## Electrometric Studies on the Reaction between Thorium and Alkali Tungstate

The reaction between $Th^{4+}$ and $WO_4^{2-}$ ions has been investigated by means of electrometric techniques involving amperometric, pH, and conductometric titrations between thorium nitrate and sodium tungstate at several concentrations in aqueous medium. The sharp breaks and inflections in titration curves provide cogent evidence for the formation and precipitation of normal thorium tungstate, $ThO_2 \cdot 2WO_3$, in the pH range 4.50–5.75. Amperometric titrations yield more accurate results and offer a simple and rapid method of determining $Th^{4+}$ ions in solutions at suitable concentrations and pH ranges. An attempt has also been made to examine the possibility of developing this reaction as an analytical procedure for the determination of thorium as tungstate amperometrically.

*Experimental.* Reagents thorium nitrate, sodium tungstate and thymol used were of AnalaR(BDH) quality and their solutions were prepared in air-free conductivity water.

Amperometric titrations: A manual polarograph with scalamp galvanometer was used for performing amperometric titrations. A dropping mercury electrode having the characteristics $m = 2.416$ mg/sec, $t = 3.58$ sec and $m^{2/3} t^{1/6} = 2.226$ mg$^{2/3}$ sec$^{-1/2}$ at $E_{d.e.} = -1.0$ v (vs. S.C.E.) was used in conjunction with saturated calomel electrode connected to the cell by agar-KCl bridge. All the amperometric titrations were performed without any supporting electrolyte and in the presence of 0.01% thymol as maximum suppressor at an electric tension of $-1.5$ v (vs. S.C.E.), which is the limiting current plateau potential of the wave produced by $Th^{4+}$ ions.

20.0 ml of the titre solution were taken into the cell each time, which was swept and stirred by bubbling hydrogen. After each addition of the titrant solution, the observed current was corrected for the dilution effect and plotted against the volume of the titrant added in ml. The end point was located graphically. Employing different concentrations of thorium nitrate and sodium tungstate, amperometric titrations were carried out with each of the reagents alternatively used as the titre. Only one figure (Figure 1, Curves I, II), having two representative curves of direct and reverse titrations, has been given for the sake of brevity. The results of amperometric study have been tabulated (Table I).

pH and conductometric titrations: pH of the solutions were measured on a Cambridge null deflection type pH meter. The glass electrode of the range 0–13 pH, calibrated frequently by buffers of different pH values, was used in conjunction with saturated calomel electrode. 20.0 ml of the solution was taken into the cell each time; it was kept immersed in an electrically maintained thermostat and the contents were stirred by means of a magnetic stirrer. The observed pH values were plotted against the volume of titrant added in ml, and from the sharp inflections in titration curves and maximum value of dpH/dV the end point was determined.

Conductance of the solutions was measured on a Kohlrausch universal bridge using an A.F. generator as a source of A.C. The conductivity values after correction for the dilution effect were plotted against the volume of titrant and the end point located graphically. The same strengths of the solutions were employed in both the techniques for the sake of comparison. The results of pH and conductometric studies have been tabulated (Table II, Figure 2).

Table I. Summary of the results of amperometric titrations

| Molarity of solutions | | Equivalence points (ml) | |
|---|---|---|---|
| $Th(NO_3)_4$ | $Na_2WO_4$ | Calculated | Observed |
| Direct titrations, Figure 1, Curve I[D] | | | |
| *M*/30 | *M*/100 | 3.00 | 3.00 |
| *M*/50 | *M*/150 | 3.33 | 3.30 |
| *M*/80 | *M*/250 | 3.20 | 3.25 |
| *M*/200 | *M*/500 | 4.00 | 4.10 |
| Reverse titrations, Figure 1, Curve II[R] | | | |
| *M*/200 | *M*/20 | 4.00 | 4.00 |
| *M*/400 | *M*/30 | 3.00 | 3.00 |
| *M*/750 | *M*/70 | 3.73 | 3.75 |
| *M*/1000 | *M*/90 | 3.60 | 3.65 |

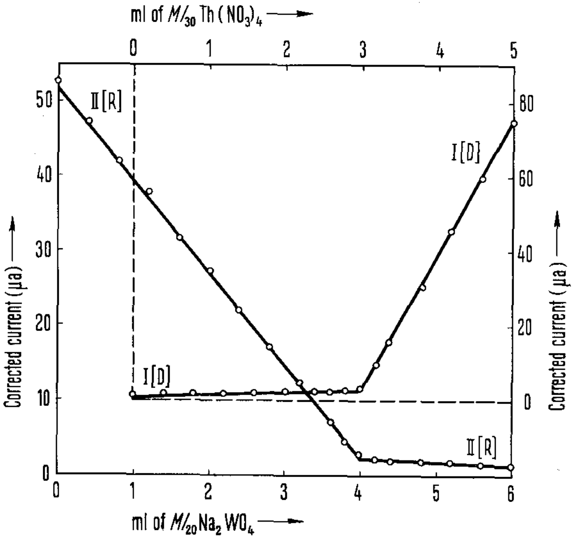

Fig. 1. Direct (I[D]) and reverse (II[R]) amperometric titrations between $Th(NO_3)_4$ and $Na_2WO_4$. Curve I[D]: ml of *M*/30 $Th(NO_3)_4$ added to 20.0 ml of *M*/100 $Na_2WO_4$. Curve II[R]: ml of *M*/20 $Na_2WO_4$ added to 20.0 ml of *M*/200 $Th(NO_3)_4$.

Table II. Summary of the results of pH and conductometric titrations

| Molarity of solutions | | Equivalence points (ml) | | |
|---|---|---|---|---|
| $Th(NO_3)_4$ | $Na_2WO_4$ | Calculated | Observed from | |
| | | | Max. dpH/dV | Conductance |
| Direct titrations Figure 2, Curves I[D] and II[D] | | | | |
| *M*/10 | *M*/30 | 3.33 | 3.35 | 3.30 |
| *M*/40 | *M*/100 | 4.00 | 3.94 | 3.95 |
| *M*/80 | *M*/250 | 3.20 | 3.25 | 3.30 |
| *M*/150 | *M*/500 | 3.00 | 3.08 | 2.95 |
| Reverse titrations, Figure 2, Curves I[R] and II[R] | | | | |
| *M*/120 | *M*/10 | 3.33 | 3.36 | 3.40 |
| *M*/250 | *M*/20 | 3.20 | 3.24 | 3.15 |
| *M*/500 | *M*/50 | 4.00 | 4.05 | 4.10 |
| *M*/750 | *M*/70 | 3.73 | 3.68 | 3.80 |

*Discussion.* Using different concentrations of thorium nitrate and sodium tungstate, a series of amperometric titrations was carried out at $E_{d.e.} = -1.5$ v (vs. S.C.E.), at which $Th^{4+}$ ions give a well-defined reduction wave while the $WO_4^{2-}$ ion does not produce any measurable diffusion current. In direct titrations (Fig. 1, curve I[D]), i.e. when sodium tungstate solution is used as the titre, the observed current of the magnitude of a few microamperes remains almost unchanged on the addition of thorium nitrate solution till the end point is reached, after which the diffusion current due to $Th^{4+}$ ions increases linearly with the addition of the latter. In cases where thorium nitrate solution is used as the titre (reverse titrations, Figure 1, curve II[R]) the reverse phenomenon is observed. Both the direct and reverse amperometric titration curves produce well-defined breaks at a point where the molecular ratio of the reactants $Th^{4+}$ and $WO_4^{2-}$ is 1:2, which suggests the formation of a white crystalline precipitate of normal thorium tungstate having the composition $ThO_2 \cdot 2WO_3$ in the pH range 4.50–5.75. The reaction can be stated as follows:

$$Th(NO_3)_4 + 2Na_2WO_4 = ThO_2 \cdot 2WO_3 + 4NaNO_3.$$

The accuracy and reproducibility of these titrations has been found to be excellent. The precipitation of normal thorium tungstate is quantitative and the reaction can be suitably employed for the determination of $Th^{4+}$ ions amperometrically as tungstate.

The pH of thorium nitrate and sodium tungstate solutions was measured with a glass electrode and found to be in the vicinity of 2.75 and 7.80 respectively. Various pH and conductometric titrations performed between thorium nitrate and alkali tungstate, both by direct and reverse methods (Fig. 2, curves I[D] and II[D] and I[R] and II[R]), provide sharp breaks and inflections as well as pronounced maxima in dpH/dV at the same molecular ratio of $ThO_2$:$WO_3$ as 1:2, at which amperometric titrations also yield sharp breaks and confirm the formation of identical compound ($ThO_2 \cdot 2WO_3$) in the pH range 4.50–5.75.

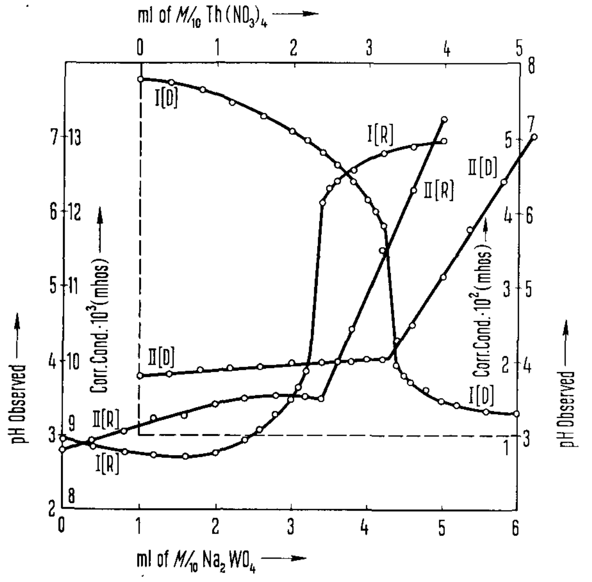

Fig. 2. Direct (I[D] and II[D]) and reverse (I[R] and II[R]) pH and conductometric titrations between $Th(NO_3)_4$ and $Na_2WO_4$. Curves I[D] and II[D]: ml of $M/10$ $Th(NO_3)_4$ added to 20.0 ml of $M/30$ $Na_2WO_4$. Curves I[R] and II[R]: ml of $M/10$ $Na_2WO_4$ added to 20.0 ml of $M/120$ $Th(NO_3)_4$.

Each titration takes about $^1/_2$ h for completion. It is observed that after each addition of the titrant it takes a little time for the diffusion current, pH, and conductance values to become steady. Thorough stirring in the vicinity of the end point has a favorable effect.

*Amperometric determination of $Th^{4+}$ as normal tungstate.* In view of the quantitative precipitation of $Th(WO_4)_2$, which is clear from Tables I and II, it was considered worth-while to study the possibility of developing this reaction as an amperometric method for the determination of $Th^{4+}$. A series of solutions containing known amounts of $Th^{4+}$ were then analysed amperometrically by titrating against normal sodium tungstate. Table III illustrates the accuracy of the method and the results of analysis.

It is quite apparent from Table III that the reaction can be suitably employed for the determination of $Th^{4+}$ content down to $1 \cdot 10^{-3} M$ with an accuracy of 1%. Cations which form precipitates with alkali tungstate, e.g. silver, cadmium, lanthanum, cerium etc., and anions which react with thorium, e.g. vanadate, molybdate, and chromate, interfere and must be absent.

A comparative study of the electrometric experiments clearly indicates that pH and conductometric titrations yield accurate results only with concentrated solutions of the reactants; at greater dilutions the breaks and inflections are not sharply defined. Amperometric titrations, however, yield very accurate end points even at sufficiently low concentrations of the reactants. The amperometric method can, therefore, be recommended for the determination of $Th^{4+}$ as normal thorium tungstate in the pH range 4.50–5.75[1].

Table III. Amperometric determination of $Th^{4+}$ as tungstate at $E_{d.e.} = -1.5$ v

Volume of the solution taken = 20.0 ml

| | | | | |
|---|---|---|---|---|
| $Th^{4+}$ present (mg) | 15.4545 | 11.6025 | 6.1180 | 0.4641 |
| $Th^{4+}$ found (mg) | 15.5473 | 11.6025 | 6.2210 | 0.4576 |
| Error | 0.0928 | 0.0000 | 0.1030 | 0.0065 |

*Zusammenfassung.* Es wurde die Reaktion zwischen $Th^{4+}$ und $WO_4^{2-}$-Ionen durch amperometrische, pH und konduktometrische Titrationen zwischen $Th(NO_3)_4$ und $Na_2WO_4$ untersucht. Elektrometrisch konnte bewiesen werden, dass sich zwischen pH 4.50–5.75 normales Thoriumtungstat $ThO_2 \cdot 2WO_3$ bildet.

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