Electro-reduction & Coulometric Determination of Titanium(III) in Calcium Nitrate Tetrahydrate Melt

C K BHASKARE*  
Department of Chemistry, Shivaji University, Kolhapur 416004  
and  
K N GANAGE  
Department of Chemistry, S S G M College,  
Kopargaon 423601  
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Polarographic investigation of the Ti(III)/Ti(II) system in calcium nitrate tetrahydrate melt has been carried out at 55°C. The reversibility of the system in the melt has been used successfully for coulometric generation of Ti(II) and its amperometric titration with potassium dichromate. The reduction is a single electron change as shown by the reciprocal of the slope of $\log \frac{i_0}{i-i}$ vs $E$ plot. L type plots are obtained in amperometric and dead stop titrations.

The electroreduction of metal ions in aqueous melts has evoked considerable interest in recent years because of its theoretical and practical importance. The aqueous melts are intermediate between the aqueous solutions of normal concentration range and anhydrous melts. Lowering has reported half wave potentials for different cations in lithium nitrate trihydrate, calcium chloride hexahydrate and calcium nitrate tetrahydrate melts. The studies on Cu(II), Cr(III) and Bi(III) by Delmarsski et al. and of Ti(I) and UO₂ ions by Plambeck et al. have generated important electrochemical data.

The electrochemistry of titanium has been studied to a greater extent in molten LiCl-KCl eutectic mixture and in molten NaCl-KCl than in any other melt. In LiCl-KCl eutectic melt, two halfwaves have been reported corresponding to the reductions Ti(III)/Ti(II) and Ti(II)/Ti. The electroreduction of titanium(III) to lower oxidation state in calcium nitrate tetrahydrate melt is of theoretical interest. In the present note we report the results of our studies on polarographic reduction of Ti(III), coulometric generation of Ti(II) and amperometric detection of the end point in the oxidation of Ti(II) to Ti(III).

A double walled, water jacketed borosilicate glass cell was used for the polarographic measurements. Hot water from a thermostat was circulated around the cell to maintain the temperature of the cell at 55 ± 1°C.

A double walled, water jacketed borosilicate glass cell (Fig. 1) was used for coulometric generation of Ti(II) and its biamperometric titration. Hot water was circulated around the cell from a thermostat to maintain the cell at 55 ± 1°C.

The generating electrodes were of platinum, the anode was placed in a fritted glass compartment whereas the cathode was placed in the outer compartment. An externally driven stirrer was used for proper stirring of the viscous melt. The constant current source for coulometry was a stabilized high voltage D.C. power supply (Sytronix Type 621). Biamperometric measurements were carried out with a dead stop titrator fabricated in our laboratory.

Calcium nitrate tetrahydrate (BDH, AnalalR) and titanium chloride (May and Baker, England) were used.

Potassium dichromate solution (0.00334 M)  
0.098 g of K₂Cr₂O₇ (BDH, AR) were dissolved in about 40 ml of calcium nitrate melt and volume made up to 100 ml in a volumetric flask with the melt. The contents of flask after attainment of homogeneity were kept in a thermostat at 55°C.

Titanium(III) solution (1.577 × 10⁻³ M)  
One ml of 12% TiCl₃ was transferred to a 50 ml volumetric flask and about 20 ml calcium nitr-
ate melt was added. The flask was shaken vigorously and finally the volume was made up to the mark with the melt. The solution was shaken to allow attainment of homogeneity and was then standardized by the literature procedure\textsuperscript{10}. The flask was kept in a thermostat at 55°C.

\textbf{Procedure Polaroay}

Polarograms of Ti(III) were run using the previously reported procedure on a Sargent-Welch polarograph model XVI with a low scan rate. The solubility of oxygen in the melt was negligible so no special precautions were taken to exclude air\textsuperscript{11}. The typical polarographic waves are shown in Fig. 2. The capillary characteristics were, \(m = 19\) mg sec\(^{-1}\), \(i = 3\) sec, \(h = 60\) cm, \(A = 0.1072\) cm\(^2\).

\textbf{Coulometric generation of titanium (II)}

A known volume of titanium chloride solution was added to 90 g of melt and the electrode system was inserted into the melt. The salt was mixed properly by stirring and a constant current (10 mA) was passed through the cell for a known interval of time (about 100 sec). The contents of the outer vessel were titrated amperometrically or biamperometrically with 0.00334 \(M\) dichromate. The amperometric titration was carried out at \(-0.95\) V using DME as the cathode and mercury pool as the anode.

The experiment was repeated by passing constant current for a longer duration until it gave constant titration reading, indicated by L shaped biamperometric curve; a similar plot was obtained for the amperometric detection. The amount of Ti(III) was determined using the relation, 1 ml of 0.00334 \(MK_2Cr_2O_7 = 0.958\) mg of Ti(III).

Polarographic investigations of Ti(III) in calcium nitrate tetrahydrate melt showed that the Ti(III)/Ti(II) couple behaved reversibly when Ti(III) concentrations were between \(0.15 \times 10^{-4}\) and \(0.80 \times 10^{-4}\) \(M\). The reciprocal of the slope of the plot of log \(i/(i_0 - i)\) versus \(E\) showed that there was one electron change during the reduction. The reciprocal of the slope of the straight line is 0.070 V as against 0.065 V for one electron change at 55°C. The diffusion coefficient of Ti(III) to Ti(II) reduction in calcium nitrate tetrahydrate melt was found to be \(7.586 \times 10^{-6}\) cm\(^2\) sec\(^{-1}\).

The constant current technique has more precision than the controlled potential coulometry for titanium because in the latter technique the concentrations of the electrolysed solutions are lower at the electrode. The titanium(II) species is found to be sufficiently stable in this melt, and this stability has been used for the determination of titanium by amperometric and biamperometric titrations. The current efficiency is found to be 100% in the constant current coulometry. The results of amperometric and biamperometric titrations are reproducible with standard deviations of 0.15 and 0.30, respectively.

Ti(III) can be successfully determined by coulometric generation of Ti(II) and its amperometric titration against dichromate due to reversibility of Ti(III)/Ti(II) system in calcium nitrate tetrahydrate. The amperometric titrations at mercury electrode give more satisfactory results as compared to the biamperometric method. Many transition metals and rare earths undergo reduction under similar experimental conditions so prior separation is necessary.

Though the estimation of titanium can be done by more simple literature procedures, the studies in the molten salt media constitute a new field which needs extensive investigations. The electroreduction of titanium in molten salt is, therefore, important from a theoretical point of view rather than analytical.

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\textbf{References}