.020	0.143
7	0.051	0.517	0.130	0.377
8	0.051	0.723	0.208	0.529
9	0.051	1.033	0.316	0.690
10	0.051	1.446	0.393	0.840
11	0.051	1.756	0.418	0.926
12	0.12	0.207	0.108	-0.109
13	0.12	0.310	0.282	0.088
14	0.12	0.517	0.452	0.337
15	0.12	0.723	0.515	0.498
16	0.12	1.033	0.597	0.666
17	0.12	1.446	0.678	0.822
18	0.12	1.756	0.717	0.912
19	0.26	0.723	0.644	0.432
20	0.26	1.033	0.698	0.618
21	0.26	1.446	0.761	0.787
22	0.26	1.756	0.781	0.882

standard deviation between measured and predicted distribution coefficient = 0.05.

Table 3. Initial extraction conditions and measured and calculated distribution coefficients of Ni(II) from 10 M HCl solution

N	$[\text{NiCl}_2]_{\text{t}}$	$[\text{R}_3\text{N}]_{\text{t}}$	Log D_{expt}	Log D_{calc}
1	0.051	0.021	-0.699	-0.834
2	0.051	0.052	-0.368	-0.417
3	0.051	0.103	-0.144	-0.092
4	0.051	0.155	0.003	0.106
5	0.051	0.207	0.099	0.245
6	0.051	0.310	0.197	0.439
7	0.051	0.517	0.413	0.680
8	0.051	0.723	0.507	0.834
9	0.051	1.033	0.597	0.997
10	0.051	1.446	0.669	1.148
11	0.051	1.756	0.843	1.235
12	0.12	0.052	-0.148	-0.569
13	0.12	0.103	0.070	-0.227
14	0.12	0.155	0.240	-0.012
15	0.12	0.207	0.380	0.143
16	0.12	0.310	0.510	0.360
17	0.12	0.517	0.734	0.627
18	0.12	0.723	0.919	0.796
19	0.12	1.033	1.041	0.969
20	0.12	1.446	1.112	1.128
21	0.12	1.756	1.134	1.218
22	0.26	0.207	0.482	-0.050
23	0.26	0.310	0.578	0.196
24	0.26	0.517	0.788	0.514
25	0.26	0.723	0.882	0.712
26	0.26	1.033	0.945	0.910
27	0.26	1.446	1.054	1.086
28	0.26	1.756	1.165	1.184

standard deviation between measured and predicted distribution coefficient = 0.06

which were predicted from the initial extraction conditions by the above method are also shown in Tables 1, 2, and 3. Figure 4 shows the distribution coefficients of Ni(II) reported in the literature and those calculated in this study. It is seen in Fig. 4 that the distribution coefficients of Ni(II) calculated in this study at each HCl concentration agreed well with those reported in the literature.

In the solvent extraction system where the ionic strength of the solution differs greatly, the variation in the activity coefficients of chemical species should be considered to predict accurately the effect of ionic strength on the extraction of metal ions. In a previous study on the ionic equilibria of NiCl₂ in HCl solution, we estimated the equilibrium constant for the formation of NiCl⁺ and Bromley interaction parameter, which could calculate solution pH of NiCl₂ up to 3 m(molality) HCl solution.¹

In order to consider the variation in the activity coefficients of chemical species with ionic strength of aqueous solution, the activity coefficients of Ni²⁺ and Cl⁻ was calculated by using Bromley equation. Bromley equation for the activity coefficient of the cation, γ_M , at 25 °C is represented below¹⁵

$$\log \gamma_M = -\frac{0.5108(z_M)^2 I^{0.5}}{1 + I^{0.5}} + F_M = -A(z_M)^2 + F_M \quad (13)$$

$$F_M = \sum_X \left[\frac{(0.06 + 0.6B_{MX}) \times |z_M z_X|}{\left(1 + \frac{1.5}{|z_M z_X|} I\right)^2} + B_{MX} \right] \times \frac{(|z_M| + |z_X|)^2}{4} [X] \quad (14)$$

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 .

The equilibrium constant (K_{ex}) for the solvent extraction reaction, defined as eq. (5), was obtained from the experimental data. By using this equilibrium constant thus obtained, distribution coefficient of nickel at each experimental condition was

predicted by solving Eqs. (10) to (12) together with the activity coefficients. However, standard deviation between the predicted and the measured distribution coefficients was 0.5, which means that it is difficult to exactly predict the distribution coefficient of nickel from initial extraction conditions.

Solvent extraction of Co(II) by Alamine336 from low to strong HCl solution was analyzed by considering the complex formation of cobalt complexes and the activity coefficients of these complexes.¹⁴ In order to develop a chemical model on the separation of Ni(II) and Co(II) by Alamine336 from strong HCl solution, activity coefficients of nickel species should be considered. It might be concluded that further study on the complex formation of nickel species and on the interaction parameter for each complex at high HCl solution should be done to predict the effect of ionic strength on the extraction of nickel from strong HCl solution.

Conclusions

Although many studies have reported that most of nickel exists as Ni²⁺ and NiCl⁺ in HCl solution, Alamine336 extracted well nickel in strong HCl solution up to 10 M. Solvent extraction data of Ni(II) by Alamine336 have been analyzed to identify solvent extraction reaction. Effective equilibrium constant of the solvent extraction at each HCl concentration was estimated from the extraction data by using chemical equilibria and mass balance. The measured distribution coefficients of Ni(II) agreed well with those calculated in this study by using the effective equilibrium constant. In order to develop a chemical model on the separation of Ni(II) and Co(II) from strong HCl solution by Alamine336, further study on the complex formation of nickel complexes and on measurement of activities of these complexes at strong HCl solution need to be done.

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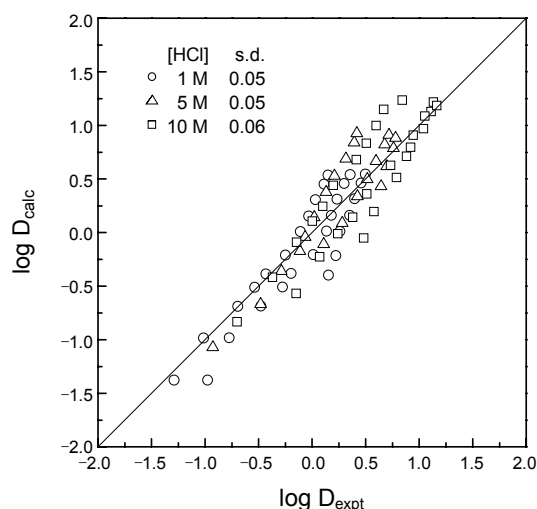


Figure 4. Comparison of the distribution coefficient of Ni(II) at several HCl concentration between measured and calculated in this study.