EXTRACTION OF INDIUM(III) AND ANTIMONY(III) FROM HYDROCHLORIC ACID SOLUTIONS BY MEANS OF SOME NEUTRAL ORGANOPHOSPHORUS REAGENTS

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Distribution of indium(III) and antimony(III) was examined between hydrochloric acid solutions and solutions of tri-n-butylphosphate (TBP), trialkyl- and triarylphosphine oxides (TGPO, G = phenyl (P), n-butyl (B), or n-octyl (O)), or tetra-n-butylammonium chloride (R_4NCl) in benzene or other organic solvents. The extractability of indium into benzene decreases in the order TOPO > TBPO > TBP ~ TPPO. In the case of TOPO and TBPO, there is a pronounced maximum on the plots of log D_{In} *vs* c(HCl) in the region of c(HCl) = 3–6 mol l^{-1}; this applies also to other organic solvents. The composition of the species transferred into the organic phase is probably $HInCl_4$.2 TGPO. The distribution ratio of antimony(III) attains considerable value even in the absence of the organophosphorus reagents, which indicates that Sb chloro complexes themselves are extracted.

In studies of extraction of trivalent indium and antimony from chloride solutions by means of neutral organophosphorus reagents, most attention has been so far paid to tri-n-butylphosphate[1-4] (TBP). In the case of indium, its extraction has been found highest from 6M-HCl solutions, the composition of the complex extracted is assumed to be[5] $InCl_3$.2 TBP or $HInCl_4$.2 TBP. The mechanism of extraction of the above compounds has not been studied in detail; in fact, in aqueous solutions indium occurs in the form of $[In(H_2O)_{6-n}Cl_n]^{3-n}$ ions, so that water molecules play here a significant part. They are relatively strongly bonded to the central atom and cause it to be generally poorly extractable chloride solutions[6].

A brief study only has been devoted to extraction of indium by means of tri-n-butyl- and tri-n-octylphosphine oxides[7,8] (TBPO, TOPO). The maxima on the extraction curves do not differ essentially from those for TBP.

Trivalent antimony is best extracted from 2·5–4·5M-HCl; the assumed composition of the complex extracted is[9,10] $SbCl_3$.TBP and $SbCl_3$.2 TBP, in solutions with $c(HCl) \geqq 5$ mol l^{-1} also $HSbCl_4$.2 TBP (ref.[11]). In the case of antimony, too, its extraction by using TOPO has been paid attention only rarely[7,8].

In order to arrive at more detailed conclusions concerning the use of trialkylphosphine oxides for extraction of the two elements, and also to specify the role of the alkyl or aryl group in the reagent molecule, we studied in this work the distribution of indium and antimony between solutions of 1 – 10M-HCl and solutions of tri-n-butylphosphine oxide (TBPO), tri-n-octylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO), or tetra-n-butylammonium chloride (R_4NCl) in benzene, chloroform, n-octane, or tetrachloromethane.

EXPERIMENTAL

Chemicals and Apparatus

All chemicals used were reagent grade purity. The organophosphorus compounds were commercial chemicals of Lachema, Brno, dried above phosphorus pentoxide prior to use.

The working solutions of $^{114m}InCl_3$ and $^{124}SbCl_3$ were prepared from their stock solutions by dilution; their concentrations were $5 . 10^{-6}$—$3 . 10^{-5}$ and $6 . 10^{-7}$—$1 . 10^{-5}$ mol l^{-1}, respectively, activities $1 . 10^4$—$3 . 10^4$ and $7 . 10^3$—$7{\cdot}5 . 10^4$ s^{-1} ml^{-1}, respectively. The gamma activity of the two nuclides was measured by means of a Nuclear Chicago 1185 Automatic Gamma System fitted with a well-type NaI(Tl) crystal. The pH of the aqueous phase was determined potentiometrically by using an EIL instrument (Electronic Instruments, Richmond, England) equipped with a GHS 23 glass electrode and an EJ 23 saturated calomel electrode.

Working Procedure

Equal volumes (5 or 10 ml) of the aqueous and the organic phases were shaken in ground-in glass test tubes on a rotary shaking machine at 20 ± 1°C for 12 h; this period was sufficient for the extraction equilibrium to establish. After the extraction and phase separation, 2 ml aliquots were sampled in glass ampoules and their gamma activity was measured. The relative standard deviation of the radiometric measurements did not exceed 2%. The pH was determined in the remaining aqueous phase.

RESULTS AND DISCUSSION

Distribution of Indium(III)

The distribution of indium(III) between the aqueous phase of 1 – 10M-HCl and solutions of TPPO, TBPO, TOPO (generally, TGPO), and R_4NCl in benzene ($c = 1 . 10^{-3}$ mol l^{-1}) is shown in Fig. 1. As the curves demonstrate, with the applied initial concentration of the reagents, indium is not extracted in the presence of TPPO (curve *1*). The possibility of using TBP was also investigated in the same conditions; its extraction curve is practically identical with curve *1*. In contrast to this, the curves for TBPO and TOPO (curves *2* and *3*) exhibit pronounced maxima in the region of $c(HCl) = 3 - 5$ mol l^{-1}. The extraction of indium proceeds best in the presence of R_4NCl, with the maximum at $c(HCl) = 6$ mol l^{-1} (curve *4*). The curve for solution of TBP, concentration 0·1 mol l^{-1}, is shown for a comparison (curve *5*); it demonstrates well the difference in the extractability of TBP and TBPO.

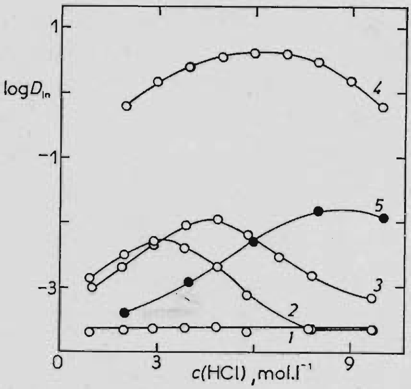

FIG. 1

Distribution of indium between hydrochloric acid solutions and 1 . 10^{-3} mol l^{-1} solutions of the reagents in benzene. *1* TPPO, *2* TBPO, *3* TOPO, *4* R_4NCl, *5* TBP (0·1 mol . . l^{-1})

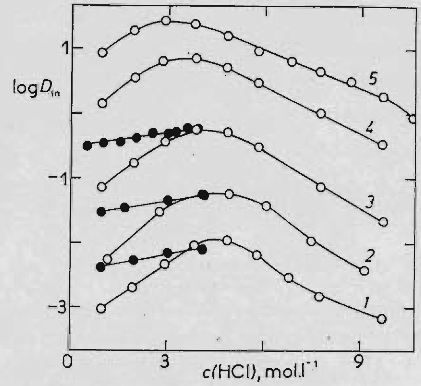

FIG. 2

Distribution of indium between hydrochloric acid solutions and solutions of TOPO in benzene. c_{TOPO} (mol l^{-1}): *1* 1 . 10^{-3}, *2* 3 . 10^{-3}, *3* 1 . 10^{-2}, *4* 5·25 . 10^{-2}, *5* 1·31 . . 10^{-1}; full circles on curves *1*—*3*: $I = 4{\cdot}0$ adjusted with HCl and NaCl

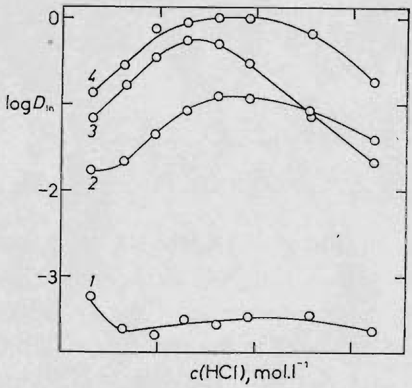

FIG. 3

Distribution of indium between hydrochloric acid solutions and 1 . 10^{-2} mol l^{-1} solutions of TOPO in organic solvents. *1* Chloroform, *2* tetrachloromethane, *3* benzene, *4* n-octane

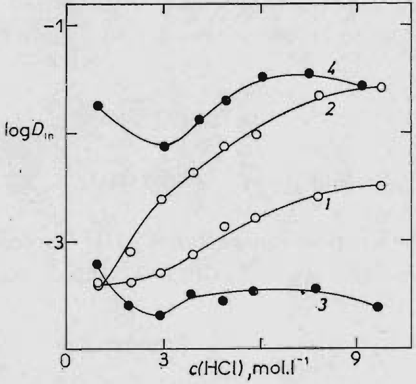

FIG. 4

Distribution of indium between hydrochloric acid solutions and solutions of TPPO *1*, *2* or TOPO *3*, *4* in chloroform. c_{TGPO} (mol l^{-1}) *1* 1 . 10^{-2}, *2* 5 . 10^{-2}, *3* 1 . 10^{-2}, *4* 0·1

In Fig. 2, the plots of log D_{In} *vs* $c(HCl)$ are shown for various initial concentrations of TOPO in the region of 10^{-3} to 0·131 mol l^{-1}. Obviously, as the initial concentration of TOPO increases, the maximum on the curve becomes less pronounced and shifts to lower values of hydrochloric acid concentration. In order to examine to what extent the effect of the chloride ions is involved, the dependence of log D_{In} on $c(HCl)$ was followed also at a constant ionic strength, $I = 4{\cdot}0$, by using HCl-NaCl solutions. It is apparent from curves *1 – 3* (full circles) that the indium distribution ratio varies only slightly with increasing acidity of the aqueous phase if the chloride ion concentration is held constant.

The effect of the organic solvent used was tested by studying the distribution of indium for solutions of TOPO in n-octane, chloroform, and tetrachloromethane ($c(TOPO) = 1 \,.\, 10^{-2}$ mol l^{-1}). As Fig. 3 shows, the extractability of indium increases in the order chlororform < tetrachloromethane < benzene < n-octane; in the case of chloroform, extraction of indium by means of TOPO is practically negligible. On the other hand, chloroform, unlike benzene, is a comparatively good solvent for TPPO. In this case the shape of the extraction curves (Fig. 4) is different in that it does not exhibit maxima observed with TOPO or TBPO, and by its nature it approaches TBP.

Slope analysis of the plots of log D_{In} *vs* $c(TGPO)$ revealed that indium is extracted into benzene or chloroform (tetrachloromethane and n-octane were not examined)

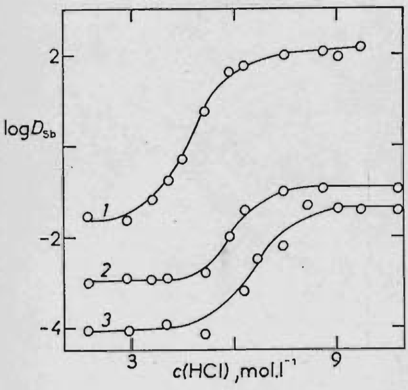

FIG. 5

Distribution of antimony(III) between hydrochloric acid solutions and organic phase free of reagents. *1* Nitrobenzene, *2* benzene, *3* n-octane

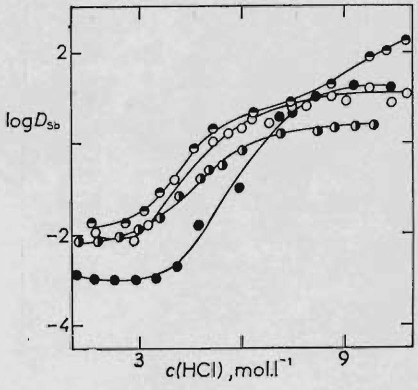

FIG. 6

Distribution of antimony(III) between hydrochloric acid solutions and $1 \,.\, 10^{-3}$ mol l^{-1} solutions of the reagents in benzene. ● TPPO, ◑ TBPO, ○ TOPO, ◓ R_4NCl

in the form of the complex species $InCl_3.2TGPO$ (TGPO = TBPO or TOPO) or $HInCl_4.2$ TGPO; the number of water molecules involved is not known. In favour of the former species is the fact that the distribution of indium is not markedly affected by the acidity of the aqueous phase (Fig 2, curves *1*–*3*); the latter alternative cannot be ruled out in view of the fact that despite the different stoichiometry, indium is well extracted into solutions of R_4NCl in benzene (Fig. 1, curve *4*), this reagent being capable of formation of practically only one well extractable ionic associate species, *viz.* $(R_4N^+, InCl_4^-)$. This was proved by the dependence of $\log D_{In}$ on $c(R_4NCl)$ at $c(HCl) = 6{\cdot}2\ mol\ l^{-1}$ being linear with the slope of 1·0.

The following conclusions can be drawn from the results obtained: With low polar organic solvent, the extractability of indium decreases in the order TOPO > TBPO > > TBP; the length of the alkyl chain thus has a bearing on the extractability, and trialkylphosphates and trialkylphosphine oxides differ in this respect considerably. The solvent effect for reagents with aliphatic chains appears in the extractability of indium increasing in the order chloroform < tetrachloromethane < benzene < < n-octane. The plots of indium distribution ratio *vs* acidity of the aqueous phase for the trialkylphosphine oxides and low polar organic phase display characteristic maxima, which are shifted to lower acidity values as the analytical concentration of the organophosphorus reagent increases. The composition of the extracted complexes is probably $InCl_3.2TGPO$ or $HInCl_4.2TGPO$ (TGPO = TBPO, TOPO); in the former case the reagent is bonded to the central atom, in the latter case it sol-

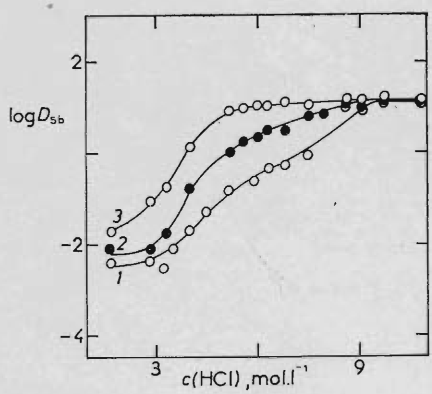

FIG. 7

Distribution of antimony(III) between hydrochloric acid solutions and solutions of TOPO in benzene. c_{TOPO} (mol l^{-1}): *1* 2 . 10^{-4}, *2* 1 . 10^{-3}, *3* 1 . 10^{-2}

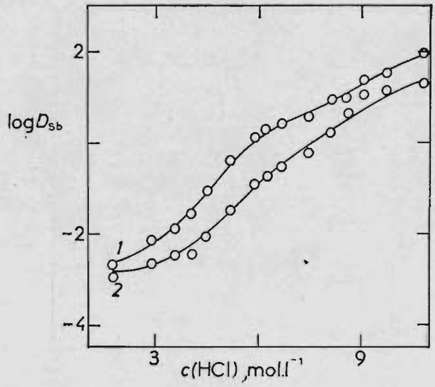

FIG. 8

Distribution of antimony(III) between hydrochloric acid solutions and solutions of TOPO in n-octane. c_{TOPO} (mol l^{-1}): *1* 1 . 10^{-3}, *2* 2 . 10^{-4}

vates the proton in the ion pair formed. The former complex seems to predominate in the region of $c(\mathrm{HCl}) < 6\ \mathrm{mol\ l^{-1}}$ in the aqueous phase, the latter, in the region of higher acidities, the simultaneous presence of both species being not ruled out[12].

Distribution of Antimony(III)

While in the case of indium, the element in the absence of reagent (TGPO, TBP, R_4NCl) does not pass into the pure organic phase in observable quantities over the entire region of hydrochloric acid concentrations used, with antimony the situation is different. Fig. 5 presents the plot of log D_{Sb} *vs* $c(\mathrm{HCl})$ for pure nitrobenzene, benzene, or n-octane as the organic phase. Obviously, if present in microconcentrations ($c_{Sb} = 1 \,.\, 10^{-5}\ \mathrm{mol\ l^{-1}}$), antimony passes into benzene and n-octane to an appreciable extent starting from $c(\mathrm{HCl}) = 6\ \mathrm{mol\ l^{-1}}$, and into nitrobenzene starting from $c(\mathrm{HCl}) = 2\ \mathrm{mol\ l^{-1}}$. This fact has not been so far taken into account. Antimony is extracted either as $SbCl_3$ or as an ionic associate (H^+, $SbCl_4^-$).

Analogous plots of log D_{Sb} *vs* $c(\mathrm{HCl})$ in the presence of the reagents in concentration $1 \,.\, 10^{-3}\ \mathrm{mol\ l^{-1}}$ are shown in Fig. 6. Similarly as in the case of indium, the reagents can be ordered according to their efficiency, the sequence being TPPO $<$ $<$ TBPO $<$ TOPO $<$ R_4NCl; this order changes in the case of TPPO at $c(\mathrm{HCl}) <$ $< 7\ \mathrm{mol\ l^{-1}}$ in the aqueous phase. Moreover, in the case of TPPO the left part of the curve (for $c(\mathrm{HCl}) < 4\ \mathrm{mol\ l^{-1}}$) is identical with that corresponding to pure

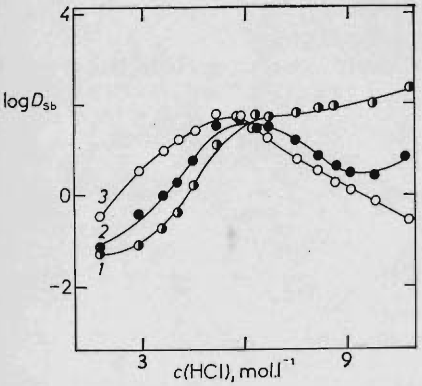

FIG. 9

Distribution of antimony(III) between hydrochloric acid solutions and solutions of TOPO in nitrobenzene. c_{TOPO} (mol l^{-1}): *1* 2 . 10^{-4}, *2* 1 . 10^{-3}, *3* 1 . 10^{-2}

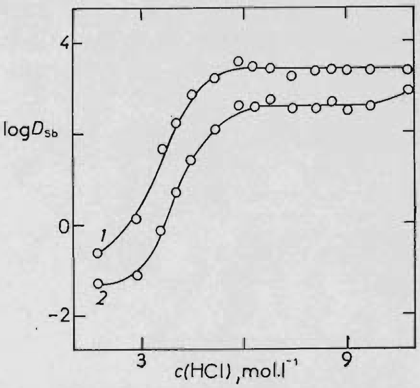

FIG. 10

Distribution of antimony(III) between hydrochloric acid solutions and solutions of TBP in benzene. *1* 55% (v/v) TBP, *2* 25% (v/v) TBP benzene. Figs 7–10 show the analogous dependences in the acidity of the aqueous phase for solutions of different concentrations of TOPO in benzene, n-octane, and nitrobenzene and for solutions of TBP in benzene. The plots are as expected, with the exception of nitrobenzene, where in the region of $c(\mathrm{HCl}) \geqq 6 \mathrm{~mol~l}^{-1}$ a reverse shape of the plots is observed. This phenomenon was not studied in detail; it can obviously be related to the high permitivity value of the solvent in question.

Slope analysis of the plots of log D_{Sb} *vs* c(TGPO, TBP) indicates that in the acidity range of $c(\mathrm{HCl}) = 4-8 \mathrm{~mol~l}^{-1}$, the complexes extracted into benzene are $\mathrm{SbCl_3}$.TGPO (TGPO = TPPO, TBPO, TOPO) and $\mathrm{SbCl_3.2TBP}$, or $\mathrm{HSbSl_4}$.TGPO and $\mathrm{HSbCl_4.2TBP}$. In the case of $\mathrm{R_4NCl}$, the $(\mathrm{R_4N^+}, \mathrm{SbCl_4^-})$ species is extracted. At acidities exceeding $8 \mathrm{~mol~l}^{-1}$ HCl, the situation is more complicated, owing to the possible formation of the $\mathrm{SbCl_5^{2-}}$ and $\mathrm{SbCl_6^{3-}}$ species; the composition of the extracted complexes was not determined.

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