



Electrochemical studies on the reduction of uranyl ions in nitric acid-hydrazine media



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ABSTRACT

The redox behaviour of uranyl ions (UO_2^{2+}) in nitric acid and nitric acid-hydrazine media were investigated by the transient electrochemical techniques cyclic voltammetry (CV) and chronopotentiometry (CP), at the working electrodes platinum, gold, titanium and glassy carbon (GC) at 298 K. At a very low concentration of 0.05 M nitric acid and in the absence of hydrazine, the reduction of uranyl ions was found to be under charge transfer and diffusion control. Nevertheless, as the acidity of the supporting electrolyte increased, the reduction was purely under kinetic control. The diffusion coefficient (D_0) values for the reduction of U (VI) at the working electrodes platinum, gold GC as well as Ti were determined. The current efficiency and conversion efficiency for the reduction of uranyl ions were found to be better under constant potential conditions than that at constant current conditions.

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1. Introduction

Partitioning of uranium from plutonium is a major step in the aqueous reprocessing of spent nuclear fuels using PUREX process [1]. Partitioning in the organic phase can be achieved by adopting either non-reductive or reductive stripping method. In the former method, separation is accomplished by forming aqueous favouring complexes of Pu (IV) with sulphate, oxalate, or by saturating the organic solvent with uranium [2]. However, this method is not a favoured process for commercial application. In the latter method, separation is achieved by reducing Pu(IV) to aqueous favouring Pu(III) using suitable reducing agents and process conditions. The reducing agents which have been investigated for the separation of plutonium from uranium include hydrazine [3,4], hydroxylamine [5,6], ferrous ion (introduced as sulphamate, acetate, nitrate, etc.) [7–9], uranous ion (introduced as nitrate) [10–15], ascorbic acid [16] and recently hydrogen in the presence of a catalyst [17,18]. Among all the reductants available for reducing Pu(IV) to Pu(III), uranous nitrate and ferrous sulphamate are widely employed. Ferrous sulphamate reduces Pu (IV) with good efficacy. However, it introduces non-volatile and corrosive ions into the process streams and complicates nuclear waste management operation, in addition to forming a strong complex with plutonium. Further, it is necessary to maintain high ferrous to the ferric ratio (20 to 40

fold) to ensure complete reduction of Pu(IV). Hence, considerable attention has been paid to the use of uranous nitrate as the reductant for Pu(IV). The data available in the literature for the preparation and reducing action of uranous nitrate in stripping Pu are exhaustive [11,12]. Uranous nitrate can be produced from uranyl nitrate by chemical [4,18], photochemical [14,15] and electrochemical methods [19–22]. The former two approaches are not employed for the commercial production. Electro-reduction method is relatively simple and suitable for large scale production. Thus, production of uranous nitrate with excellent conversion efficiency is an important process step in nuclear fuel reprocessing.

Conversion of U(VI) to U(IV) with high current efficiency can be achieved in continuous as well as in batch mode electro-reduction process if it is voltage-controlled [22]. Reduction of U(VI) at Ti cathode in nitric acid-hydrazine media was studied by Kim et al. [23]. These authors reported that a high activation potential was required for the reduction of uranyl ions at Ti cathode. The electrochemical behaviour of U (VI) in nitric acid solutions of concentration 0.1 to 3 M on platinum and titanium electrodes was investigated [10,24]. Polarographic studies in strong acid solutions, conducted by Kolthoff and Harris [25] revealed that at a higher acid concentration, the primary reduction product was UO_2^+ , which undergoes disproportionation in the presence of H^+ to yield U (VI), U(IV) and H_2O . Wei et al. [20] studied the effect of acidity on the reduction of U(VI) by cyclic voltammetric technique and had reported that high acidity is electrochemically favourable for the reduction of U(VI) to U(IV). Their observation is consistent with the results reported by Ghandour et al. [10], based on polarographic studies. Though several researchers had studied the electrochemical behavior of U(VI) at different electrodes

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in various media including room temperature ionic liquids [26,27] as well as the stability of U(V) in basic carbonate and in aqua complexes [28–30] by cyclic voltammetric technique, kinetic studies on the reduction of U(VI) in nitric acid medium is not reported reliably. Nevertheless, chronopotentiometric oxidation and reduction of Pu in mineral acid solutions using Pt wire micro-electrodes were investigated by Peters and Shults [31] and cyclic voltammetric studies of Pu and Np in nitric acid media were reported by Cassadio et al. [32].

To understand the mechanism of reduction of uranyl ions and to determine the kinetic parameters for the reduction reaction, the redox behavior of uranyl ions in nitric acid medium at different working electrodes was investigated in the present study using the transient electrochemical techniques, cyclic voltammetry (CV) and chronopotentiometry (CP). The reduction behavior of U(VI) in the presence of hydrazine was also investigated to compare the results with those data generated in the nitric acid medium. The value of heterogeneous electron transfer rate constant (k_s) estimated for uranyl reduction at a low concentration of nitric acid (0.05 M) using Klingler and Kochi equation [33] based on peak separation method was validated using Nicholson equation [34]. The current, as well as conversion efficiencies in the reduction of uranyl to uranous ions at Ti working electrode, were compared on constant potential/current conditions.

2. Experimental

2.1. Chemicals

The chemicals and reagents used were nuclear grade U_3O_8 (supplied by NFC, Hyderabad), AR grade nitric acid (Hi-Pure Chemicals, Chennai), potassium hydrogen phthalate (GR, 99.9%, Merck, Mumbai), sodium hydroxide and sulphuric acid (GR, 98%, Merck, Mumbai), hydrazine hydrate (AR, 99%, S d fine Chem Ltd., Mumbai), potassium dichromate (GR, 99.5%, Merck, Mumbai), potassium oxalate (AR, 99.5%, Ranbaxy Fine Chemicals Ltd., New Delhi) and Ferroin indicator (Merck, Mumbai). Solutions of uranyl nitrate in different concentrations of nitric acid (0.05, 1.0 and 1.5 M) and hydrazine (0.25 M) were prepared by dissolving accurately weighed quantities of U_3O_8 in hot nitric acid. 0.25 M hydrazine nitrate was added as the holding reductant to scavenge nitrous acid (produced as an intermediate in the reduction of nitric acid), which would otherwise catalyse the oxidation of U(IV) ions.

2.2. Estimation of uranyl [U(VI)] and uranous [U(IV)] ions

Uranyl ions in the stock solutions were quantitatively analyzed by Davis and Gray method [35] after reducing U(VI) to U(IV) in a strong phosphoric acid medium using Fe(II) and titrating the resultant U(IV) ions against standard potassium dichromate solution potentiometrically, using Metrohm auto titroprocessor-670. The amount of U(IV) generated during electro-reduction was estimated periodically in the sulphuric acid medium by titrating against standard potassium dichromate in the presence of ferroin indicator. The end point was the disappearance of reddish orange and the appearance of blue colour. Uranous ions were also characterized by UV-Visible spectrophotometry.

2.3. Simultaneous determination of free acidity and hydrazine

As uranium (heavy metal ion) present in the electrolyte solution interferes in the estimation of free acidity by forming hydroxide with the titrant (NaOH) at very low concentrations of acid, it was essential to mask the uranyl ions by complexing with pre-neutralized potassium oxalate, before the determination of free acidity. Further, to eliminate the interference of hydrazine present in the solution, the pH of the potassium oxalate solution was adjusted to 5.6, because during free acidity determination, hydrazine (the weak base) would produce the conjugate acid, whose pKa value is 7.96. As per Henderson-Hasselbalch equation, the equivalence point for the neutralisation reaction to form

hydrazinium nitrate occurs at pH 5.6 (for the concentrations of nitric acid and hydrazine encountered in the test solutions). Thus, for the estimation of the free acid, 0.1 ml of the aliquot (test solution) was added to 30 ml of 0.1 M (pH adjusted) potassium oxalate solution. Owing to the presence of free acid in the sample, the pH of potassium oxalate solution decreased, and it was brought back to the initial pH of 5.6 by titrating against standardized NaOH solution and using a combined glass electrode in an auto titroprocessor. From the titre value, the concentration of free acid in the sample was calculated. To determine the concentration of hydrazine in the sample was calculated. To determine the concentration of hydrazine, 3 ml of 30% formaldehyde was added to the same solution, the pH of which was 5.6. Formaldehyde releases HNO_3 from $N_2H_4.HNO_3$ and binds hydrazine, the quantity of which is equivalent to the amount of acid liberated from $N_2H_4.HNO_3$. As free acid was released from hydrazine nitrate, the pH of the solution was found to decrease below pH 5.6, which was again adjusted back to 5.6 with standardized sodium hydroxide. The concentration of acid determined from the titre value is equal to the concentration of hydrazine.

2.4. Electrochemical setup

Electrochemical behaviour in the reduction of U(VI) was investigated by performing CV and CP experiments at 298 K in a standard three-electrode cell comprising Pt foil (Surface area, SA: 1.2 cm^2) as a counter electrode and Ag-AgCl as a reference electrode. Platinum (SA: 0.416 cm^2), glassy carbon (SA: 0.448 cm^2), Titanium (SA: 0.328 cm^2) and Gold (SA: 0.228 cm^2) were employed as working electrodes for the electrochemical studies using Autolab Model PGSTAT 30 (Eco-Chemie, the Netherlands) electrochemical system, equipped with General Purpose Electrochemical Software. 25 ml of 50 mM uranyl nitrate in different concentrations of nitric acid (0.05, 1.0 and 1.5 M), without or with hydrazine (0.25 M) served as the electrolyte. The voltammograms were recorded at different scan rates from 0.01 to 0.1 Vs^{-1} . Similarly, chronopotentiograms were recorded at various applied constant currents. All the experiments were performed after de-oxygenation of the test solutions by purging with argon gas.

3. Results and discussion

3.1. Cyclic voltammograms of U(VI) in HNO_3 medium

The cyclic voltammograms of 50 mM U(VI) in 0.05 M nitric acid, recorded at a platinum working electrode over the potential range 0.3 to -0.65 V against Ag/AgCl reference electrode at the scan rates 0.01 and 0.1 Vs^{-1} are shown in Fig. 1. The CV recorded for the supporting

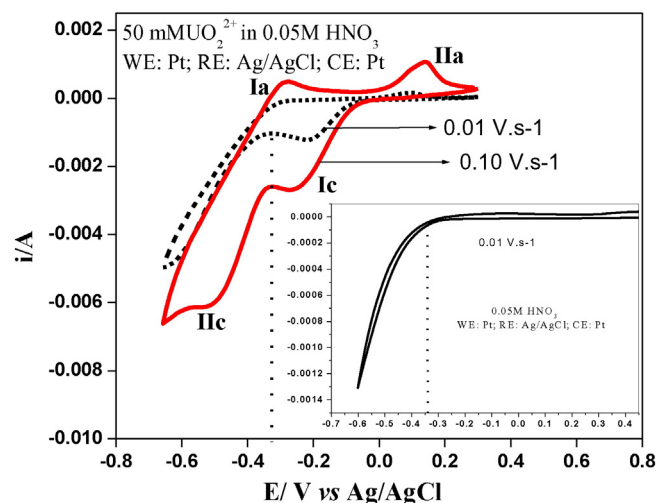


Fig. 1. Cyclic voltammograms of U(VI) in 0.05 M HNO_3 recorded with Pt electrode at 298 K.

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