

Solvent Extraction of Zinc from Strong Hydrochloric Acid Solution with Alamine336

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Solvent extraction reaction of Zn(II) by Alamine336 from strong HCl solution up to 10 M was identified by analyzing the data reported in the literature. The equilibrium constant of this reaction was estimated by considering the complex formation between zinc and chloride ion. The necessary thermodynamic parameters, such as equilibrium constant for the formation of complexes and the interaction parameters, were evaluated from the thermodynamic data reported in the literature. The following solvent extraction reaction and the equilibrium constant was obtained by considering the activity coefficients of solutes present in the aqueous phase with Bromley equation. $Zn^{2+} + 2Cl^- + R_3NHCl_{org} = ZnCl_2R_3NH_{org}$, $K_{ex} = 6.33 \times 10^2$. There was a good agreement between measured and calculated distribution coefficients of Zn(II).

Key Words: ZnCl₂, HCl, Alamine336, Solvent extraction

Introduction

Solvent extraction of Zn(II) has been widely practiced in separating zinc from the aqueous solution containing metal ions, such as Co(II), Ni(II), Cu(II) and Fe(III).¹ Organophosphorus and carboxylic acid extractants have been used in the solvent extraction of zinc from sulphate solutions.^{2,3} Zinc ion can form various chloride complexes in HCl solution and this tendency can be utilized to separate zinc from chloride solution. Especially recovery of zinc from spent hydrochloric acid pickling solutions can be accomplished by using amine extractant.^{1,4}

Alamine336 (Tertiary amine, R₃N, R = CH₃(CH₂)₇) is an anionic extractant and is extensively used in the solvent extraction of various metal ions.^{3,5-7} Sayar *et al.* reported the data on the solvent extraction of zinc by Alamine336 from HCl solution up to 10 M.³ They proposed the following equation to simulate the solvent extraction behavior of zinc in their system.³

$$E = 100 - [a_1 \exp(d_1 I_c) + (100 - a_1) \exp(d_2 I_c)] \quad (1)$$

In the above equation, E represents extraction percentage of zinc and I_c the volumetric percentage of Alamine336. They obtained the parameters (a_1 , d_1 , and d_2) from their results by regression analysis.³ The extraction percentage of zinc predicted by using the above equation agreed well with those measured in their study.³ However, it is difficult to apply the above equation in predicting the separation behavior of zinc from other metal ions by using Alamine336.

In aqueous solution, ionic strength of a solution has a great effect on the activity of solutes present in that solution. Therefore, the effect of ionic strength on the activity of solutes should be considered in predicting the impact of operating variables on the solvent extraction of metals. In this study, the

data reported by Sayar *et al.*³ were analyzed to identify the solvent extraction reaction and the corresponding equilibrium constant was estimated by considering the activity coefficients of solutes present in the aqueous phase with Bromley equation. The necessary thermodynamic values were evaluated from the data reported in the literature.

Theoretical Background

Zinc ion forms various complexes with chloride ion, which can be represented by



The equilibrium constant for eq. (2) at a given ionic strength, K_i^1 , is related to the equilibrium constant at zero ionic strength, K_i^0 , and to the activity coefficient as follows

$$K_i^0 = K_i^1 \frac{\gamma_{ZnCl_i^{2-i}}}{\gamma_{Zn^{2+}} (\gamma_{Cl^-})^i} \quad (3)$$

Taking logarithm on both sides of the above equation results in

$$\log K_i^1 = \log K_i^0 + \log \gamma_{Zn^{2+}} + i \log \gamma_{Cl^-} - \log \gamma_{ZnCl_i^{2-i}} \quad (4)$$

The activity coefficient of solute was calculated by Bromley equation. Bromley equation for the activity coefficient of the cation, γ_M , is represented by the following equations.⁸

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

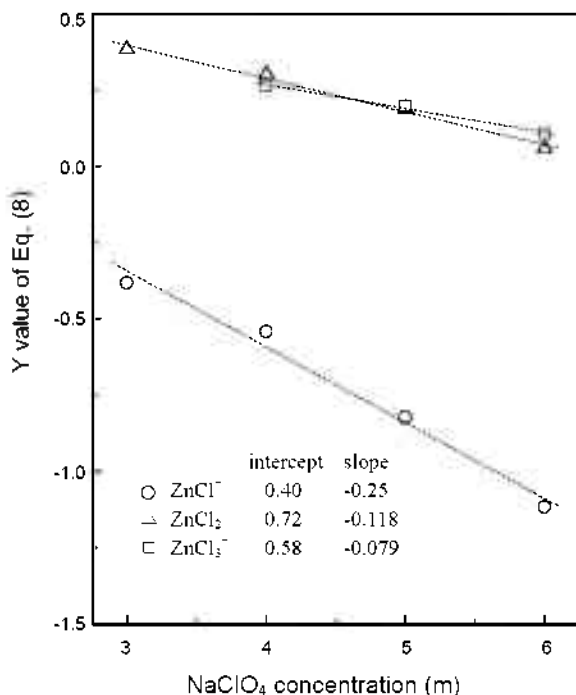


Figure 1. Evaluation of the equilibrium constant for the formation of complexes at zero ionic strength and the interaction parameter from the reported data.

$$F_M = \sum_X \left[\frac{(0.06 + 0.6B_{MX}) \times |z_M z_X|}{\left(1 + \frac{1.5I}{|z_M z_X|}\right)^2} + B_{MX} \right] \times \frac{(|z_M| + |z_X|)^2}{4} [X] \quad (6)$$

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 coefficients of each species into Eq. (4) gives

$$\log K_1^1 = \log K_1^0 + (I^2 - 5I)A + F_{Zn^{2+}} + IF_{Cl^-} - F_{ZnCl_2^{2+}} \quad (7)$$

The equilibrium constants for the formation of zinc chloride complexes at different $NaClO_4$ concentration have been reported in the literature.⁹ The concentrations of Zn^{2+} , Cl^- and $ZnCl_2^{2+}$ are negligible compared to the $NaClO_4$ concentration in these data.^{10,11} Hence, F term for the activity coefficient of the anion is related only to the cation Na^+ of the ionic medium, while F term for the activity coefficient of cation is related to the anion ClO_4^- of the ionic medium. In this case, Eq. (7) for $ZnCl_2^{2+}$ reduces to

$$\log K_1^1 + 4A - \left[\frac{2(0.06 + 0.6B_{Zn^{2+}, ClO_4^-})}{\left(1 + \frac{1.5I}{2}\right)^2} + B_{Zn^{2+}, ClO_4^-} \right] \times \frac{9}{4} [ClO_4^-]$$

$$= - \left[\frac{(0.06 + 0.6B_{Na^+, Cl^-})}{(1 + 1.5I)^2} + B_{Na^+, Cl^-} \right] \times [Na^+] \\ = \log K_1^0 - \left[\frac{(0.06 + 0.6B_{ZnCl_2^{2+}, ClO_4^-})}{(1 + 1.5I)^2} + B_{ZnCl_2^{2+}, ClO_4^-} \right] \times [ClO_4^-] \quad (8)$$

The equation for the formation of $ZnCl_2^0$ and $ZnCl_3^-$ could be obtained in the same manner. Bromley reported interaction parameters between Zn^{2+} and ClO_4^- and between Na^+ and Cl^- .⁸ These values and the concentrations of Na^+ and ClO_4^- were inserted into the equations for the respective complex. Eq. (8) indicates that a straight line would be obtained by plotting the value of left-hand side of this equation against the concentration of $NaClO_4$. The equilibrium constant for the formation of zinc chloride complexes is related to the intercept of the straight line, while the interaction parameter is related to the slope of the straight line. In the case of $ZnCl_2^0$, the slope of the straight line is directly related to the activity coefficient of this species in $NaClO_4$ solution. Fig. 1 shows these plots for the formation of $ZnCl^+$, $ZnCl_2^0$, and $ZnCl_3^-$. Table 1 represents the equilibrium constants at zero ionic strength and interaction parameters thus obtained in this study.

Results and Discussion

Solvent extraction of Zn(II) from chloride solution by Alamine336. Some studies have shown that amine extractants can react with inorganic acid to form amine salt when the amount of inorganic acid is in excess to that of amine.¹²⁻¹⁴ The following reaction represents the formation reaction of Alamine336 salt (R_3NHCl) with HCl.



In the above equation, subscript *org* means organic phase. Solvent extraction reaction of Zn(II) from chloride solution by Alamine336 can be represented as



where m represents stoichiometric coefficient for Alamine336 salt.

The value of m was determined from the extraction data by the following method. First the definition of distribution coefficient was inserted into the equilibrium constant of Eq. (10) and taking logarithm on both sides of the resulting equation leads to

$$\log D \cong \log K_{ex} + 2 \log [Cl^-] + m \log [R_3NHCl] \quad (11)$$

Equation (11) indicates that a plot of $\log D$ against $\log [R_3NHCl]$ gives a straight line with a slope of m when the concentration of HCl is constant. Figs. 2-4 show these plots for the solvent extraction data reported by Sayar.³ In Fig. 2, the initial concentration of Zn was 0.046 M. The distribution

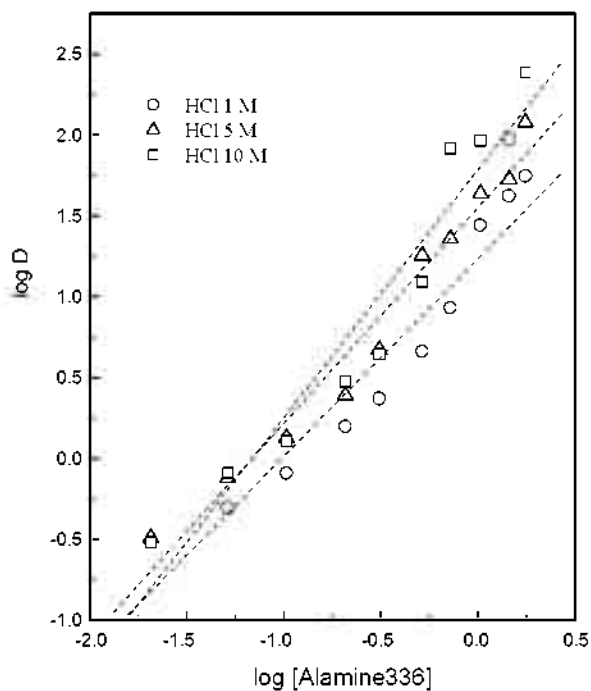


Figure 2. Effect of Alamine336 concentration on the extraction of Zn(II) at various HCl concentration (Initial concentration of Zn(II) = 0.046 M).

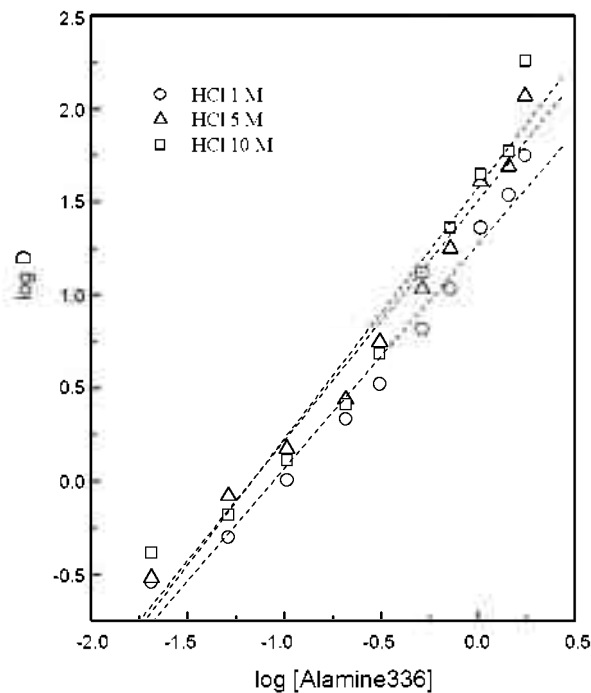


Figure 4. Effect of Alamine336 concentration on the extraction of Zn(II) at various HCl concentration (Initial concentration of Zn(II) = 0.23 M).

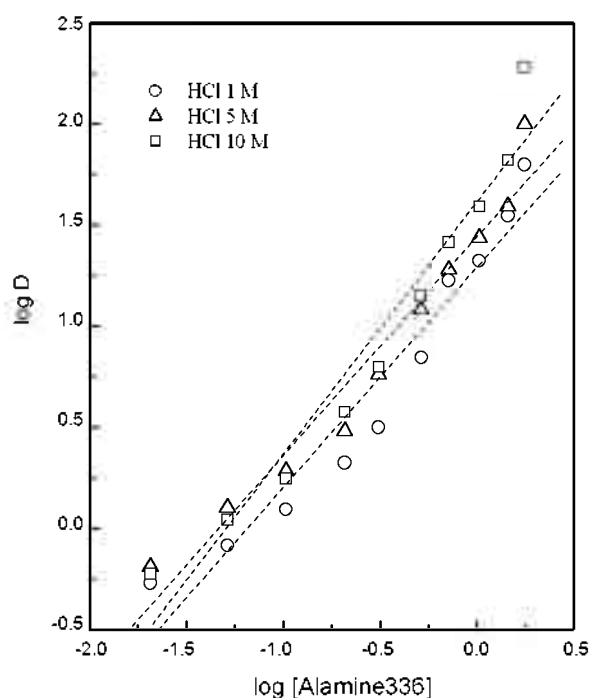


Figure 3. Effect of Alamine336 concentration on the extraction of Zn(II) at various HCl concentration (Initial concentration of Zn(II) = 0.107 M).

coefficients of Zn increased linearly with Alamine336 concentration at various HCl concentrations and the slope of this plot is close to unity. In Figs. 3 and 4, the initial concentration of Zn was 0.107 and 0.23 M, respectively. In both figures, the

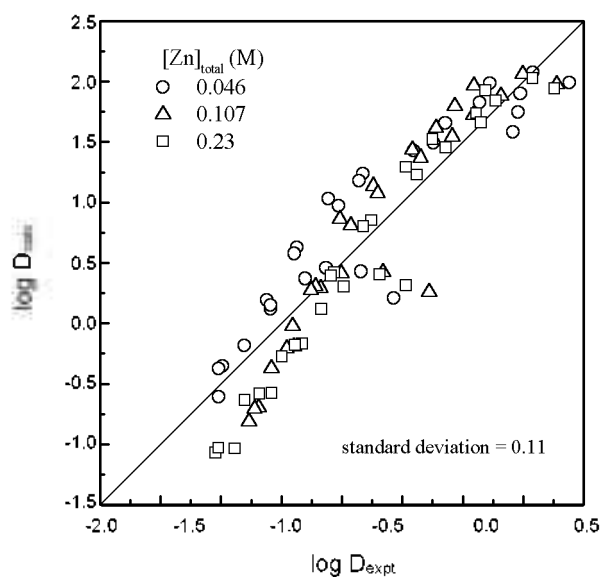
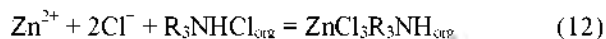


Figure 5. Comparison of the distribution coefficients of Zn(II) between reported in the literature and calculated in this study.

slope is also close to unity. Therefore, the solvent extraction reaction of Zn(II) from HCl solution by Alamine336 could be represented as follows



Prediction of the distribution coefficient of Zn(II) from the initial extraction conditions. In order to predict the distribution coefficients of Zn from the initial extraction conditions, equi-

Table 1. Estimated equilibrium constant and interaction parameter.

Reaction	K	Interaction parameter
$\text{Zn}^{2+} + \text{Cl}^- = \text{ZnCl}^+$	0.40	$B_{\text{ZnCl}^+, \text{ClO}_4^-}$ 0.24
$\text{Zn}^{2+} + 2\text{Cl}^- = \text{ZnCl}_2^0$	0.72	
$\text{Zn}^{2+} + 3\text{Cl}^- = \text{ZnCl}_3^-$	0.58	$B_{\text{Na}^+, \text{ZnCl}_3^-}$ 0.076

Table 2. Initial and equilibrium conditions together with calculated results at the initial Zn concentration of 0.046 M.

N	[HCl] _t	[R ₃ N] _t	logD _{expt}	LogD _{cal}
1	1.0	0.021	-0.519	-0.413
2	1.0	0.052	-0.306	0.083
3	1.0	0.103	-0.088	0.461
4	1.0	0.207	0.197	0.675
5	1.0	0.310	0.370	0.776
6	1.0	0.517	0.659	0.895
7	1.0	0.723	0.930	0.900
8	5.0	0.021	-0.489	-0.495
9	5.0	0.052	-0.120	-0.019
10	5.0	0.103	0.126	0.364
11	5.0	0.207	0.389	0.745
12	5.0	0.310	0.673	0.955
13	5.0	0.517	1.256	1.216
14	5.0	0.723	1.357	1.387
15	5.0	1.033	1.639	1.575
16	5.0	1.446	1.724	1.762
17	5.0	1.756	2.078	1.877
18	10.0	0.021	-0.519	-0.612
19	10.0	0.052	-0.088	-0.166
20	10.0	0.103	0.107	0.187
21	10.0	0.207	0.475	0.547
22	10.0	0.310	0.644	0.748
23	10.0	0.517	1.091	0.997
24	10.0	0.723	1.916	1.158
25	10.0	1.033	1.958	1.330
26	10.0	1.446	1.976	1.493
27	10.0	1.756	2.381	1.590

logD_{expt}: measured distribution coefficients of ZnLogD_{cal}: calculated distribution coefficients of Zn

Equilibrium concentrations of all the chemical species in both phases after extraction should be known. In strong acid solution, the concentration of hydroxide ion can be ignored. When we consider the complex formation reactions and solvent extraction reaction, the number of chemical species in both phases after extraction would be ten (Cl^- , H^+ , Zn^{2+} , ZnCl^+ , ZnCl_2^0 , ZnCl_3^- , R_3NHCl , $\text{ZnCl}_3\text{R}_3\text{NH}$, H_2O , xylene). In order to calculate the concentrations of the eight species excluding H_2O and xylene, 8 independent equations are required. We obtained these eight equations from 3 chemical equilibria, solvent extraction reaction, three mass balance equations (Zn, Cl, R₃N), charge balance. From the chemical equilibria together with solvent extraction reaction, mass and charge balance equations were obtained as follows when the volume ratio of aqueous to organic was unity.

$$[\text{Zn}]_{\text{total}} = [\text{Zn}^{2+}] + [\text{ZnCl}^+] + [\text{ZnCl}_2^0] + [\text{ZnCl}_3^-] + [\text{ZnCl}_3\text{R}_3\text{NH}] \quad (13)$$

Table 3. Initial and equilibrium conditions together with calculated results at the initial Zn concentration of 0.107 M.

N	[HCl] _t	[R ₃ N] _t	logD _{expt}	LogD _{cal}
1	1.0	0.021	-0.269	-0.721
2	1.0	0.052	-0.083	-0.233
3	1.0	0.103	0.093	0.205
4	1.0	0.207	0.323	0.641
5	1.0	0.310	0.496	0.683
6	1.0	0.517	0.840	0.812
7	1.0	0.723	1.223	0.865
8	5.0	0.021	-0.189	-0.764
9	5.0	0.052	0.101	-0.290
10	5.0	0.103	0.282	0.132
11	5.0	0.207	0.481	0.604
12	5.0	0.310	0.759	0.861
13	5.0	0.517	1.082	1.161
14	5.0	0.723	1.278	1.348
15	5.0	1.033	1.434	1.548
16	5.0	1.446	1.590	1.743
17	5.0	1.756	1.996	1.862
18	10.0	0.021	-0.224	-0.830
19	10.0	0.052	0.042	-0.378
20	10.0	0.103	0.244	0.004
21	10.0	0.207	0.572	0.425
22	10.0	0.310	0.795	0.662
23	10.0	0.517	1.150	0.945
24	10.0	0.723	1.411	1.121
25	10.0	1.033	1.587	1.304
26	10.0	1.446	1.816	1.475
27	10.0	1.756	2.279	1.575

$$[\text{Cl}]_{\text{total}} = [\text{Cl}^-] + [\text{ZnCl}^+] + 2[\text{ZnCl}_2^0] + 3[\text{ZnCl}_3^-] + 3[\text{ZnCl}_3\text{R}_3\text{NH}] + [\text{R}_3\text{NHCl}] \quad (14)$$

$$[\text{R}_3\text{N}]_{\text{total}} = [\text{R}_3\text{NHCl}] + [\text{ZnCl}_3\text{R}_3\text{NH}] \quad (15)$$

In strong HCl solution, charge balance equation reduces to

$$[\text{H}^+] = [\text{HCl}]_{\text{total}} - [\text{R}_3\text{NHCl}]_{\text{total}} \quad (16)$$

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

These nonlinear equations were solved by using Newton-Raphson method. The activity coefficients of solutes present in the aqueous phase was calculated by Bromley equation.⁸ However, few equations are available to calculate the activity coefficient of chemical species present in the organic phase. Therefore the activity coefficients of Alamine336 salt and zinc extracted species were assumed to be unity. The unit of concentration employed in estimating the interaction parameters shown in Table 1 was molality. The unit of concentration in the data reported by Sayar *et al.* was molarity.³ The difference between molar and molal concentration was assumed to be small and the thermodynamic values shown in Table 1 were used without correction. With this assumption, the equilibrium constant for the solvent extraction of Zn by Alamine336 is represented as

Table 4. Initial and equilibrium conditions together with calculated results at the initial Zn concentration of 0.230 M.

N	[HCl] _i	[R ₃ N] _i	logD _{expt}	LogD _{cal}
1	1.0	0.021	-0.545	-1.038
2	1.0	0.052	-0.304	-0.590
3	1.0	0.103	0.003	-0.194
4	1.0	0.207	0.331	0.316
5	1.0	0.310	0.517	0.607
6	1.0	0.517	0.814	0.682
7	1.0	0.723	1.032	0.783
8	5.0	0.021	-0.520	-1.060
9	5.0	0.052	-0.081	-0.616
10	5.0	0.103	0.170	-0.228
11	5.0	0.207	0.435	0.278
12	5.0	0.310	0.743	0.624
13	5.0	0.517	1.032	1.029
14	5.0	0.723	1.250	1.260
15	5.0	1.033	1.610	1.489
16	5.0	1.446	1.689	1.702
17	5.0	1.756	2.078	1.829
18	10.0	0.021	-0.386	-1.094
19	10.0	0.052	-0.182	-0.657
20	10.0	0.103	0.111	-0.287
21	10.0	0.207	0.410	0.165
22	10.0	0.310	0.678	0.462
23	10.0	0.517	1.122	0.823
24	10.0	0.723	1.360	1.037
25	10.0	1.033	1.652	1.247
26	10.0	1.446	1.773	1.435
27	10.0	1.756	2.258	1.542

$$K_{\text{ex}} = \frac{[\text{ZnCl}_3\text{R}_3\text{NH}]}{[\text{Zn}^{2+}][\text{Cl}^-]^2[\text{R}_3\text{NHCl}]} \times \frac{1}{\gamma_{\text{Zn}^{2+}}(\gamma_{\text{Cl}^-})^2} \quad (17)$$

In order to estimate the above equilibrium constant from the extraction data, an evaluation function was defined as follows:

$$\text{Err} = \frac{1}{N} \sum (D_{\text{calc}} - D_{\text{meas}})^2 \quad (18)$$

where N denotes the number of experimental data and D_{calc} and D_{meas} represent the distribution coefficient of Zn calculated in this study and measured by Sayar *et al.*,³ respectively. The following equilibrium constant was obtained by minimizing the Err function.

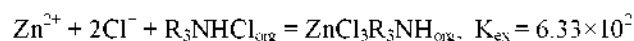
$$K_{\text{ex}} = 6.33 \times 10^2 \quad (19)$$

Table 2, 3, and 4 show the initial extraction conditions together with the distribution coefficients of Zn(II) reported in the literature.³ The distribution coefficients of Zn was predicted from the initial extraction conditions by using the above equilibrium constant and these predicted values are also shown in Table 2, 3, and 4. Figure 5 shows the measured distribution coefficients of Zn(II) and the calculated values. Standard

deviation between the two values was 0.11. The concentration range of HCl was from 1 to 10 M. Since ionic strength of a solution has a great effect on the reaction, it can be concluded that the measured distribution coefficients of Zn(II) agreed well with those predicted in this study.

Conclusions

Solvent extraction data reported in the literature were analyzed to determine the solvent extraction reaction of Zn(II) by Alamine336 from low to high HCl solution up to 10 M. The equilibrium constant for this solvent extraction reaction was estimated by considering the activity coefficient of chemical species present in the aqueous phase with Bromley equation. Complex formation of zinc chloride, such as ZnCl⁺, ZnCl₂⁰ and ZnCl₃⁻ were considered. The thermodynamic values related to the formation of these complexes were evaluated from the data on the variation of the formation constant with ionic strength. Solvent extraction reaction of Zn from HCl solution by Alamine336 and the corresponding equilibrium constant can be represented as follows



The measured distribution coefficients of Zn(II) agreed well with those calculated in this study by using the above equilibrium constant. The above solvent extraction reaction together with the equilibrium constant can be employed in calculating the number of equilibrium stages for the solvent extraction of zinc chloride by Alamine336.

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