SOLVENT EXTRACTION OF ANTIMONY (III) FROM CHLORIDE SOLUTIONS WITH TRI-n-BUTYL PHOSPHATE (T.B.P.)

Part I.—Extraction from Acid Solutions

S. S. M. A. KHORASANI

Department of Chemistry, University of Dacca, Dacca

Extraction of antimony (III) from chloride solutions with pure and also diluted TBP has been examined. At tracer concentrations, Sb(III) is extracted as a hydrated species, $SbCl_3 2TBP (H_2O)_x$. At *macro* concentrations, extraction takes place possibly through the formation of one or more hydrated and/or polynuclear TBP solvates. In the extracted species, $SbCl_3$ never associates itself with any HCl, which is contrary to the normal behaviour of trivalent metal chlorides.

Introduction

Considerable interest has recently grown in the use of tri-*n*-butyl phosphate (TBP) for the extraction of metals from chloride solutions.[1] So far we know, extraction of antimony from such solutions by TBP has not been reported. We have found that both Sb (III) and Sb (V) are highly extractable from chloride solutions with TBP. A method for the quantitative separation of Sb (III) from Ni (II), Cr (III) and small amounts of Pb(II) employing TBP extraction has been developed.[2] In this paper are presented the results of our experiments with the view to elucidating the mechanism behind the extraction of $SbCl_3$ from chloride solutions with TBP.

Experimental

Reagents.—Antimony Stock Solution I.—A solution of carrier-free Sb-124 in 6 M HCl was prepared by diluting the solutions of $SbCl_3$ (containing Sb-124) supplied by the Radiochemical Centre, Amersham, England. The final metal concentration was ~10^{-6} M.

Antimony Stock Solution II: An approximately 0.1 M $SbCl_3$ solution in 6 M HCl was prepared by rapidly dissolving a weighed amount of anhydrous $SbCl_3$ (B.D.H. Reagent) in the acid. This solution was kept in a closed bottle provided with a semi-*micro* delivery burette. Aliquots were measured out, and their metal contents verified iodimetrically.

HCl Stock Solution.: AnalaR conc. HCl solution was kept in a closed bottle having a delivery burette. Aliquots were taken out and standardized accurately with standard alkali.

TBP: The solvent was obtained from A.E.R.E., Harwell, England. It was purified according to the method given by McKay *et. al.*[3]

Diluent: Petroleum ether (B.D.H.); boiling range, 60–80°C.

Other Reagents, Chemicals etc.—All other reagents and chemicals used were either B.D.H. AnalaR grade or Merck's certified products. Solutions were prepared by usual methods and their concentrations ascertained individually through conventional methods.

Procedure

Equilibration of tracer solution with TBP were carried out at 25±0.5°C. in centrifuge tubes, employing thorough stirring. Next, the solutions were centrifuged and the solvent and aqueous phases was separated. Aliquots of both the phases were taken in separate liquid G-M counters and their radioactivity was measured in the usual way, as already described.[2] Acidity of the solutions was measured by alkali titrations.

For salting out experiments and TBP dilution experiments, recommended techniques[4] were employed.

For studying co-extraction of $SbCl_3$ and HCl into TBP, inactive $SbCl_3$ solutions were used. Determination of HCl and $SbCl_3$, when present together, were carried out by a method specially developed for this purpose.[5]

Results and Discussion

Effect of the HCl Concentration on Distribution of the Tracer.—The effect of aqueous HCl concentration on the distribution of Sb (III) tracer between TBP and aqueous phases at equilibrium can be seen from the data in Table 1. In Fig. 1, D the distribution coefficient has been plotted against equilibrium aqueous HCl concentration.
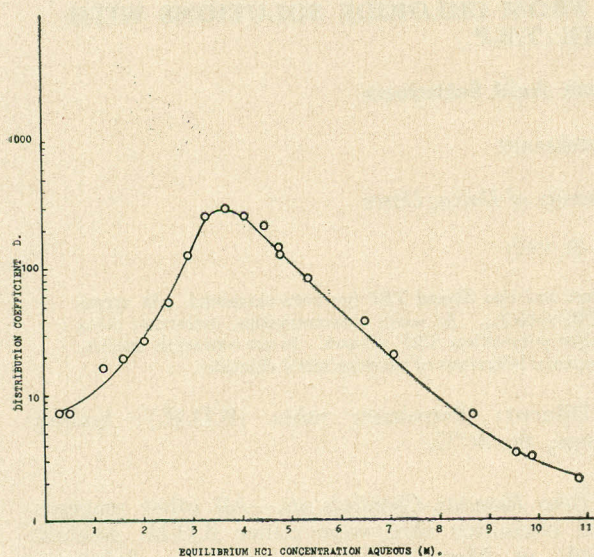
Fig. 1— Effect of HCl Concentration on the Distribution of
Sb (III) Tracer between Pure TBP and Aqueous Phase.

TABLE 1.—EXTRACTION OF Sb (III) TRACER BY
TBP FROM HCl SOLUTIONS.
EFFECT OF AQ. HCl CONCN. ON PARTITION OF
THE TRACER.

Equilibrium HCl concentration (aq.) M	$D = \dfrac{[Sb]\ TBP}{[Sb]\ aq.}$
0.313	7.371
0.511	7.371
1.185	16.379
1.598	19.476
2.017	26.902
2.542	53.690
2.928	125.800
3.314	258.770
3.692	294.160
4.102	259.240
4.479	214.250
4.824	146.460
4.848	123.590
5.360	82.774
6.501	38.923
7.173	20.314
8.684	6.987
9.570	3.401
9.878	3.169
10.844	2.115

From an aqueous solution 0.31 M in HCl,
quite a significant amount of the tracer is

extracted (~88%). We did not go below this
acidity as there was a possibility of Sb(III) under-
going hydrolysis. At 0.51 M HCl, extraction does
not improve and the distribution coefficients for
these two acid concentrations are identical. Above
0.51 M HCl, however, D progressively increases,
attains a maximum value 294 at 3.69 M HCl
and then decreases.

Between 0.51 and 0.31 M HCl, there is every
likelihood that SbCl$_3$ hydrolyses as shown by
the constant value of D, resulting in all probability
from the difficulties encountered in extraction
and due to the formation of undesirable hydrolytic
products. Above 0.51 M HCl however, possibly
there is no further hydrolysis, and extraction in-
creases. The increase in extraction (up to the
maxima), may be due to the progressive forma-
tion of the extractable species. Decrease in ex-
traction beyond 3.69 M HCl (aq.) may be due
to competition between the extractable species
and HCl for the available TBP molecules.

The nature of the distribution curve is similar
to that found for other metal chlorides,[1] but the
rise and fall in D and the maxima are very clearly
defined in this system.

Salting Out Experiments.—Keeping the chloride
concentrations constant (3.7 M-optimum), a
part of the HCl was replaced by increasing
amounts of NaCl and extractions were under-
taken. Results are given in Table 2. In Fig. 2,

TABLE 2.—EXTRACTION OF Sb (III) TRACER BY
TBP FROM NaCl-HCl SOLUTIONS.

Equilibrium concentrations (aq.)		$D = \dfrac{[Sb]\ TBP}{[Sb]\ aq.}$
NaCl M	HCl M	
0.00	3.70	296.45
1.10	2.60	143.32
2.14	1.56	36.08
2.93	0.77	23.31
3.63	0.07	18.48

D has been plotted against the solution composi-
tion. It is rather interesting to observe that in-
stead of the expected increase in D, with the
increase of NaCl (a non-extractable salt), there
is actually a progressive decrease. This may be
due to the following reasons: (i) SbCl$_3$ is pos-
sibly extracted as a chloro-acid (HSbCl$_4$, H$_2$SbCl$_5$,
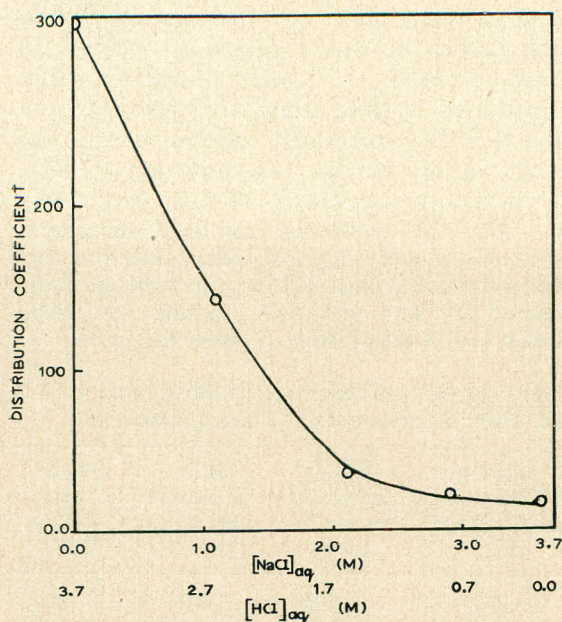H$_3$SbCl$_6$ etc.). Now as HCl is gradually re-

Fig. 2.—Effect of NaCl on the extraction of Sb (III) tracer from HCl solutions.

placed by NaCl, the formation of extractable Sb (III) species is hindered, and this might result in a decrease of extraction. (ii) $SbCl_3$ is possibly extracted as a hydrate, $SbCl_3.H_2O$,[6] or $SbCl_3$. $(H_2O)_x$. As more and more NaCl is introduced into the system, more and more of the water molecules capable of hydration of $SbCl_3$ are utilized for keeping NaCl in solution, and thus they cannot easily attach themselves with $SbCl_3$ to form extractable species, resulting in extraction decreases. (iii) Both chloro-acids and hydrates or possibly hydrated chloro-acids may be the actual extractable species. Under all these conditions, replacement of HCl by NaCl would suppress extraction. (iv) Decrease in extraction might also result from formation of non-extractable $SbCl_3$. NaCl type double chlorides, from chloro-acids as HCl is replaced by NaCl.

TBP Dilution Experiments.—These experiments were performed in order to find out the number of TBP molecules associated with each antimony (III) atom in the extractable species.[4] Normal inert diluents such as hydrocarbons, CCl_4 and $CHCl_3$ etc. were all found to extract the tracer more or less, and therefore much difficulty was encountered in finding out a really 'inert' diluent for our work. A particular grade of petroleum ether (boiling range, 60-80°C.) was finally chosen as it did not extract the tracer. Values of the distribution co-efficient D for extraction with varying concentrations of TBP in the solvent phase

are given in Table 3. Log-log plot of D against TBP concentrations (Fig. 3) is a straight line with a slope very close to 2. This at once indicates that two TBP molecules are associated with each antimony (III) in the extracted species. On this basis, partial formula of the extracted species may be given as $SbCl_3$. 2 TBP.

TABLE 3.—TBP DILUTION EXPERIMENTS: VARIATION OF DISTRIBUTION CO-EFFICIENT WITH TBP CONCENTRATION (IN THE ORGANIC PHASE): DILUENT PETROLEUM ETHER. AQUEOUS ACIDITY 3.70 M HCl.

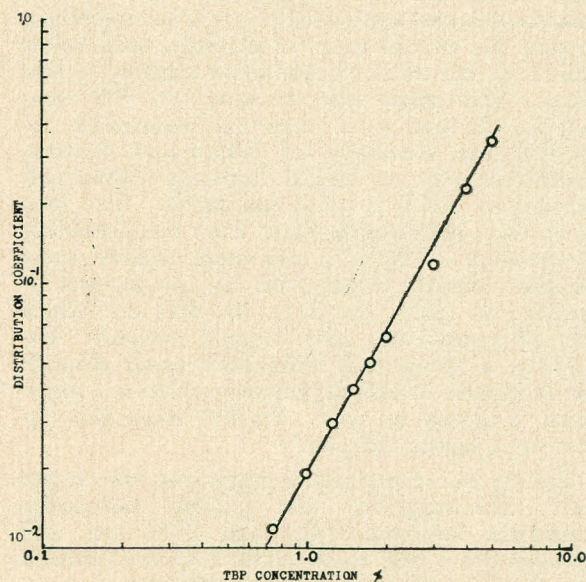| TBP concentration % (v/v)	Distribution Co-efficient-D
0.75	0.0118
1.00	0.0191
1.25	0.0298
1.50	0.0400
1.75	0.0511
2.00	0.0630
3.00	0.1188
4.00	0.2289
5.00	0.3354

Fig. 3.—Dependance of extraction on TBP concentration. Evaluation of the TBP number.

This gives antimony a co-ordination number 5. We know from Pani and co-workers' studies, [7–15] that in its complexes, Sb (III) usually has a co-ordination number of 4. It is further known

that, SbCl$_3$ can form complexes with covalencies rising to 6-, giving compounds, viz., M$_2$ [SbCl$_5$] and also M$_3$ [SbCl$_6$].[16] We can therefore expect Sb (III) to have co-ordination numbers as large as 5 or 6. It is also known [17] that compounds having metals in the 5- or 7- co-ordination states, are very rare and that instead 6- and 8- states are preferred. It is therefore reasonable to expect that Sb (III) in our compound would probably have a co-ordination number 6. This can be assigned if HCl and/or water molecules are assumed to be associated with Sb (III) in the extracted species. Tentative formulae for these compounds may be

    1. SbCl$_3$ (HCl). 2 TBP,
    2. SbCl$_3$ (H$_2$O). 2 TBP,
or 3. [SbCl$_3$ (HCl) $_x$ (H$_2$O)$_y$. 2 TBP]$_n$

The extreme dilutions at which the tracer was employed rules out the possibility of the existence of any polynuclear Sb (III) complexes. But it is possible that either chloro-acid or hydrated species are formed which are associated with the TBP molecules. Both SbCl$_3$-HCl-TBP and SbCl$_3$-H$_2$O-TBP types of compounds may simultaneously be formed so that the overall distribution of the co-ordinating ions or molecules for each antimony comes to 6.

It has been recently pointed out [18] that, at least for solvents like ethers, alcohols and ketones, mixed-solvate-hydrate-conditions arise sometimes so that the central atom of the extractable solute makes up the usual co-ordination number of that atom. This might also be true for TBP extractions. If this is so, then our assumption regarding the formation of chloro-acid solvates, hydrate-solvates or mixed hydrated chloro-acid solvates by SbCl$_3$ is quite reasonable. The idea of Sb (III)-chloro-acids comes from the possibility of existence of HSbCl$_4$ and other similar compounds. Similar chloro-acids are also formed by Fe(III), Al (III), Au (III), In (III) etc. which are all extractable into organic solvents. For Fe(III), we know that extractions occur through the formation of HFeCl$_4$-solvates which are sometimes hydrated as well. Sb(III) may also behave in a similar manner.

Salting out experiments employing the tracer have also suggested that possibly association complexes between SbCl$_3$ and HCl and also between SbCl$_3$ and H$_2$O might have been formed and these are the actual extractable species.

Tracer techniques were found to be inadequate for providing further information regarding the actual nature and composition of the extractable species and therefore extractions at macro concentrations were studied to ascertain these.

Co-extraction of SbCl$_3$ and HCl into TBP from Chloride Solutions at Macro Concentrations.—Effect of HCl Concentration.— To study the above effect, extractions of a fixed amount (3.912×10^{-4} moles) of SbCl$_3$ from fixed volumes (10 ml.) of solutions having various concentrations of HCl, were performed employing 10 ml. portions of TBP. After the equilibrium had been established, aliquots of the solvent phase were taken out and analysed for SbCl$_3$ and HCl by a method specially developed for this purpose.[5] Results are given in Table 4 and graphically represented in Fig. 4

TABLE 4.—CO-EXTRACTION OF SbCl$_3$ AND HCl BY TBP: INCREASING HCl CONCENTRATIONS.

Equilibrium HCl concentration (TBP) M	SbCl$_3$ extracted moles $\times$ 10^{-4}	HCl extracted moles $\times$ 10^{-4}	Molar ratio HCl/ SbCl$_3$
0.3750	3.902	7.500	1.922
0.6085	3.927	12.170	3.098
0.9615	3.785	19.230	5.081
1.3210	3.597	26.420	7.343
1.6850	3.503	33.700	9.618
2.1250	3.170	42.250	13.320

As equilibrium acidity (HCl) of the TBP phase increases from 0.375 to 2.125 M, the amount of HCl extracted also increases from 7.5×10^{-4} to 42.25×10^{-4} moles. For this range, the amount of SbCl$_3$ extracted varies from 3.902×10^{-4} to 3.170×10^{-4} moles (a small but perceptible gradual decrease). On the comparison of this with the increase in amounts of HCl extracted ($\sim$6-fold) we find that actually there is insignificant decrease in the amount of SbCl$_3$ extracted. The HCl/SbCl$_3$ molar ratio (in TBP), however, progressively increases from 1.922 to 13.320.

On the basis of the above results it can be said that:

(1) HCl is more extractable than SbCl$_3$, and that (2) there is hardly any competition (mole-for-mole basis) between SbCl$_3$ and HCl for the solvent molecules available.

If we assume that there is an association of SbCl$_3$ with HCl in the TBP phase, this would require the maintenance of at least a rough stoicheometric relation between the amounts of the two in the organic phase; but this is not so. Moreover, if there is any association, then the HCl molecules during transfer to the TBP phase would drag definite amounts of SbCl$_3$ with them; this is also not in keeping with the results. Therefore we conclude that irrespective of the amounts of HCl extracted by TBP, practically constant amounts of SbCl$_3$ enter the

organic phase. From the nature of the curves in Fig. 4 it can be expected that $SbCl_3$ would extract into TBP even from solutions containing no HCl. This could be actually confirmed experimentally when extractions of $SbCl_3$ from concentrated NH_4Cl solution into TBP showed 70% recovery.
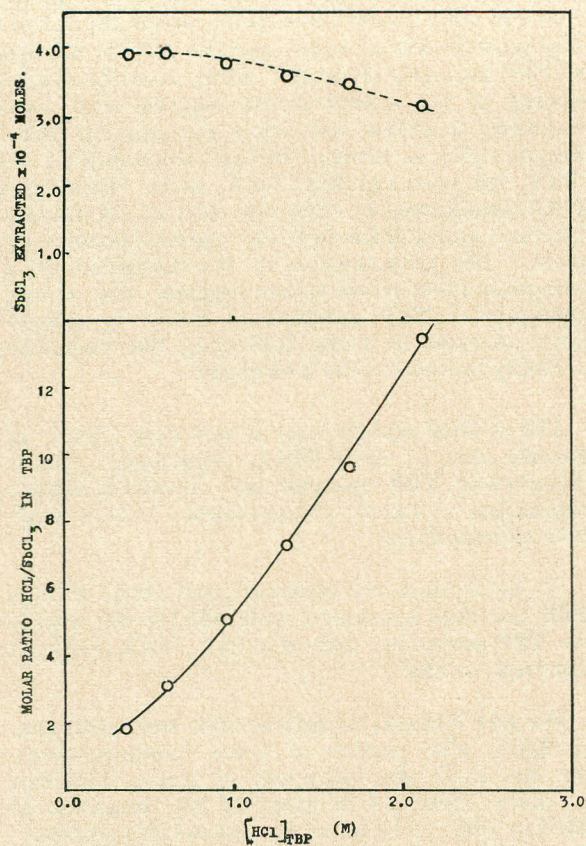
and HCl were carried out by our method.[5] Results are given in Table 5 and are graphically represented in Fig. 5.

TABLE 5.—CO-EXTRACTION OF $SbCl_3$ AND HCl BY TBP: INCREASING $SbCl_3$ CONCENTRATIONS.

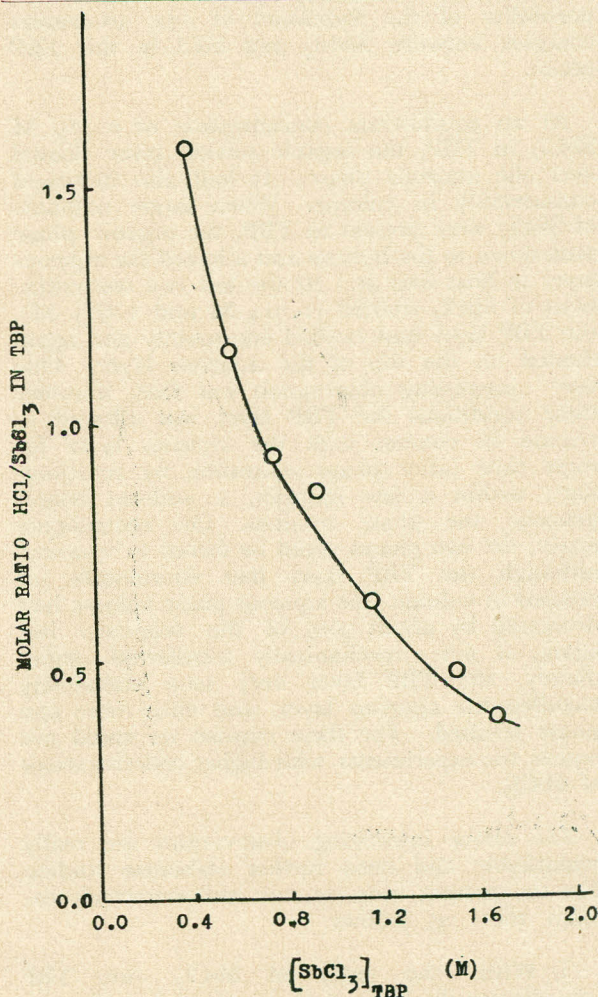| Equilibrium $SbCl_3$ concentration (TBP) M	Equilibrium HCl concentration (TBP) M	Molar ratio $HCl/SbCl_3$
0.409	0.612	1.582
0.584	0.609	1.157
0.757	0.607	0.931
0.934	0.603	0.857
1.154	0.601	0.623
1.514	0.602	0.474
1.665	0.598	0.376

Fig. 4.—Co-extraction of HCl and $SbCl_3$ into TBP at macro Concentration. Effect of HCl concentration.

Co-extraction of $SbCl_3$ and HCl into TBP from Chloride Solutions.—Effect of $SbCl_3$ Concentration.—After the above work had been completed, we thought that, keeping the aqueous acidity constant, if more and more $SbCl_3$ could be forced into the TBP (at equilibrium), the amounts of HCl and $SbCl_3$ going into the TBP phase might indicate whether there is competition, association etc., if any, between the two in the organic phase.

With this end in view, a set of experiments was performed in which the initial aqueous $SbCl_3$ concentration was increased manifold, but the HCl concentration was kept constant (3.7 M). Analyses of the TBP extracts for $SbCl_3$

Fig. 5.—Co-extraction of HCl and $SbCl_3$ into TbP at macro concentration. Effect of $SbCl_3$ concentration

It can be seen that equilibrium HCl concentration in the TBP phase does not change much, although considerable amounts of SbCl₃ can be forced into the organic phase. Moreover, irrespective of the amount of SbCl3 coming into the TBP, practically the same amount of HCl always enters the organic phase. Thus there can neither be competition (mole-for-mole basis) nor association between SbCl₃ and HCl during extraction into the organic phase. The overall HCl/SbCl₃ ratio decreases from 1.58 to 0.376 as SbCl₃ concentration is gradually increased. This is according to our expectations.

For reasons given in the subsequent paragraphs, we could not proceed beyond a concentration of 1.665 M SbCl₃. However, an examination of the values of molar ratio HCl/SbCl₃ over the range of concentrations studied, leads us to rule out the possibility of the formation of any association complex between SbCl₃ and HCl in the TBP phase.

At an equilibrium concentration of 0.409 M SbCl₃ in TBP, the organic solvent layer floated over the aqueous phase. It had also increased considerably in volume. When larger amounts of SbCl₃ were present in TBP, the organic phase sank down to the bottom and allowed the aqueous layer to float over it. At the last two concentrations of SbCl₃ studied (1.514 M and 1.665 M), the TBP layer had swelled enormously and again floated on the top of the aqueous layer. One very interesting observation was that, if under these conditions the TBP layer was allowed to remain in contact with the aqueous layer for some time (after phase separation by centrifuging), within a few minutes, a uniform homogeneous one phase resulted. On centrifuging again, the two phases could be forced to separate, although the TBP layer had enormously increased in volume (the aqueous phase volume had decreased by about 90% of the original), but again, if not mechanically transferred immediately, the TBP layer very soon completely engulfed the aqueous layer, and once more one phase resulted. For these reasons we could not repeat the experiments with higher concentrations of SbCl₃.

The above interesting observations are really remarkable and need further elaborate studies. For the present moment, we can tentatively explain these as follows:

(i) With the entry of SbCl₃ into TBP (simultaneously H₂O may also enter the solvent), its volume increases as a result whereof the density of the TBP layer decreases.

(ii) Due to an increase in the weight of the TBP phase (as a result of the entry of SbCl₃ and H₂O), its density would increase and this would work against the former effect.

When SbCl₃ concentration in the TBP phase is increased, at first, the first effect becomes prominent, indicating that H₂O may follow SbCl₃ into the TBP. Later more SbCl₃ enters the solvent and possibly less of water, and the volume increase of TBP may also be small. Thus, only the overall density of the solvent would increase and consequently it would sink below the aqueous layer. Finally, after a certain critical concentration of SbCl₃ has been reached, once more SbCl₃ and H₂O simultaneously enter the solvent; its volume increases and it floats over the aqueous phase once more. The phenomenon of the formation of a one-phase meta-stable system suggests the strong tendency of TBP solutions of SbCl₃ to absorb large amounts of water, indicating the formation of SbCl₃ hydrates in the TBP phase.

The overall picture here is not very clear, as possibly one or more SbCl₃ (hydrated) and/or polynuclear TBP solvates are involved during extractions at macro concentration. It is however indicated that:

(i) SbCl₃ does not associate itself with HCl in TBP, nor does it compete with HCl for the available TBP molecules, and that (ii) SbCl₃-hydrates can exist in TBP.

We feel inclined to believe that this behaviour of SbCl₃ also persists at trace concentrations. On this basis, the behaviour at tracer level can be easily explained in terms of the formation of SbCl₃.2 TBP. (H₂O)ₓ as the extractable species.

As there was no evidence for the molecular association of SbCl₃ and HCl in the TBP, SbCl₃ must behave differently from other trivalent metal halides which, as a rule, extract into oxygenated organic solvents as complex acids-HMX₄.[19]

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