SOLVENT EXTRACTION OF TIN(IV) WITH PC-88A FROM SULFURIC ACID SOLUTIONS CONTAINING CHLORIDE IONS

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Solvent extraction of tin(IV) with PC-88A in EXXSOL D-80 diluent from sulfuric acid solutions containing chloride ions was investigated to elucidate the effect of the concentration of the reactant species and the stoichiometric relation of the extraction reaction. Because of a difference in extraction mechanism from the usual cation exchange mechanism for metals with acidic extractants, tin(IV) was more strongly extracted from high concentrations of sulfuric acid and the extraction increased with increasing sulfuric acid concentration. By plotting the distribution ratio against activity of sulfuric acid, it was found to have a 3rd order dependence on the activity. The distribution ratio was found to have a first order dependency on the concentration of the dimeric reagent. The extraction increased with increasing concentration of chloride at low chloride concentrations while it decreased at high chloride concentrations. From these experimental results, it was inferred that tin(IV) is extracted as the complex, $SnCl(HSO_4)SO_4 \cdot 2HR$.

1. Introduction

In a previous paper [1], we investigated the solvent extraction of indium(III) with PC-88A in EXXOL D-80 diluent from sulfuric acid solutions containing chloride ions which were added in order to suppress the formation of the precipitates of tin which usually coexists with indium not only in natural ores but also in some wastes such as spent indium tin oxide (ITO) which is used in transparent electrodes for liquid crystal displays. Since, as is well known, tin(IV) is apt to be easily hydrolysed to give rise to very fine precipitates even under significantly acidic conditions, investigations on solvent extraction of tin have been conducted under more acidic conditions than is usually the case. Levin et al. reported that divalent tin is extracted also as tetravalent state complexes with D2EHPA in heptane from hydrochloric acid solution in the presence of air and this was confirmed by means of Moessbauer spectroscopy [2,3].

Some work has been conducted on the extraction of tin(IV) with D2EHPA from hydrohalic acids. Tarasova et al reported that tin is extracted as a species $SnR_2X_2 \cdot 2HR$ (X = Cl, Br) from hydrochloric or hydrobromic acids and examined the diluent effect [4].   Mukai et al. investigated tin extraction also with D2EHPA in benzene from hydrochloric acid and found that it is extracted as the $SnR_4 \cdot 4HR$ species [5]. In the present work, we investigated the solvent extraction of tin(IV) under nearly the same conditions as the extraction of indium(III) investigated in the previous work [1] and elucidated the extraction reaction by examining the effects of the concentrations of the reactant species.

2. Experimental

PC-88A kindly donated by Daihachi Chemical Industries Co. Ltd., was used as received without further purification after diluting with EXXSOL D-80 diluent.   Aqueous tin(IV) solutions were prepared by dissolving reagent grade tin(IV) chloride in varying concentrations of sulfuric acid containing chloride ions which was added as ammonium chloride.   The initial tin concentration was 5 mmol/dm^3 for all experimental runs.

Equal volumes of both phases were shaken overnight in a flask immersed in a water bath incubator maintained at 30℃ to attain equilibrium.   Equilibrium was confirmed to be attained within 6 h in a preliminary experiment.   Tin concentration in the aqueous solution was measured by using a Seiko Model SAS7500 atomic absorption spectrophotometer.   The tin concentration in the organic phase was calculated from the difference in the concentration in the aqueous phase before and after extraction. Hydrogen ion concentration was measured by titration using phenolphthalein as the indicator.

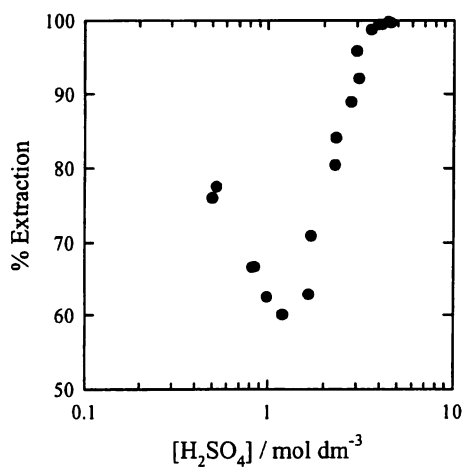## 3. Results and Discussion

Fig. 1   Plot of % extraction of tin(IV) with 50 mmol/dm^3 PC-88A in EXXSOL D-80 from varying concentrations of sulfuric acid containing 0.1 mol/dm^3 chloride: effect of sulfuric acid concentration.

Figure 1 shows the effect of sulfuric acid concentration on the % extraction of tin(IV) from varying concentrations of sulfuric acid containing 0.1 mol/dm^3 chloride.   At low sulfuric acid concentrations, < 1 mol/dm^3 , tin extraction decreases with increasing sulfuric acid concentration similar to the extraction of other metals with acidic extractants but extraction then increases with further increasing acid concentration at high sulfuric acid concentrations as was observed in the solvent extraction of indium(III) from sulfuric acid solutions containing fluoride [6].
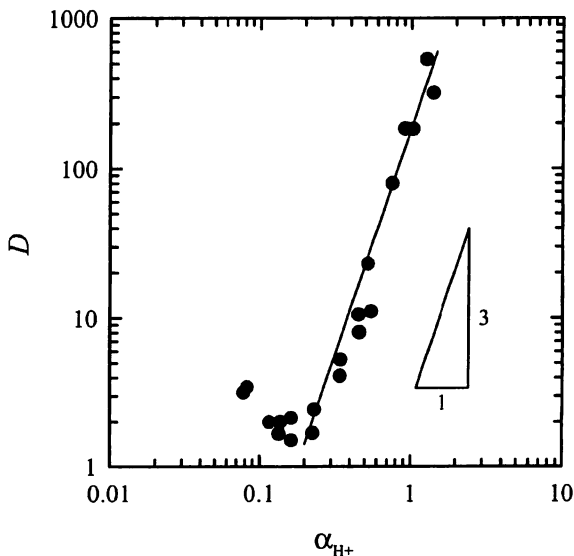

Fig. 2   Plot of the distribution ratio of tin(IV) from sulfuric acid solution containing 0.1 mol/dm^3 chloride with 50 mmol/dm^3 PC-88A in EXXSOL D-80 against the activity of the hydrogen ion.
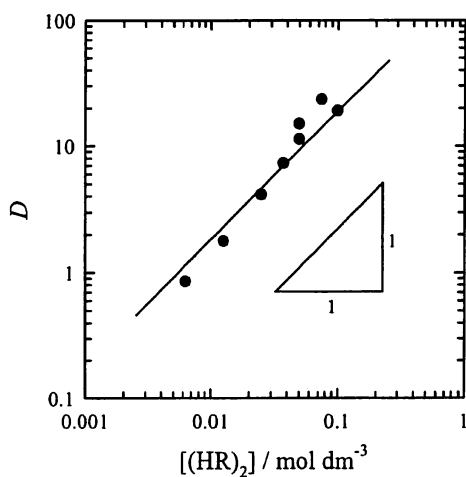

Fig. 3   Plot of the distribution ratio of tin(IV) against the concentration of the dimeric reagent on extraction from 2.04 mol/dm^3 sulfuric acid containing 1.0 mol/dm^3 chloride.

Figure 2 shows the replot of the data shown in Fig. 1 against the activity of hydrogen ion, α_{H+}, which was calculated from the concentration of sulfuric acid and the literature value of the activity coefficient [7].   Except for the points in low concentrations of sulfuric acid, the points appear to cluster on a straight line with a slope of 3.

Figure 3 shows the plot of the distribution ratio against the concentration of dimeric reagent on extraction from 2.04 mol/dm^3 sulfuric acid containing 1.0 mol/dm^3 chloride.   The points appear to lie on a straight line with a slope of unity, suggesting that two molecules of the monomeric reagent take part in the extraction reaction.
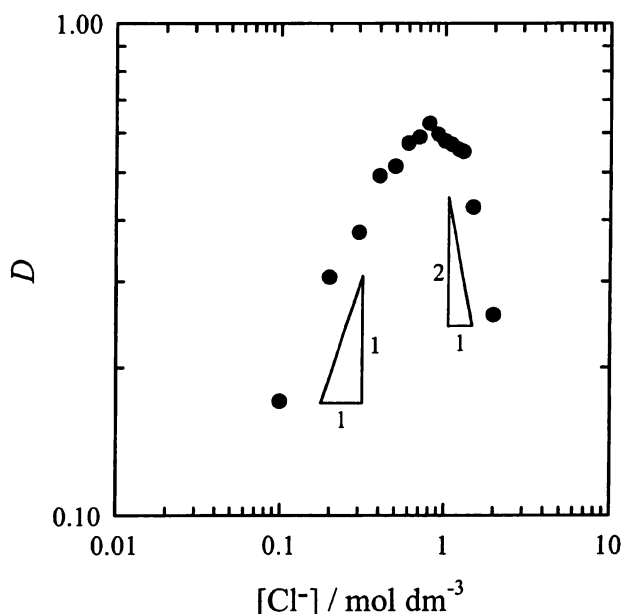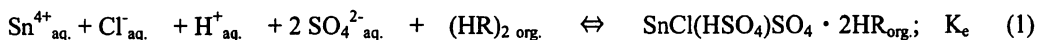

Fig. 4   Plot of the distribution ratio of tin(IV) against chloride concentration on extraction with 50 mmol/dm^3 PC-88A in EXXSOL D-80 from 4 mol/dm^3 sulfuric acid containing varying concentrations of chloride.

Figure 4 shows the plot of the distribution ratio against the concentration of chloride on extraction with 50 mmol/dm^3 PC-88A from 4 mol/dm^3 sulfuric acid.   The points lie on a convex curve; at low chloride concentrations, they appear to lie on a straight line with the slope of about 1 while at high chloride concentrations they lie on a straight line with the slope of -2, which is considered to indicate a variation in the composition of the tin(IV)-chloro complexes in the aqueous phase.

From the above-mentioned experimental results of the dependencies of the distribution ratio on the concentration and activity of the reactant species, it may be inferred that tin(IV) is extracted according to the following solvation reaction with PC-88A at high sulfuric acid concentrations.

$$Sn^{4+}_{aq.} + Cl^-_{aq.} + H^+_{aq.} + 2\,SO_4^{2-}_{aq.} + (HR)_{2\;org.} \Leftrightarrow SnCl(HSO_4)SO_4 \cdot 2HR_{org.}; \quad K_e \qquad (1)$$

Tin(IV) gives rise to chloro-complexes in the aqueous phase as follows [8]:

$$Sn^{4+} + j\,Cl^- \Leftrightarrow SnCl_j^{(j-4)-}; \quad \beta_j \quad (j = 1 \sim 6) \qquad (2)$$
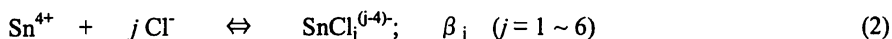
The fraction of free species, Sn^{4+}, is expressed as follows:

$$[Sn^{4+}]/C_0 = 1/\{1 + \Sigma\,\beta_j\,[Cl^-]^j\} \qquad (3)$$

where C_0 is the total concentration of tin in the aqueous solution.   From the equilibrium reaction relation given in Eq.(1) and from Eq.(3), the distribution ratio is described as follows:

$$D = K_e \cdot \alpha_{H^+}^{\;3} \cdot [(HR)_2][Cl^-]/\{1 + \Sigma\,\beta_j\,[Cl^-]^j\} \qquad (4)$$

Equation (4) gives the same concentration dependencies with respect to the reactant species as was observed in Figs. 2, 3 and 4; i.e., it gives first order dependency with respect to chloride ion concentration at low chloride concentrations and as it increases, after passing through the maximum, the distribution ratio is expected to decrease with dependencies of the order of –1, -2, -3, -4 and finally –5.

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