Physico-chemical Properties of Chloramine-T: Part III—Conductometric Study of the Interaction of Chloramine-T with Th(IV) & Zr(IV) Solutions

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Aqueous solution of chloramine-T, the sodium salt of *p*-toluene sulphochloramide produces a white turbidity when aqueous solutions of $Th(NO_3)_4$, $ThCl_4$, $ZrOCl_2$ and $Zr(NO_3)_4$ are added to it. The turbidity has been identified as dichloramine-T on the basis of conductometric and potentiometric titrations, elemental analysis, and UV and IR spectral studies. The breaks obtained in the conductance curves also substantiate the formation of the free acid, N-chloro-*p*-toluenesulphonamide, for which no other experimental proof has been presented till now.

CHLORAMINE-T (CAT), p-$CH_3C_6H_4SO_2NClNa$. $3H_2O$, is the sodium salt of p-toluenesulphochloramide (I). It has been widely used for the oxidation of many inorganic and organic compounds. A survey of literature shows that very little work has been done on the salts of I (RNHCl). During our attempts[1,2] to prepare other salts of I, it was noticed that the addition of CAT solution to aqueous solutions of Th(IV) and Zr(IV) produced a white turbidity. In this paper the composition of the white turbidity produced has been established by performing conductometric titrations supported by potentiometric titrations, elemental analysis, UV and IR spectral studies. It was also found essential to carry out conductometric and potentiometric titrations of CAT with HCl and H_2SO_4 solutions to supplement the observations.

Materials and Methods

All solutions were prepared using triply distilled water (sp. cond. $<1·0 \times 10^{-6}$ ohm^{-1} cm^{-1}). Thorium nitrate, thorium chloride, zirconium nitrate (BDH reagent grade) and zirconium oxychloride (Riedel) were used. The purity of thorium and zirconium salts was checked by standard methods. Chloramine-T (E. Merck) was purified by the method of Morris *et al.*[3] and its aqueous solutions standardized iodometrically. Reagent grade chemicals were used in preparing other solutions. The experimental details are described elsewhere[1].

Results and Discussion

Some typical conductance plots are shown in Figs. 1 and 2. In the direct titration (Fig. 1, curves a and b) the breaks observed correspond to about 1:3 molar ratio with respect to Th^{4+} ion and CAT whereas in the indirect titration (Fig. 1, curve c) besides a break at 3:1 molar ratio a second break is also observed roughly at 1:1 molar ratio.

In the direct titration of Zr(IV) solution (Fig. 2, curve a) a break is observed roughly at 1:1 molar
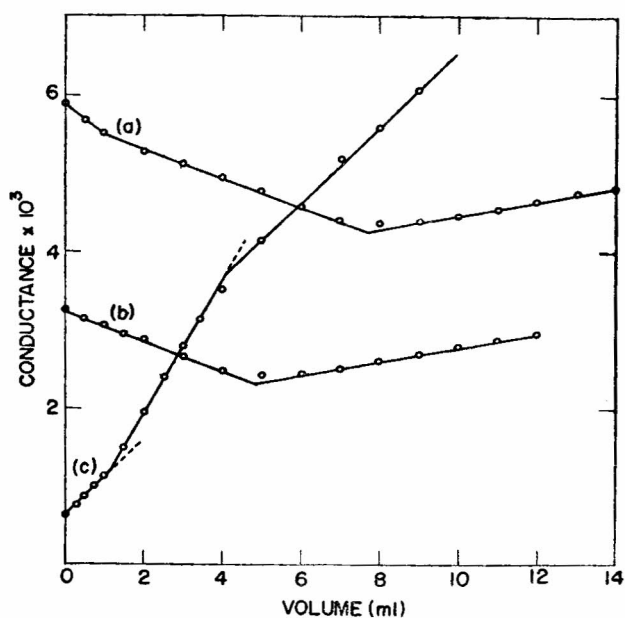
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Fig. 1 — Conductometric titration curves [(a) $Th(NO_3)_4$ ($0·009977M$) vs CAT ($0·1000M$); (b) $ThCl_4$ ($0·005363M$) vs CAT ($0·06979M$); and (c) CAT ($0·006037M$) vs $ThCl_4$ ($0·05357M$)]

ratio. In the titration of H_2SO_4 with CAT (Fig. 2, curve b) a break is seen at 1:2 molar ratio. The reverse titrations support the above data (Fig. 2, curve c).

The direct pH titration curves of Th^{4+} and Zr^{4+} are similar and identical with those obtained by Morris *et al.*[3] in the potentiometric titration of CAT with HCl. The reverse potentiometric titration curves are also identical and resemble the normal acid-base titration curves.

The white precipitate formed during the titrations was filtered and the precipitate shaken with dil. H_2SO_4. Th^{4+} and Zr^{4+} ions could be detected in the acid solution, while the precipitate was free from these ions. This indicates that $Th(OH)_4$ and $Zr(OH)_4$ get adsorbed on the precipitate during
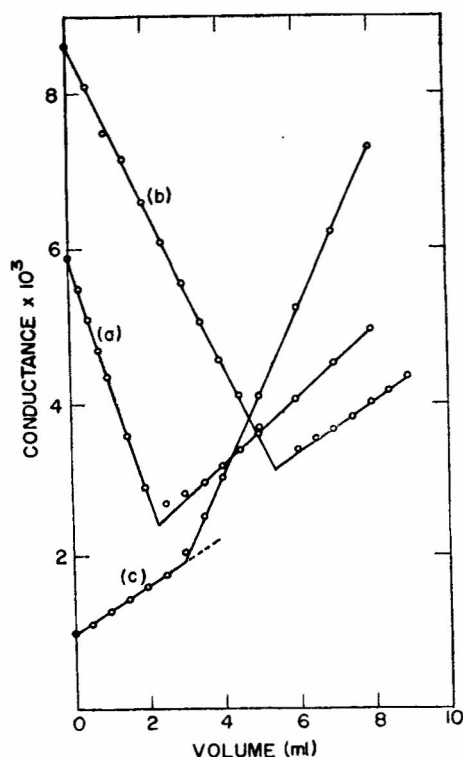
Fig. 2 — Conductometric titration curves [(a) ZrOCl$_2$ (0·01020M) vs CAT (0·1040M); (b) H$_2$SO$_4$ (0·01109M) vs CAT (0·09770M); and (c) CAT (0·01040M) vs ZrOCl$_2$ (0·1000M)]

the later stages of precipitation. Further when carefully neutralized solutions of Th^{4+} and Zr^{4+} ions with NaOH were mixed with CAT, no precipitation was observed. These results indicate that H$^+$ ion produced during the hydrolysis of these ions in aqueous solution is the actual reactant in the precipitation reactions.

The hydrolysis equilibria of Th(IV) ion in aqueous solutions have been studied by several workers[4-6]. While the presence of monomers such as Th(OH)$^{3+}$ and Th(OH)$_2^{2+}$ and the dimer Th$_2$(OH)$_2^{6+}$ has been speculated, Baes et al.[7] have concluded that the hexamer Th$_6$(OH)$_{15}^{9+}$ is the most important species present in Th(IV) ion solutions, which is formed as a result of reaction (1):

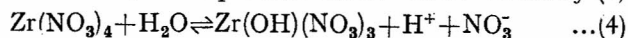$$6Th(OH)_2^{2+}+3H_2O\rightleftharpoons Th_6(OH)_{15}^{9+}+3H^+ \qquad ...(1)$$
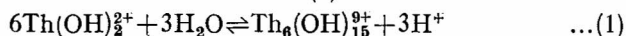
Formation of Th(OH)$^{3+}$ results[8] from the equilibrium reaction (2) producing one H$^+$ ion:

$$Th^{4+}+H_2O\rightleftharpoons Th(OH)^{3+}+H^+ \qquad ...(2)$$
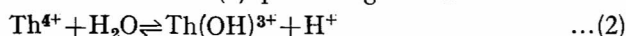
The hydrolysis[9] of zirconium oxychloride follows the course given in Eq. (3)

$$ZrOCl_2+H_2O\rightleftharpoons ZrO(OH)Cl+H^++Cl^- \qquad ...(3)$$
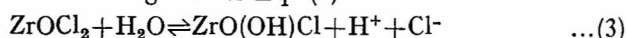
It may be assumed that Zr(NO$_3$)$_4$ hydrolyses in a similar manner to produce one H$^+$ ion as shown by (4)

$$Zr(NO_3)_4+H_2O\rightleftharpoons Zr(OH)(NO_3)_3+H^++NO_3^- \qquad ...(4)$$

It is seen from Eq. (4)[1] that three H$^+$ ions and one H$^+$ ion per mole are available from the hydrolysis equilibria on Th^{4+} and Zr^{4+} ion solutions respectively. By a knowledge of these hydrolysis equilibria, an explanation of the breaks observed in the conductance graphs can be given.
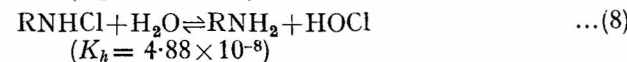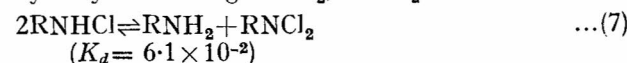
Bishop and Jennings[10] have shown that CAT is a strong electrolyte in aqueous solution and disassociates as

$$RNCl\ Na=RnCl^-+Na^+ \qquad ...(5)$$

The anion picks up a proton forming RNHCl.

$$RNCl^-+H^+\rightleftharpoons RNHCl \qquad ...(6)$$
$$(K = 3·58\times10^4)$$

The free acid undergoes disproportionation and/or hydrolysis forming RNH$_2$, RNCl$_2$ and HOCl:

$$2RNHCl\rightleftharpoons RNH_2+RNCl_2 \qquad ...(7)$$
$$(K_d = 6·1\times10^{-2})$$

$$RNHCl+H_2O\rightleftharpoons RNH_2+HOCl \qquad ...(8)$$
$$(K_h = 4·88\times10^{-8})$$

The turbidity obtained in the conductometric titrations could be due to dichloramine-T (RNCl$_2$) which is only sparingly soluble in water (7·75 $\times$ 10i^{-5} moles per litre at 25°). The break obtained at 1:1 molar ratio with respect to CAT and Zr^{4+} ion (Fig. 2, curve a) probably indicates the formation of RNHCl. The break observed at 3:1 with respect to CAT and Th^{4+} ion solutions (Fig. 1, curves a and b) and for CAT and H$_2$SO$_4$ at 2:1 mole ratio could possibly indicate the number of protons available for the formation of the free acid.

The initial decrease in conductance of salt solution when CAT is added from the burette could be attributed to the removal of H$^+$ ion from the solution, while the increase noted after the break is due to the addition of excess titrant. In the reverse titrations, the initial increase in conductance of the solution is due to the addition of metal ions, chloride or nitrate ions, although (RNCl)$^-$ ions are removed from the solution by the added H$^+$ ions according to Eq. (6). The steep increase noted after the break is due to the addition of excess titrant (metal solution).

Identification of the precipitate — The precipitate obtained in the above titrations was suspected to be dichloramine-T (DCT). A check for mass balance was carried out in all the cases and as a typical example, the mass balance for ThCl$_4$ and CAT reaction is given in Table 1. This shows that the reaction between H$^+$ ion and CAT takes place approximately in 1:1 molar ratio. The precipitate was filtered, washed with water and was estimated iodometrically in glacial acetic acid medium[11]. The unreacted CAT in the filtrate was determined iodometrically. The amount of H$^+$ ions reacted was calculated by titration against standard NaOH. It is seen from Table 1 that CAT and H$^+$ ions have reacted approximately in 1:1 molar ratio and the amount of DCT formed is nearly half the amount

TABLE 1 — MASS BALANCE IN ThCl$_4$-CAT REACTION

CAT added (mM)	CAT unreacted (mM)	DCT obtained (mM)	H$^+$ reacted (mM)	CAT reacted (mM)
0·4784	0·1243	0·1449	0·3281	0·3541
0·9360	0·4013	0·2199	0·4255	0·5347
0·2600	0·08719	0·07501	0·1255	0·1729
0·2600	0·08206	0·08366	0·1235	0·1780

of CAT reacted. The precipitate was further identified as DCT by elemental analysis (Found: S, 13·7; Cl, 28·8. p-$CH_3C_6H_4SO_2NCl_2$ requires S, 13·33; Cl, 29·6%), UV and IR spectral studies.

UV spectrum of the precipitate in aqueous solution ($\sim$0·1 mM) showed a broad absorption band $\sim$43860 cm^{-1} (log $\epsilon_M$$\sim$4·1). DCT prepared by the method of Jacob and Nair[11] showed an identical band in aqueous solution. The IR spectra of the sample obtained in the present study and that obtained by Jacob and Nair[11] were superimposable.

The above results show that the turbidity produced in the above titrations is dichloramine-T formed by reactions (6) and (7). It may be pointed out that no thorium or zirconium salt of the free acid RNHCl similar to AgCAT and Hg(CAT)$_2$ reported by the authors[1], can be prepared even by the addition of excess of reagents. However, the results of the present investigations are significant, for the conductance breaks can be taken as positive evidence for the formation of the free acid RNHCl, for the existence of which no other experimental proof has been presented until now. The mass balance given in Table 1 supports the view that H$^+$ ions are removed by reaction (6) where the equilibrium is mainly to the right and DCT is formed by reaction (7). Higuchi et $al.$[12] have studied the disproportionation reaction (7) and they have shown that at pH 2·3 and initial concentration of 1 mM, the half way point in the approach of equilibrium is of the order of 1 min. It is seen that reaction (7) is fastest at pH 4 and thereafter the rate decreases. This could as well account for the decrease in the amount of precipitation after pH 4. It is probable that RNHCl formed around pH 3 disappears above this pH by reaction (7), giving rise to DCT and RNH$_2$.

Acknowledgement

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