

SOLVENT EXTRACTION OF ANTIMONY (III) FROM CHLORIDE SOLUTIONS WITH TRI-*n*-BUTYL PHOSPHATE (TBP)

Part II.—Extraction of Macro-Amounts from Ammonium Chloride and Lithium Chloride Solutions

S. S. M. A. KHORASANI AND Q. A. HAKIM

Department of Chemistry, University of Dacca, Dacca

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From ammonium chloride solutions, macro-amounts of antimony (III) is extracted into TBP as $\text{SbCl}_3 \cdot 2 \text{TBP} \cdot (\text{H}_2\text{O})_x$, while from lithium chloride solutions extraction occurs through the formation of $2 \text{LiCl} \cdot \text{SbCl}_3 \cdot 2 \text{TBP} \cdot (\text{H}_2\text{O})_n$, where *n* may assume different values depending on TBP concentration in the organic phase. In both the systems initial distribution equilibrium is very rapidly established but is followed by slow hydrolysis of antimony(III) which, however, is much reduced in the latter system.

The mechanism of extraction of SbCl_3 from HCl solutions into TBP has been studied earlier by Khorasani.¹ The present work was taken up to examine extraction in the absence of added HCl. To keep the antimony(III) in solution, ammonium chloride and lithium chloride were used; the former does not extract into TBP while the latter is extracted. Since, at tracer concentrations, there is no reliable method available for detecting hydrolysis of the metal, it was decided to use moderate concentrations. Although extraction behaviour under these conditions is not usually expected to be analogous to that for tracer extractions, such studies should help a complete understanding of the mechanism.

Experimental

Reagents.—*Antimony Stock Solution I:* A 0.1 M SbCl_3 solution in 5.58 M aq. ammonium chloride.

Antimony Stock Solution II: A 0.1 M SbCl_3 solution in pure anhydrous TBP.

Ammonium Chloride Solution: 8.0 M, aqueous.

Lithium Chloride Solution: 12.0 M, aqueous.

TBP: The commercial sample was purified and dehydrated in the usual way.²

Diluent: Redistilled (E. Merck) pure carbon tetrachloride.

Other reagents and solutions were prepared from pure compounds.

Concentration of all solutions were individually checked by conventional methods.

Procedure.—Equal volumes (5.0 ml. each) of the aqueous and organic phases made up by mixing together aliquots of different stock solutions, were taken up in graduated centrifuge tubes and equili-

brated. Later the two phases were separated by centrifuging and aliquots were analysed for antimony(III) by iodimetric titration and for total chloride by Volhard's method. All experiments were performed at $30 \pm 0.2^\circ\text{C}$.

Preliminary Observations

In the first system studied, it was observed that the distribution equilibrium is very rapidly established (within 1.5 minutes), but it is followed by slow hydrolytic reactions in both the phases (particularly in TBP) which gradually become turbid. Rapid equilibration followed by immediate separation of phases enabled the authors to prevent the onset of hydrolysis. At high SbCl_3 concentrations there was a tendency of formation of an emulsion-like phase after equilibration. Amount of emulsion was, however, too small to affect the distribution equilibria except at very high metal concentrations when experiments were abandoned.

The behaviour in the system SbCl_3 -LiCl- H_2O -TBP was quite similar to the previous system. The distribution equilibrium was again rapidly set up (within 2.0 minutes), but the hydrolytic tendency of the metal was drastically reduced and formation of 'emulsion' was also very much suppressed. Extractions at very high LiCl concentrations were not attempted for two reasons, (i) because of high value of the distribution coefficient, the analytical method was not considered adequately accurate, and (ii) the high viscosities of TBP extracts and observation of mixing lines on shaking, which are believed to be due to formation of LiCl-TBP aggregates,^{3,4} was expected to make the system more complicated.

At macro-concentrations, SbCl_3 was not significantly extracted by CCl_4 to affect the results, and therefore CCl_4 could be used as a satisfactory inert diluent for TBP.

Results and Discussion

The System $SbCl_3-NH_4Cl-H_2O-TBP (+Diluent)$.—As it appears from the results presented in Table 1, equilibrium aqueous chloride concentration has very little influence on extraction of the trichloride by 100% TBP. This, of course, is true only for the limited range of chloride concentrations over which the authors could study partition of antimony (III) avoiding complications stated earlier.

TABLE 1.—INFLUENCE OF AQUEOUS CHLORIDE CONCENTRATION ON PARTITION OF ANTIMONY (III) BETWEEN AQ. NH_4Cl AND 100% TBP.

Total aq. chloride (M)	Distribution co-efficient $D_{Sb(III)}$
3.31	1.49
3.88	1.48
4.44	1.46
5.01	1.41
5.58	1.41

Total $SbCl_3$ used for each experiment 4.92×10^{-5} g. moles.

In this system the aqueous phase probably contains only chloro and chloro-hydroxy complexes of the metal.^{5,7} An almost two-fold increase in aqueous chloride concentration results only in less than 8.0% variation of the distribution co-efficient, which indicates that chloro-complexes may play only a minor role in the extraction, which must therefore, depend largely on chloro-hydroxy complexes ($SbCl_3$ -hydrates).

Results of dilution experiments performed at a constant aqueous phase composition are given in Table 2. In Fig. 1, the log-log plot of the distribution co-efficient against organic phase composition, is a straight line (A) of slope very close

TABLE 2.—INFLUENCE OF TBP CONCENTRATION IN THE ORGANIC PHASE ON PARTITION OF ANTIMONY (III) BETWEEN AQ. NH_4Cl AND CCl_4 -TBP.

TBP concentration in the organic phase % (v/v)	Distribution co-efficient $D_{Sb(III)}$
18.2	0.0247
27.3	0.0560
36.4	0.1010
45.4	0.1770
54.5	0.2800
63.6	0.4190
90.9	1.1800

Total $SbCl_3$ used for each experiment 20.80×10^{-5} g. moles.
Total aq. chloride concentration 5.58 M.

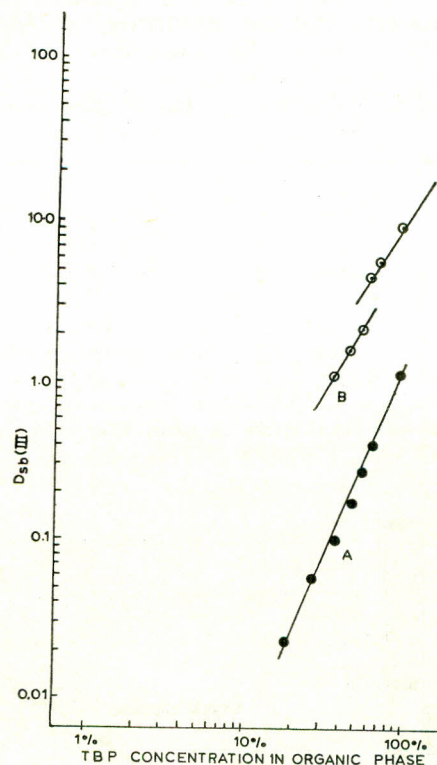


Fig. 1.—Dependence of $D_{Sb(III)}$ on TBP conc. in organic phase.

to 2.0 indicating that in this system as well, two molecules of TBP are associated with each antimony (III) in the extracted species, which, in analogy to the $SbCl_3-HCl-H_2O-TBP$ system studied earlier,¹ may be formulated as $SbCl_3 \cdot 2 TBP \cdot (H_2O)_x$.

The System $SbCl_3-LiCl-H_2O-TBP (+diluent)$.—In this system there is a major influence of aqueous chloride concentration on the distribution co-efficient of the tri-chloride for 100% TBP as is evident from the results given in Table 3. In Fig. 2., the distribution curve has been plotted and for comparison the curve for extraction from ammonium chloride solutions is also included. The curve for the present system is of different shape from those of other metal chloride extractions,⁸ and resembles those for extraction of nitrates.⁹ Extraction behaviour indicates that chloro-complexes of antimony(III) may play a major role in extraction.

Morris and Short¹⁰ have recently found evidence for extraction of Ni(II) from such solutions in the form of an associated electrolyte of suggested composition $[Li \cdot xTBP \cdot (4-x)H_2O]_2[NiCl_4]$. To exa-

TABLE 3.—INFLUENCE OF AQUEOUS CHLORIDE CONCENTRATION ON PARTITION OF ANTIMONY (III) BETWEEN Aq. LiCl AND 100% TBP.

Total aq. chloride (M)	Distribution co-efficient $D_{Sb(III)}$
2.946	2.88
4.178	7.54
4.917	8.62
5.655	7.89
5.903	8.00
6.871	12.10
8.118	17.50
8.465	20.01

Total $SbCl_3$ used for each experiment 15.84×10^{-5} g. moles.

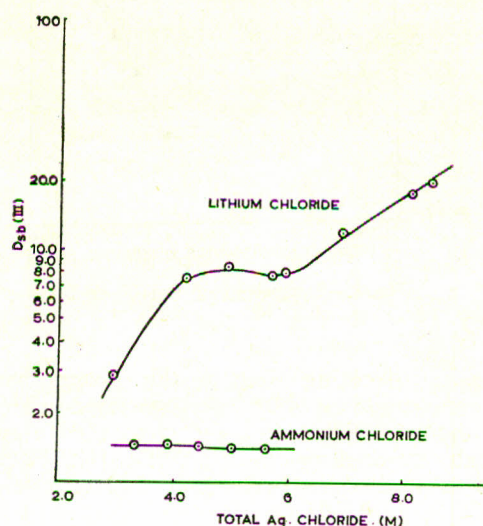


Fig. 2.—Influence of Aq. Chloride Conc. on $D_{Sb(III)}$

mine the possibility of such a situation occurring in the present system, the co-extraction of LiCl and $SbCl_3$ into TBP was studied and the results are given in Table 4. It will be seen that over the range 4.96–5.656 M total aqueous chloride, where the distribution co-efficient is expected to be not much affected by chloride concentration (Fig. 2), extraction of LiCl and $SbCl_3$ are inter-dependant. Plots of molar ratio $LiCl/SbCl_3$ against $SbCl_3$ concentration in the TBP phase (Fig. 3) indicates stoichiometric interaction to form a compound $2 LiCl \cdot SbCl_3$.

Results of dilution experiments (Table 5) bring out further interesting behaviour of the system.

TABLE 4.—CO-EXTRACTION OF LiCl AND $SbCl_3$ INTO 100% TBP.

Total Aq. Chloride (M)	$SbCl_3$ in TBP Moles/litre	Molar ratio $LiCl/SbCl_3$ in TBP
5.656	0.00323	16.04
5.411	0.00419	11.68
5.412	0.00467	12.80
5.409	0.00826	8.17
5.412	0.01795	3.17
5.175	0.02657	1.86
5.080	0.03614	2.11
4.956	0.04500	1.99

Total $SbCl_3$ used 3.96 to 79.20×10^{-5} g. moles.

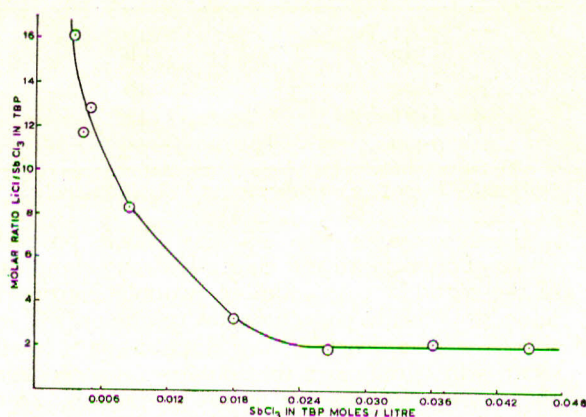


Fig. 3.—Co-extraction of LiCl and $SbCl_3$ by 100% TBP.

TABLE 5.—INFLUENCE OF TBP CONCENTRATION IN THE ORGANIC PHASE ON PARTITION OF ANTIMONY(III) BETWEEN Aq. LiCl AND CCl_4 -TBP.

TBP concentration in the organic phase % (v/v)	Distribution co-efficient $D_{Sb(III)}$
36.0	1.15
44.0	1.67
52.0	2.22
60.0	4.72
68.0	5.83
92.0	10.00

Total $SbCl_3$ used for each experiment 31.68×10^{-5} g. moles.
Total aq. chloride concentration 5.00M.

Upto 52.0% TBP in the organic phase log-log plot of the distribution co-efficient against TBP concentration in the organic phase, is a straight

line of slope ~ 2.0 . At higher TBP concentrations discontinuity is observed and another straight line emerges (B and C in Fig. 1). It would appear that upto 52.0% TBP the extractable species is a di-solvate and at higher TBP concentrations it suffers some change in composition. Since the slope of the second straight line (C in Fig. 1) is again close to 2.0, the molar ratio TBP/SbCl₃ in the extracted species should remain constant (~ 2.0) and the only difference between the two species may be in the degree of hydration.

The above results are understood if we consider the extractable complex to have the formula $2\text{LiCl}\cdot\text{SbCl}_3\cdot 2\text{TBP}(\text{H}_2\text{O})_n$, where n may assume different values depending on the concentration of the active (solvating) solvent (TBP) in the organic phase.

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