NOTES

Amperometric Titrations of Thorium with Alkali Tungstate

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In view of the interesting results reported[1] in the amperometric studies of rare metal molybdates and tungstates, it was considered that it would be of interest to make a detailed study of the similar reaction between thorium nitrate and alkali tungstate from an analytical point of view. A perusal of the literature, however, revealed that no amperometric investigation seems to have been carried out on the thorium nitrate - alkali tungstates system. Only the preparation of thorium tungstate has been described long ago by Berzelius,[2] who mixed a solution of each of these salts.

Reagent-grade thorium nitrate and sodium tungstate were used. The strengths of these solutions were checked by the standard gravimetric methods.

Much anomalous polarographic behaviour of thorium at d. m. e. has been reported.[3] Amperometric titrations of thorium have also been described.[4,5] In view of this, it was considered worthwhile to investigate for analytical purposes the nature of the reduction wave produced by Th^{4+}. In this investigation the current voltage curves were obtained as usual by means of a manual polarograph with a lamp and scale galvanometre. The capillary had the following characteristics: ($m=2.416$ mg./sec., $t=3.6$ and $m^{2/3}\ t^{1/6}=2.235$ at -1.0 V.). Polarograms were run on 0.2 to 2 mM Th^{4+} solutions in a supporting electrolyte (1 M with respect to LiCl). Gelatin (0.01%) was used as a maximum suppressor. After making a correction for the residual current, the value of the limiting current at each concentration was determined at an applied potential $=-1.60$ versus SCE. The values of i_e/C were calculated; it was found that these values are fairly constant from a 1 mM to a 2 mM concentration of Th^{4+}. Though the wave seems to be catalytic, it may serve our purpose for carrying out amperometric titrations between a thorium salt and an alkali tungstate in this narrow range of Th^{4+} concentrations.

Twenty-five milliliters of a solution containing 1 mM of thorium as thorium nitrate is pipetted into the supporting electrolyte, 1 M lithium chloride, contained in the titration vessel. Oxygen is removed by passing nitrogen through for ten minutes. A standard solution of sodium tungstate is then added in small increments, and nitrogen is bubbled through the solution for one minute. The current is read at a potential value of -1.60 V. one minute after being diverted over the tip of the solution. The readings thus obtained are then plotted against the volume of the titrant after correcting for the volume added. The equivalence point is obtained in the usual manner from the point where the straight lines interesect.

In direct titration, where sodium tungstate is used as the titre, it is noted that at $E_{de}=-1.60$ V. versus SCE the WO_4^{2-} ion yields no measurable diffusion current, because, as is well known, this ion gives no polarographic wave in a neutral or an alkaline medium.[6] Little change in the value of current was observed on the addition of

1) C. M. Gupta, *J. Inorg. Nucl. Chem.*, **14**, 297 (1960); *Naturwissenchaften*, **50**, 545 (1963); *Z. anal. Chem.*, **204**, 3, 181 (1964); *Ind. J. Chem.*, **2**, (1965); This Bulletin, in press.

2) Berzelius, *Pogg. Ann.*, **16**, 385 (1829).

3) J. H. Paterson and C. V. Banks, *Anal. Chem.*, **20**, 897 (1948); Masek, *Chem. Listy*, **52**, 7 (1958).

4) A. Langer, *Ind. Eng. Chem. (Anal. Ed.)*, **12**, 511 (1940).

5) V. P. Vasilenko, *Zhur. Anal. Khim.*, **16**, 433 (1961).

6) I. M. Kolthoff and J. Lingane, "Polarography," Part II (1952), p. 461.

thorium salt until the stoichiometric end point is reached; after this point, however, it is found to increase linearly with the addition of the titrant. In the case of inverse titrations, the current falls. It falls as more of the precipitant is added; this continues until all of the Th^{4+} in the test solution is precipitated. Beyond the equivalence point, it reaches the residual current value. The amperometric titration curves have an L shape and feature a break at the point where the molecular ratio of Th:W is 1 : 2; this corresponds to the formation of normal tungstate of thorium $ThO_2 \cdot 2WO_3$ in the pH range from 3.5 to 7.5.

The accuracy and reproducibility of these titrations are found to be quite satisfactory, even at low concentrations of thorium salt (1 mM) or alkali tungstate. The titrations can be easily completed in twenty minutes. Cations which form a precipitates with alkali tungstate, e. g., silver, cadmium, cerium, mercury(I) and mercury-(II), and anions which react with Th^{4+}, e. g., vanadate, chromate, molybdate, tellurite, selenite and oxalate, interfere and so must be excluded.

The above results have been corroborated by making pH measurements on a battery-operated Cambridge pH meter. Direct and reverse pH titrations show a sharp break at the 1 : 2 (Th : W) ratio. The pH titrations indicate a sharp change in pH value from the acidic to the neutral side of the end point. These titrations suggest the possibility of estimating metal thorium within a 2% error.

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