EXTRACTION EQUILIBRIUM OF ZINC CHLORIDE WITH LONG-CHAIN ALKYLAMINE

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As a basic study of solvent extraction of metals with high molecular-weight amines, the measurement of the distribution equilibrium of zinc chloride between Amberlite LA-2, long-chain secondary alkylamine (*n*-lauryl trialkylmethylamine), dissolved in *n*-hexane and an aqueous solution of hydrochloric acid was carried out at 30°C over wide concentration ranges of amine, zinc chloride and hydrochloric acid.

It was clarified that zinc chloride is extracted by the following reaction:

The equilibrium constant for this reaction and the stability constants of the chloro complexes of zinc were determined.

Introduction

Solvent extraction with high molecular-weight amines is now in extensive hydrometallurgical use, for example in the uranium purification process named the Amex Process, and a great number of basic and applied studies of the extraction of many kinds of acids and metals with amines have been made¹⁹⁾. The solvent extraction of zinc chloride with amines also has been studied by many investigators from the standpoint of physical chemistry and analytical chemistry. The purposes of these studies are to evaluate the stability constants of the chloro complexes of zinc^{7,12,15-17)}, to determine the role of aggregates in the organic phase^{1-6,24)}, to compare the extraction efficiency with various kinds of amines and diluents^{11,22)} and so on. Most of these studies were made using tertiary amines or quaternary ammonium salts, and those using primary or secondary amines are few. Furthermore, most of these concern the extraction equilibrium in the low concentration ranges of zinc in the organic phase. There are few studies over a wide range of zinc-loading to amine.

The authors studied the extraction equilibrium of zinc chloride with Amberlite LA-2, the long-chain secondary alkylamine (*n*-lauryl-trialkylmethylamine, shortened to LA-2 hereinafter) dissolved in *n*-hexane and the effects of the concentrations of zinc chloride, hydrochloric acid in the aqueous phase and LA-2 in the organic phase on the distribution equilibrium were investigated over a wide concentration range of these components.

The information obtained in this study is used

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in the analysis of the extraction rate mechanism of zinc chloride with LA-2⁹⁾.

1. Experimental

LA-2 was washed alternatively with 10 wt% hydrochloric acid and aqueous sodium hydroxide solution several times and with ion-exchanged water. After dilution with *n*-hexane to the required concentration, LA-2 was completely transformed into the ammonium salt by reaching equilibrium with a large amount of a 1-mol/l aqueous solution of hydrochloric acid.

The aqueous solution of zinc chloride was prepared by dissolving commercial GR grade zinc chloride in an aqueous hydrochloric acid solution of the required concentration. In these procedures, commercial GR grade hydrochloric acid and *n*-hexane were used without further purification.

Equal volumes of the aqueous and organic phases of known concentrations were shaken in a flask and allowed to attain equilibrium in a water bath maintained at 30±0.1°C. After about twelve hours, the phases were separated from each other and analysed for zinc content.

The concentration of LA-2 in the organic phase was determined as follows. Before the saturation with hydrochloric acid, it was determined by titration with hydrochloric acid dissolved in methanol-butanol mixture and bromocresol green as indicator. After the saturation, the hydrochloric acid concentration in the organic phase was determined by titration with an ethanol solution of potassium hydroxide and phenolphthalein as indicator. Then it was confirmed that LA-2 was completely transformed into the ammonium salt.

Fig. 1 Effect of C_{B0} on the distribution equilibrium ($[HCl] = 1.0 \text{ mol/l}$)

Fig. 2 Effect of $[HCl]$ on the distribution equilibrium ($C_{B0} = 0.2 \text{ mol/l}$)

Zinc chloride content in the aqueous phase was determined by titration with DETA and xylenol orange as indicator in the range of high concentration and by spectrophotometric analysis using the zincon method in the range of low concentration. The concentration of zinc in the organic phase was obtained from mass balance or determined by titration of organic phase in much the same way as for the aqueous phase.

2. Experimental Results

The equilibrium concentrations of zinc in both phases are shown in Figs. 1 and 2. Figure 1 shows the results in which the concentration of hydrochloric

acid in the aqueous phase was maintained at 1.0 mol/l and that of LA-2 in the organic phase was varied from 0.1 to 0.55 mol/l . From these results, it is evident that the plotted points of C_{ZnO}/C_{B0} against C_{ZnW} lie on a single curve regardless of C_{B0} . Figure 2 shows the results in which C_{B0} was maintained at 0.2 mol/l and the concentration of hydrochloric acid in the aqueous phase was varied from 0.1 to 6.0 mol/l .

From these results, it is evident that the value of C_{ZnO}/C_{B0} approaches the constant value of $1/2$ with increase of C_{ZnW} and is proportional to C_{ZnW} regardless of hydrochloric acid in the low concentration range of C_{ZnO} . The former seems to suggest that zinc in the aqueous phase reacts with the ammonium salt of LA-2 in the organic phase in the ratio of $1:2$ to form a complex in the organic phase. And the latter seems to suggest that the complex formed in the organic phase exists as a mononuclear complex of zinc.

Furthermore, it is evident that at lower loading ratios, C_{ZnO}/C_{B0} increases remarkably with increase of hydrochloric acid concentration in the range less than 2.0 mol/l but decreases slightly in the range greater than 2.0 mol/l . These results are considered to correspond to the variation of composition of the chloro complexes of zinc in the aqueous phase with chloride ion concentration, as is explained in the following section.

3. Discussion

From the results mentioned in the previous section, it is considered that zinc extracted into the organic phase exists as the species, $(BH)_2ZnCl_4$.

On the basis of the facts mentioned above and the results of the distribution equilibrium of hydrochloric acid with LA-2 reported in the previous paper⁸⁾, the experimental results were examined as follows.

It is well-known that zinc in aqueous hydrochloric acid solution exists as the chloro complexes shown below.

Although the stability constants of these chloro complexes of zinc have been obtained by many investigators by various methods such as potentiometry, polarography, cation exchange, anion exchange and solvent extraction with high molecular-weight amine analogous to the present study, the values of these stability constants vary widely among the investigators, as shown in Table 1.

In the organic phase, it is considered from the results reported in the previous paper⁸⁾ that in the

Table 1 Comparison of values of the stability constants of the Zn (II) chloro complexes

No	Temp. [°C]	β_1	β_2	β_3	β_4	Method	Literature
1	25	2.7×10^0	4.1×10^0	2.1×10^0	1.6×10^0	anion exchange	14)
2	20	5.3×10^0	3.1×10^0	6.5×10^{-1}	1.5×10^0	cation exchange	20)
3	25	4.8×10^{-1}	8.9×10^{-1}	5.0×10^{-1}	7.1×10^{-1}	emf	18)
4	25	6.5×10^{-1}	1.5×10^0	4.0×10^{-2}	3.0×10^{-2}	amine extraction	17)
5	20	3.2×10^{-1}	1.0×10^{-1}	1.0×10^0	1.0×10^{-1}	anion exchange	13)
6	25	3.2×10^{-1}	1.0×10^0	8.5×10^{-1}	—	polarography	10)
7	25	6.5×10^{-1}	2.5×10^{-1}	1.4×10^0	—	emf	21)
8	25	1.7×10^{-1}	—	—	1.7×10^{-1}	amine extraction	12)
9		3.1×10^0	1.0×10^0	8.3×10^0	1.1×10^0	amine extraction	15)
10		5.4×10^0	2.8×10^0	1.1×10^0	2.7×10^{-1}	amine extraction	16)
11	30	2.1×10^{-1}	1.8×10^{-2}	1.9×10^{-1}	—	amine extraction	this work

higher concentration range of hydrochloric acid ($[HCl] > 0.1 \text{ mol/l}$) most of the LA-2 exists as the dimer of the ammonium salts of LA-2, $(BH \cdot Cl)_2$.

Zinc in the aqueous phase is extracted into the organic phase by addition ($j=2$ in Eq. (5)) or anion exchange reaction ($j=3$ or 4 in Eq. (5)) with LA-2¹⁹⁾.

From those mentioned above and experimental results, the extraction reaction is considered to proceed as:

With the assumption that the activity constants of each species in both phases are maintained constant over the whole range of this experimental condition, the concentration of $ZnCl_j^{(j-2)-}$, the species which takes part in the extraction reaction shown by Eq. (5), is expressed as follows from Eqs. (1)–(4).

$$[ZnCl_j^{(j-2)-}] = \frac{\beta_j \cdot [Cl^-]^j}{1 + \sum_{i=1}^4 \beta_i \cdot [Cl^-]^i} \cdot C_{ZnW} \quad (6)$$

Total concentration of LA-2 in the organic phase is expressed as:

$$C_{B0} = 2[(BH \cdot Cl)_2] + 2[(BH)_2ZnCl_4] \quad (7)$$

Then, from Eqs. (5), (6) and (7), the relations of the equilibrium concentrations of zinc in both phases are described by

$$\frac{C_{ZnO}}{C_{B0}} = \frac{1}{2} \cdot \frac{f([Cl^-]) \cdot C_{ZnW}}{1 + f([Cl^-]) \cdot C_{ZnW}} \quad (8)$$

where

$$f([Cl^-]) = \frac{K_e \beta_j \cdot [Cl^-]^2}{1 + \sum_{i=1}^4 \beta_i \cdot [Cl^-]^i} \quad (9)$$

From Eq. (8), it is expected that the relation between C_{ZnO}/C_{B0} and C_{ZnW} is not influenced by C_{B0} and that C_{ZnO}/C_{B0} approaches the value of $1/2$ as C_{ZnW} increases, which is in agreement with the experimental results shown in Fig. 1.

Furthermore, in the lower concentration range of C_{ZnO} , where $[(BH \cdot Cl)_2] \gg [(BH)_2ZnCl_4]$, Eq. (8) is ap-

—: calculated result by the stability constants obtained in the present study
: calculated result by the stability constants obtained by other investigators.
 The numbers on the dotted lines denote No. in Table I.

Fig. 3 Relationship between $f([Cl^-])$ and $[HCl]$

proximated as follows.

$$\frac{C_{ZnO}}{C_{B0}} = \frac{1}{2} \cdot f([Cl^-]) \cdot C_{ZnW} = \frac{1}{2} \cdot \frac{K_e \beta_j \cdot [Cl^-]^2}{1 + \sum_{i=1}^4 \beta_i \cdot [Cl^-]^i} \cdot C_{ZnW} \quad (10)$$

It is evident that in this region, C_{ZnO}/C_{B0} is proportional to C_{ZnW} and its proportional coefficient depends only on the concentration of chloride ion, which is in agreement with the experimental results shown in Fig. 2.

On the basis of Eq. (10) and the experimental results shown in Fig. 2, the relation between $f([Cl^-])$ and hydrochloric acid concentration in the aqueous phase was obtained as shown in Fig. 3.

Assuming that the extraction reaction proceeds only by the addition reaction⁹⁾, i.e. assuming that $j=2$ in Eq. (5), the stability constants of the chloro complexes of zinc (β_i) and the equilibrium constant of this reaction (K_e) were obtained as follows.

As expected from Eq. (9), the plotted points in Fig. 3 lie on a straight line the slope of which is 2 and intersects the ordinate at $K_e \beta_2$ in the lower concentration range of $[Cl^-]$. Accordingly, the value, $K_e \beta_2 = 6.6 \times 10^1 \text{ [l/mol}^3\text{]}$, was obtained. On the other hand,

it is expected that $f([Cl^-])$ becomes proportional to $[Cl^-]^{-2}$ in the higher concentration range of $[Cl^-]$ where the ionic species, $ZnCl_4^{2-}$, is predominant²³⁾. However, it seems that the plotted points in Fig. 3 lie on a straight line the slope of which is not -2 but is nearly equal to -1 in the concentration range where $[HCl]=4-6$ mol/l and the ionic species, $ZnCl_3^-$, is predominant in such a concentration range. Then, in this study, the stability constants were evaluated with the assumption that the species, $ZnCl_4^{2-}$, exists only in a small proportion compared to other chloro complexes and that the term $\beta_4 [Cl^-]^4$ in the denominator of Eq. (9) can be ignored in the concentration range of this experiment. The values of β_i ($i=1, 2$ and 3) which were obtained by least square analysis using the results shown in Fig. 3 and the value of $K_e\beta_2$ mentioned above on the basis of Eq. (9) are shown in Table 1 and compared with the values reported by other investigators. From the values of β_2 and $K_e\beta_2$, the equilibrium constant of this extraction reaction was obtained as $K_e=3.8 \times 10^3$ [l/mol].

The solid line in Fig. 3 is the calculated result by Eq. (9) using these values. Dotted lines are the calculated results using the stability constants reported by other investigators and the value, $K_e\beta_2=6.6 \times 10^1$.

The solid lines in Figs. 1 and 2 are the calculated results obtained by Eqs. (8) and (9) using the constants obtained in this work. In this calculation, the chloride ion concentration ($[Cl^-]$) in Eq. (9) was evaluated by the mass balance of chloride ion in the aqueous phase shown by Eq. (11), taking account of the variation of $[Cl^-]$ caused by increase of C_{ZnW} .

$$[HCl] + 2C_{ZnW} = [Cl^-] + [ZnCl^+] + 2[ZnCl_2] + 3[ZnCl_3^-] \\ = [Cl^-] + \frac{\sum_{i=1}^3 i\beta_i \cdot [Cl^-]^i}{1 + \sum_{i=1}^3 \beta_i \cdot [Cl^-]^i} \cdot C_{ZnW} \quad (11)$$

Dotted lines in Fig. 2 are the calculational results based on the assumption that the chloride ion concentration is irrelevant to the zinc concentration i.e. $[Cl^-]=[HCl]$. These lines are in good agreement with solid lines over the whole concentration range of C_{ZnW} in the higher concentration range of $[HCl]$, though there are significantly large discrepancies between these lines in the higher concentration range of C_{ZnW} when $[HCl]$ is less than 1 mol/l.

These calculated results are in fairly good agreement with the experimental results in the range of lower loading ratio of zinc to LA-2.

However, in the range of higher loading ratio, all experimental results deviate downward from the calculated results. Though it is considered that these deviations are caused by variation of the activity coefficient in the aqueous phase due to change of ionic strength or to formation of complicated aggregates in

the organic phase, further detailed research is necessary on these problems.

Conclusion

The distribution equilibrium in the extraction of zinc chloride by Amberlite LA-2, a long-chain secondary alkylamine, was investigated over wide concentration ranges of LA-2 in the organic phase, and of zinc chloride and hydrochloric acid in the aqueous phase.

It was found that zinc chloride is extracted into the organic phase by the reaction

The equilibrium constant for this reaction and the stability constants of the chloro complexes of zinc such as $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$ were determined.

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Nomenclature

B	= species of free LA-2 (=RR'NH)
$(BH \cdot Cl)_2$	= species of the dimer of ammonium salt of LA-2
C_{B0}	= total concentration of LA-2 in the organic phase [mol/l]
C_{ZnO}	= concentration of zinc in the organic phase [mol/l]
C_{ZnW}	= total concentration of zinc in the aqueous phase [mol/l]
$f([Cl^-])$	= function of $[Cl^-]$ defined by Eq. (9) [l/mol]
K_e	= equilibrium constant for the reaction shown by Eq. (5) [(mol/l) ⁻¹⁻³]
β_i	= stability constant of the i -th chloro complex of zinc [(l/mol) ^{i}]
[]	= concentration [mol/l]
overline	= organic phase
<Subscripts>	
(aq.)	= aqueous phase
(org.)	= organic phase

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EXTRACTION KINETICS OF ZINC CHLORIDE WITH LONG-CHAIN ALKYLAMINE

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The solvent extraction of zinc chloride from aqueous hydrochloric acid solution with Amberlite LA-2, a long-chain secondary alkylamine, dissolved in *n*-hexane was carried out at 30°C by the single drop method.

The extraction rate mechanism was fairly well explained by the Handlos-Baron model, taking account of the interfacial reaction at the drop surface as a rate-determining step.

Furthermore, it was found that the diffusion of zinc around a droplet is very rapid compared both to that inside a droplet and to the interfacial reaction under this experimental condition. Zinc in the continuous phase is extracted into the dispersed phase as a neutral species, ZnCl_2 .

Introduction

Solvent extraction processes with high-molecular weight amines are now in extensive use in the field of hydrometallurgy⁹⁾. A great number of basic and applied studies of the extraction of many kinds of acids and metals with amines have been made¹⁰⁾.

However, most of these are concerned with the distribution equilibrium or its hydrometallurgical application, and those related to the extraction kinetics are very few, as was mentioned in the authors' review⁹⁾. Kataoka *et al.* measured the extraction rate of cadmium chloride with Amberlite LA-2 and tri-*n*-octylamine⁸⁾, and that of uranyl nitrate with tri-*n*-octylamine⁷⁾, using a stirred transfer cell. They con-

cluded that the extraction rates of these systems are controlled only by diffusion processes in the aqueous and organic phases. On the other hand, Južnič⁵⁾ measured the transfer rate of zinc chloride labelled with radioisotope into a solution of tri-*n*-octylamine in *m*-xylene using the capillary-cell method and reported that there are some mass transfer resistances at the interface even under such a stagnant condition.

In extraction with high-molecular weight amines, metals in the aqueous phase are extracted in accordance with one of the following two mechanisms¹⁰⁾ where amine (B) is transformed previously into the ammonium salt (BH·X) by neutralization with acid (HX).

Anion exchange reaction:

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