The Extraction of Thallium(III) from Hydrochloric Acid Solutions with Ethyl Acetate

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The extraction of thallium(III) from hydrochloric acid solutions into ether and other organic solvents has been reported by several investigators.[1-4] It has been developed into an analytical method for the separation of thallium from most elements, excepting iron(III), gallium(III), gold(III), and a few others. Irving and Rossotti,[5] while studying the extraction of indium(III) from hydrochloric acid solutions, have given a comparative account of the extraction of the HMX_4 species ($M = Ga^{3+}, In^{3+}, Fe^{3+}, Au^{3+}$; $X = Cl, Br, I$) with various organic solvents, including ethyl acetate. However, no information is available on the extraction of the corresponding halothallic acids ($HTlX_4$). The present communication will give the details of the extraction of thallium(III) from its solutions in hydrochloric acid, using ethyl acetate as an extracting solvent.

Experimental

Stock solutions of thallic chloride were prepared by dissolving freshly-precipitated thallium(III) oxide in hydrochloric acid solutions of the desired strength.

Ethyl acetate (British Drug House) was distilled once and used in that form. All the other reagents and solutions were prepared from "Analar" compounds, and their concentrations were ascertained by conventional methods.

Known volumes of an aqueous thallic chloride solution of the desired strength in hydrochloric acid of an appropriate concentration were shaken for a constant time (1 min.) with an equal volume of ethyl acetate (pre-equilibriated with acid of a corresponding strength), in a glass-stoppered measuring cylinder. The layers were allowed to separate, and the final volumes were recorded. Known aliquots from the organic and the aqueous layers were withdrawn and analysed volumetrically for their thallium and chloride contents.

Results and Discussion

Optimum Conditions for Extraction.—The extraction yield of thallium(III) at 1.0 N hydrochloric acid was found to be as high as 72%; the percentage extraction and the distribution coefficient increase gradually with an increase in the acid concentration, attain a maxima at 6.0 N hydrochloric acid, and then fall to a lower value (Fig. 1). As the changes in the phase miscibility, due to the hydrolysis of ethyl acetate, are relatively small up to 6.0 N hydrochloric acid, the experimental conditions at this stage correspond approximately to the ideal state, but at a higher concentration of the acid, the hydrolysis of the ester becomes significant and the volume of the organic layer decreases. This consequently brings about a decrease in the activity of the extractable species, and results in the lower values for the percentage extraction and the distribution coefficient.

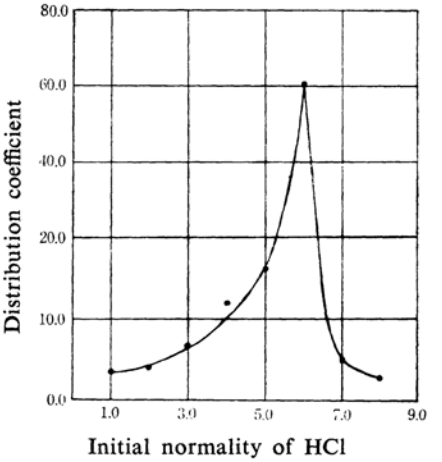

Fig. 1. Distribution of thallium(III) between ethyl acetate and hydrochloric acid.

The Nature of the Extracted Species.—The empirical formula of the extracted species corresponds to $HTlCl_4$, because almost equimolar quantities of thallic chloride and hydrogen chloride are extracted from aqueous solutions containing less than 6.0 N hydrochloric acid.

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1) H. M. Irving, *Quart. Revs.*, **5**, 200 (1951).

2) H. M. Irving and F. J. C. Rossotti, *Analyst*, **77**, 2440 (1957).

3) D. L. Horrocks and A. F. Voigt, *J. Am. Chem. Soc.*, **79**, 2440 (1957).

4) K. S. Venkateswarlu and P. C. Das, *J. Inorg. & Nuclear Chem.*, **25**, 730 (1963).

5) H. M. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, **1955**, 1906, 1918.

Beyond this concentration, an increasingly greater quantity of hydrochloric acid is co-extracted. This fact cannot be attributed to the formation of a thallium complex with a larger amount of hydrochloric acid, e. g., H_2TlCl_5, as this species has already been shown by Horrocks and Voigt³⁾ to be inextractable. A plausible explanation may be a salting-out effect of thallium(III).

The Effect of the Metal Concentration.—The studies of the extraction of thallium(III) at various concentrations in 6 N hydrochloric acid solutions have shown that the percentage extraction and the distribution coefficient increase with the increase in the concentration of the metal. This may be due to a self-salting-out effect caused by thallium(III) itself, similar to that reported for the extraction of gallium(III) and iron(III) from hydrochloric acid solutions.⁶⁾ The mechanism of this phenomenon may be explained by assuming the formation of $[Tl(H_2O)_6]^{3+}$ ions in more concentrated solutions of thallium, which replace the protons in the species $[H^+(TlCl_4)]$, thereby giving enhanced values of the distribution coefficient and of the percentage extraction.

Salting-out Effects.—The extraction of thallium(III) from its solution in 2 N hydrochloric acid and in the presence of 1.0 M MCl_x (where M=Li, Na, K, NH_4, Ca, Mg, and Al, and x, the valency of the cation) was studied. The presence of metal chloride results in a considerable increase in the percentage extraction and distribution coefficient. When univalent chlorides were used, the distribution coefficient followed the order $Li>K—Na>NH_4$. For other metal chlorides, an order of the $Li>Al>Mg>Ca>NH_4$ type is obtained. This may be attributed to the relative differences in the water activity in the presence of these cations. Lithium, being the most strongly hydrated, has the greatest effect.

The Effect of the Dilution of the Solvent.—Ethyl acetate diluted with such solvents as petroleum ether (B. range 85—100°C), benzene, chloroform and carbon tetrachloride was employed for the extraction of thallium(III). The results indicate that the distribution coefficient decreases with the increasing molar polarisation of the diluent. This happens to be in conformity with a generalisation given previously.⁷⁾

A plot of the log of the distribution coefficient against the log of the concentration of ethyl acetate did not give a definite value of n, the solvation number. It appears that the solvation of the metal varies significantly with the extent of dilution; hence, a definite stiochiometric ratio can not be obtained.

The Separation of Thallium(III) from Al^{3+}, Ga^{3+}, and In^{3+}.—Experimentation on other metals of the III-B group has, however, shown that the extraction percentages of aluminum, gallium and indium are 0, 96.7, and 3.72 respectively at an initial hydrochloric acid concentration of 6.0 N. Aluminum does not from a tetrahedral-extractable species of the chloride complex in an aqueous solution, while indium under similar conditions shows a marked tendency to remain predominantly octahedral⁷⁾; hence, very low values for the percentage extraction are obtained.

The fact that thallium(III) is extracted by 72.26% at a 1.0 N hydrochloric acid concentration, at which concentration gallium and indium are only negligibly extracted, has been utilised in separating it from these two metals. A batch-by-batch extraction with ethyl acetate at 1.0 N hydrochloric acid effects a quantitative separation of thallium from other members of the III-B group. The presence of other metals, particularly aluminum, on the other hand, results in a salting-out effect of thallium and enhances the percentage extraction.

Summary

Ethyl acetate has been employed as a solvent for extracting thallium(III) from its hydrochloric acid solutions. The empirical formula of the extracted metal entity has been found to be $HTlCl_4$. Optimum conditions for the extraction of the metal have been determined, and the effect of various factors, e. g., metal concentration, salting-out agents, and the dilution of the solvent, have been investigated. It has been possible to separate thallium(III) from aluminum(III), gallium(III) and indium(III) by performing a batch-by-batch extraction at a 1.0 N hydrochloric acid concentration.

1) The extracted species is an acid with an approximate formula of $HTlCl_4$, the distribution of the species between the two phases depends upon the concentration of the hydrochloric acid present in the system.

2) The extracted species is ionic and may associate in the organic phase to from ion pairs, ion triplets and higher clusters. This is evident from the fact that an increase in the metal concentration causes an increase in the distribution coefficient.

3) There is no primary solvation of thallium, which is tetrahedrally surrounded by chloride ions and which is apparently saturated. This is supported by the observation that the metal

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6) N. H. Nachtrieb and R. E. Fryxell, *J. Am. Chem. Soc.*, **71**, 4035 (1949); **70**, 3522 (1948).

7) Y. Marcus, *Chem. Revs.*, **63**, 139 (1963).

could not be extracted from its solution in perchloric acid.

4) The proton of the chlorothallic acid may be solvated (and possibly hydrated, too) in the organic phase, the solvation number being indefinite.

5) Ion pairing results in the formation of an extractable complex and a general mechanism of the type:

$$H(S)^+ + [Tl(S)_2Cl_4]^- \rightleftharpoons [(HS^+)(Tl(S_2)Cl_4)^-]$$

may be expected, where S is either H_2O or ethyl acetate.

The above equation may well represent qualitatively various reactions at different relative water and ethyl acetate activities.

In general, the system is a simple ion-association extraction system and is quite similar to the extraction of iron(III) and gallium(III) chloride with oxygenated solvents.

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