

EFFECT OF CHLORIDE IONS ON THE SOLVENT EXTRACTION OF INDIUM WITH PC-88A FROM SULFURIC ACID

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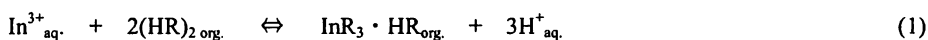
The effect of chloride ions on the distribution equilibrium in the solvent extraction of indium(III) with PC-88A in EXXSOL D-80 diluent from sulfuric acid solution containing lithium chloride at 30 °C was investigated to elucidate the stoichiometric relation and equilibrium constant of the extraction reaction by examining the effect of the concentrations of reactant species such as hydrogen and chloride ions and extraction reagent. It was found that indium(III) is extracted as the species, $\text{InClR}_2 \cdot 2\text{HR}$, while the extracted complex was found to be $\text{InR}_3 \cdot \text{HR}$ in the absence of chloride ions. The equilibrium constant of the extraction reaction was evaluated taking account of the formation of chloride-complexes of indium(III) in the aqueous phase.

1. Introduction

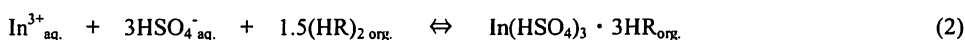
Demand for indium has rapidly increased in recent years as a raw material for various electronic devices such as indium phosphide semiconductors, indium solar batteries and indium tin oxide (ITO) transparent electrodes in particular for liquid crystal displays along with the rapid advances of IT industries. Indium does not occur by itself and is mainly found together with lead-zinc, copper and tin ores. It is extracted from various conversion products (cake, blue powder, roasting dusts, slimes and so on) generated at zinc-lead and copper smelters wherein it becomes concentrated during the ore treatment. At present, the majority of indium is being recovered from the above-mentioned feed materials by means of repeated dissolutions and precipitations followed by cementation by zinc to produce sponge-indium as the final product [1]. However, this conventional process is inefficient because of the consumption of large amounts of labor and energy and a long treatment time. Therefore, an alternative, more efficient process making use of solvent extraction has been desired [2]. In both purification and recovery of indium, its separation from tin is of prime importance because it coexists together with indium in the majority of cases. In

sulfuric acid solution which is usually employed as the leach liquor for the above-mentioned feed materials, tin is apt to be hydrolysed to form very refractory fine precipitates even at high acid concentration. These fine precipitates give rise to the formation of stable crud at the interface between the two phases and impedes phase separation and, consequently, the smooth operation of the solvent extraction process.

In the previous papers, the addition of chloride or fluoride ions suppressed the formation of the tin hydroxide precipitate, which suggests the possibility of successful separation of these metals by means of solvent extraction free from crud formation [3,4]. After the removal of tin from sulfuric acid containing fluoride or chloride ions, indium should be recovered from the raffinate by means of solvent extraction. In a previous paper, we investigated the solvent extraction of indium(III) with PC-88A in kerosene from sulfuric acid solution containing fluoride and found that the extraction is not influenced by the fluoride ion and indium is extracted according to the following reactions [4]:



at low concentration of sulfuric acid



at high concentration of sulfuric acid

On the other hand, we also found that indium(III) is extracted as the species, $\text{H} \cdot \text{InCl}_4(\text{reagent})_2$, in solvent extraction with trialkylphosphine oxides such as TOPO and Cyanex 925 from sulfuric acid solutions containing chloride ion [3]. That is, although chloride is coextracted with indium(III), fluoride is not.

In the present work, we investigated the solvent extraction of indium(III) with PC-88A from sulfuric acid solutions containing chloride ions to elucidate the extraction reaction.

2. Experimental

PC-88A, the solvent extraction reagent, kindly donated by Daihachi Chemical Industry Co. Ltd., was used as received without further purification after diluting with EXXOL D-80, an aliphatic kerosene with only 0.8 wt.% aromatic content, purchased from EXXON Chemicals Co. Ltd..

Aqueous solutions of indium(III) were prepared by dissolving indium(III) sulphate in sulphuric acid solution. The initial concentration of indium was 5 mmol/dm^3 for all experimental runs. The concentration of chloride ion was adjusted by adding lithium chloride.

Equal volumes of both phases were shaken overnight in a flask immersed in a water bath incubator maintained at 30°C to attain equilibrium. Here, the equilibrium was confirmed to be attained within 5 h in a preliminary experiment. Indium concentration in the aqueous solution was measured by using a Seiko Model SAS 7500 atomic absorption spectrophotometer. Its concentration in the organic phase was calculated from the difference in the initial concentration in the aqueous phase and that found after the extraction. Hydrogen ion concentration was measured by means of a neutralization titration using

phenolphthalein as an indicator.

3. Results and Discussion

Prior to the extraction from sulfuric acid solution containing chloride ions, the extraction in the absence of chloride was investigated to confirm the extraction reaction under the chosen conditions.

Figure 1 shows the log-log plot of the distribution ratio of indium(III) against hydrogen ion concentration in the extraction with 0.5 mol/dm^3 PC-88A from varying concentrations of sulfuric acid solution. The experimental points lie on a straight line with the slope of -3 as was observed in the extraction from sulfuric acid solution containing fluoride [4], suggesting that indium(III) is extracted according to a cation exchange mechanism releasing 3 hydrogen ions per unit ion of indium(III).

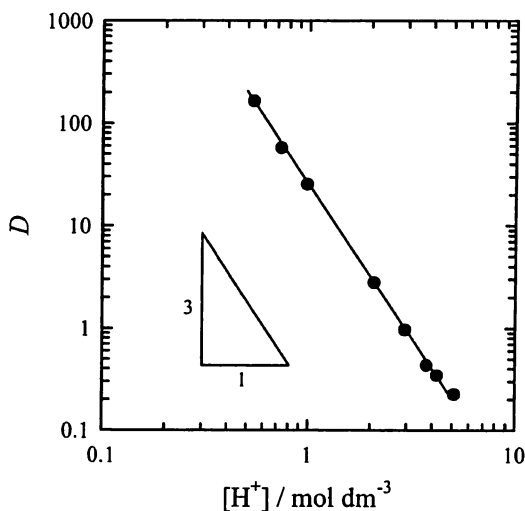


Fig. 1 Effect of hydrogen ion concentration on the distribution ratio of indium(III) in the absence of chloride in the aqueous phase. Initial indium concentration = 5 mmol/dm^3 . Concentration of PC-88A = 0.5 mol/dm^3 . Shaking time = 24 h.

Figure 2 shows the log-log plot of the distribution ratio against the concentration of the dimeric extractant in the organic phase in the extraction from 2.0 mol/dm^3 sulfuric acid solution. Also similar to the previous experimental result of the extraction from sulfuric acid solution containing fluoride, the points lie on a straight line with a slope of 2, suggesting that 2 dimeric extractant molecules take part in the extraction reaction of indium(III).

From the above experimental results, it can be concluded that indium(III) is extracted according to

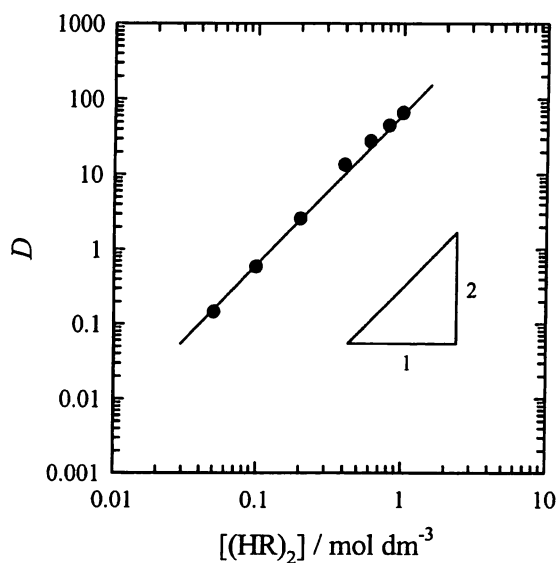


Fig. 2 Effect of the concentration of the dimeric reagent on the distribution ratio of indium(III) in the absence of chloride in the aqueous phase. Initial indium(III) concentration = 5 mmol/dm³. Sulfuric acid concentration = 2.0 mol/dm³. Shaking time = 24 h.

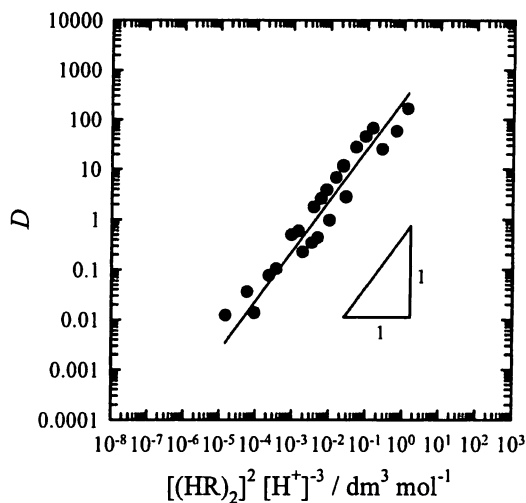


Fig. 3 Plot of all data in the absence of chloride in the aqueous solution according to Eq. (4)

the following extraction reaction which is in accordance with that reported in the previous paper for the extraction from sulfuric acid containing fluoride [4].



This extraction reaction is different from that reported in the previous paper on the extraction from nitric acid with 3 different acidic organophosphorus extractants, D2EHPA, PC-88A and Cyanex 272, in toluene, where it was extracted as a 1:6 metal:reagent complex, $\text{InR}_3 \cdot 3\text{HR}$, with all of these extractants [5]. According to the above-described extraction reaction, the distribution ratio, D , is expressed as follows:

$$D = K_{ex}[(\text{HR})_2]^2/[\text{H}^+]^3 \quad (4)$$

Figure 3 shows the replot of all experimental data shown in Figs. 1 and 2 according to this equation. In this figure, the points appear to cluster on a straight line with a slope of unity as expected from the above equation. From the intercept of the straight line with the ordinate, the equilibrium constant for the extraction reaction was evaluated as $K_{ex} = 2.0 \times 10^2 \text{ mol/dm}^3$.

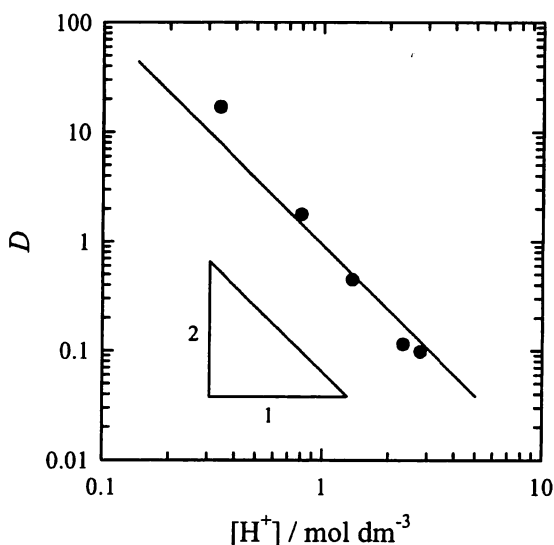


Fig. 4 Effect of hydrogen ion concentration on the distribution ratio of indium(III) in the presence of chloride in the aqueous phase. Initial indium(III) concentration = 5 mmol/dm^3 . Concentration of PC-88A = 0.5 mol/dm^3 . Chloride concentration = 1.0 mol/dm^3 . Shaking time = 24 h.

Figure 4 shows the pH dependency of the distribution ratio of indium(III) in the extraction with 0.5 mol/dm^3 PC-88A from varying concentrations of sulfuric acid solution containing 1.0 mol/dm^3 chloride. Contrary to the case in the absence of chloride shown in Fig. 1, the points lie on a straight line with a slope of -2 , suggesting that the positive charge of indium(III) is only partly neutralized with the anionic species of the extractant molecules.

Figure 5 shows the concentration dependency of the dimeric extractant in the organic phase on the distribution ratio in the extraction from 0.58 mol/dm^3 sulfuric acid solution containing 1.0 mol/dm^3 chloride.

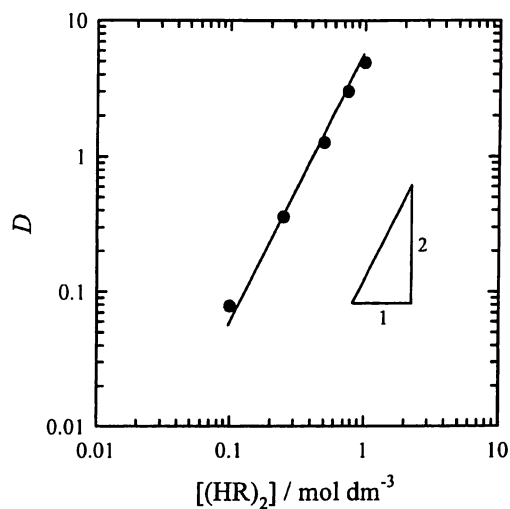


Fig. 5 Effect of the concentration of the dimeric reagent on the distribution ratio of indium(III) in the presence of chloride in the aqueous phase. Initial indium(III) concentration = 5 mmol/dm³. Sulfuric acid concentration = 0.58 mol/dm³. Chloride concentration = 1.0 mol/dm³. Shaking time = 24 h.

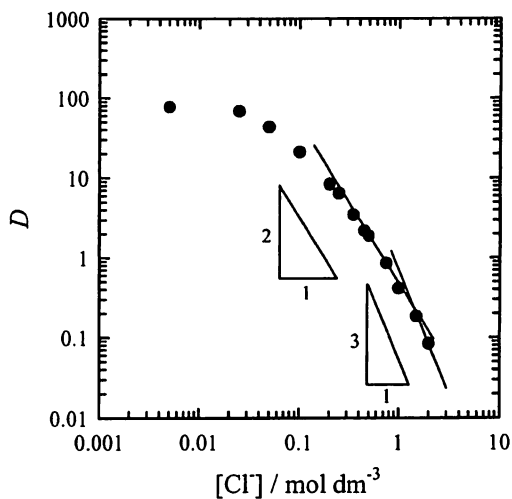
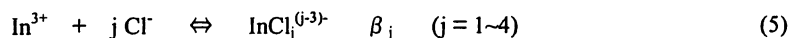


Fig. 6 Effect of chloride concentration on the distribution ratio of indium(III) in the aqueous phase. Initial indium(III) concentration = 5 mmol/dm³. Sulfuric acid concentration = 0.54 mol/dm³. Concentration of PC-88A = 0.5 mol/dm³. Shaking time = 24 h.

The points lie on a straight line with the slope of 2 similar to the extraction in the absence of chloride shown in Fig. 2.

Figure 6 shows the log-log plot of the distribution ratio against chloride concentration in the extraction with 0.5 mol/dm³ PC-88A from 0.5 mol/dm³ sulfuric acid solution containing varying concentrations of chloride. The distribution ratio decreases with increasing chloride concentration, and the points appear to lie on a straight line with the slope of -2 or -3 at high chloride concentration, suggesting that the chloride ion takes part in the extraction reaction unlike the fluoride ion.

As is well known, indium(III) forms chloro-complexes in chloride-containing aqueous solutions as follows [6]:



Taking into consideration that the concentration dependency of the hydrogen ion on the distribution ratio is -2 then from the formation of the above-described chloro-complexes, the extraction reaction of indium(III) from the solution containing chloride may be expressed as follows:



On the basis of the above-described extraction reaction and the formation of chloro-complexes in the aqueous phase, the distribution ratio is expressed by the following equation.

$$D = K_{\text{ex}'} [(\text{HR})_2]^2 [\text{Cl}^-] / [\text{H}^+]^2 \{1 + \sum \beta_j [\text{Cl}^-]^j\} \quad (7)$$

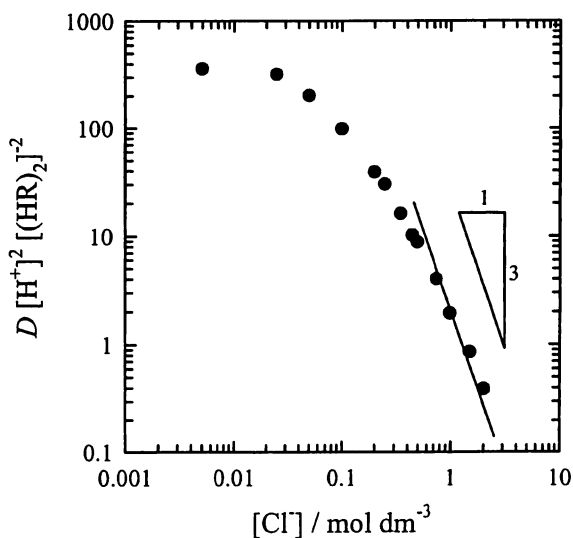


Fig. 7 Replot of the data in Fig. 6 according to Eq. (7).

At high concentrations of chloride ions where $\beta_4 [\text{Cl}^-]^4 \gg 1 + \beta_1[\text{Cl}^-] + \beta_2[\text{Cl}^-]^2 + \beta_3[\text{Cl}^-]^3$, the distribution ratio can be approximately expressed by the following equation.

$$D \approx K_{ex}'' \frac{[(\text{HR})_2]^2}{[\text{H}^+]^2 [\text{Cl}^-]^3} \quad (8)$$

$$\text{where } K_{ex}'' = K_{ex}' / \beta_4 \quad (9)$$

Figure 7 shows the replots of the data shown in Fig. 6 according to Eq.(7); as expected from this equation the points lie on a straight line with the slope of -3 at high chloride concentrations. From the intercept of the straight line of slope of -3 with the ordinate, the apparent equilibrium constant of the extraction reaction in the presence of chloride, K_{ex}'' , was evaluated as $2.4 \text{ (mol/dm}^3)^3$.

4. Conclusion

The following is concluded from the experimental results of the solvent extraction of indium(III) with PC-88A in EXXSOL D80 from sulfuric acid solution containing chloride.

1. In the absence of chloride, indium is extracted according to the following extraction reaction.



The equilibrium constant, K_{ex} , was evaluated as $2.0 \times 10^2 \text{ mol/dm}^3$.

2. In the presence of chloride, indium is extracted according to the following extraction reaction.



The apparent equilibrium constant of the extraction reaction in the presence of chloride, K_{ex}'' ($= K_{ex}' / \beta_4$), was evaluated as $2.4 \text{ (mol/dm}^3)^3$.

References

- 1) C.E.T.White and J.A.Slattery, Hydrometallurgy of Copper, Its Byproduct and Rare Metals, ed. by L.A.Haas and D.R Weir, AIME, New York (1982), p.95
- 2) P.Halsall, Trans.Inst.Min.Metall., Sec.C, C93 (1988)
- 3) K.Inoue, K.Yoshizuka, and S.Yamaguchi, J.Chem.Eng.Japan, 27, 737 (1994)
- 4) K.Inoue, T.Asakawa, and K.Yoshizuka, Solv.Extr.Res.Develop.Jpn., 4, 213 (1997)
- 5) K.Inoue, Y.Baba, and K.Yoshizuka, Hydrometallurgy, 19, 393 (1988)
- 6) E.Hogfeldt, Stability Constants of Metal Ion Complexes, Part A, Pergamon Press, Oxford (1982), p.226