Preparation of High Concentrations of Trivalent Uranium by Acid Control and Studying It's Stability

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Abstract:

High aqueous trivalent uranium concentrations (≥2.0 M) in hydrochloric acid medium have been prepared , using zinc amalgam and by controlling the acid concentration during preparation .Stabilities of 1.5M U(III) in different HCl concentrations(3, 4, 5 and 7)M were studied. It was found that U (III) is more stable in low acid concentration, due to the formation of chloro-complex compound with U (III) at high concentrations.The half oxidation time was calculated from experimental data. It was found that the half oxidation time of U(III) is (6 - 211) days and it decreased with increase of acid concentration.Addition of low concentrations (2mmole) of Cu^{+2}, Cr^{+3}, Ni^{+2} and Fe^{+2} ions (impurities) to 1.5M aqueous solution of U(III) in 3M HCl , decreased the U(III) half oxidation time dramatically (2-6 hours).It was concluded that the presence of impurities in U(III) solution act as a catalyst for oxidation of U (III).

Key wards: Trivalent uranium, hydrochloric acid.

Introduction:

Trivalent uranium ions are unstable in aqueous solutions, due to the very low electrochemical potential which allows the direct reaction between trivalent uranium U(III) and water molecules or hydrogen ions according to the following equations : [1]

$$U(III) + H^{+} \rightarrow U(IV) + \tfrac{1}{2} H2$$
$$U(III) + 2H2O \rightarrow U(IV) + H2 + 2OH^{-}$$

Low U(III) concentration (mmole range) had been obtained by reduction of uranyl salt with zinc amalgam in acids [1-4] . The rate of oxidation increased with increasing concentration of zinc (II). A uranium (III) solution prepared by reduction of uranyl ions with amalgam was very unstable [1]. On the other hand, Sato A. reported that the stability of trivalent uranium in 0.5M HCl was fairly stable [4]. It had been observed that the rate of oxidation increases with the increasing of acid concentration [1].The oxidation of U (III) is strongly catalyzed by Cu (II), Pb (II) and less strongly by Ag (II) and Cd (II). [1-5] Trivalent actinides like U, Pu, Np , are extremely redox-sensitive against oxygen , therefore the stabilization of trivalent actinides in solution is a major task for performing experiments .[2]U(III)was also prepared by mercury cathode electrolysis [5]. Vertical mercury cathode cells were employed to prepare high concentration of U (III). [6]The aim of this work was to prepare higher concentration of U (III) with different concentration of hydrochloric acid using zinc amalgam as a reductant and studying the stability of U (III) at experimental conditions.

Experimental:

All of the chemicals used were analytical reagent grade and aqueous solutions were prepared using demineralized water and de-aerated by saturation with nitrogen gas (99.9999%).Ammonium diurinate was heated to 350°C to obtain UO3 .The UO2Cl2 stock solution was prepared by dissolving UO3 in hydrochloric acid solution.UO2Cl2 solutions in hydrochloric acid medium were triple purified with 30% tri-butyl phosphate (TBP) in odorless-kerosene to deduct impurities, then washed with kerosene to remove the organic residues, and concentrated by evaporation to about 2M UO2Cl2 concentration .

Preparation of liquid zinc amalgam:

About 15g of pure granular zinc were washed well with dilute sulfuric acid and heated on water bath for bout an hour with 300g of mercury in a small quantity of dilute sulfuric acid (1+10), The yield was cooled and stored in dilute sulfuric acid. The amalgam was washed thoroughly with water preusage, using a separating funnel. Hydrogen chloride gas was freshly prepared by dropping a concentrated hydrochloric acid solution from a separating funnel into a Buckner flask containing a concentrated sulfuric acid. The concentration of impurities in stock solution was measured by flameless atomic absorption (type shimadzo-AA 680).

Copper, nickel, chrome and iron metals were dissolved in hydrochloric acid solutions which were used as added impurities. Acid concentration was measured by titration with NaOH in presence of Kf.[7] Total uranium concentration was measured as described by Cherry, J. [8]

Preparation of trivalent uranium:

All experiments were carried out in an inert gas glove box. Figure 1. shows the apparatus utilized for preparation of trivalent uranium. The reduction of UO2Cl2 experiment was carried out in a 100ml volume test tube contained zinc amalgam, in which, ten milliters of UO2Cl2 (2-2.5M) in 1M HCl were pipetted and shaked vigorously by hand, the liberated hydrogen gas was released frequently, the color of solution changed into olive-green then to dark brown, the solution of U(III)was separated from zinc amalgam , this process lasted 30 minutes.

It was found that, a dark gray precipitate formed with residual zinc amalgam and the hydrochloric acid was consumed. One can conclude that this precipitate is a hydrolysis product of mercury and zinc; due to these phenomena we could not get a complete reduction of U(VI). To avoid this problem the experiment was run in a controlled acidic medium, the uranium solution was bubbled with hydrogen chloride gas during shaking with zinc amalgam .We have achieved more than 95% reduction of U(VI)) by running the experiment in this acid controlled medium. Unreduced U(IV) was extracted by 30% TBP in odorless- kerosene. The acidity of the prepared U(III) solution was adjusted by bubbling with hydrogen chloride gas. U (III) concentration was adjusted to 1.5M by diluting with the equivalent HCl concentration.

The measurements of U(III) were conducted using a spectrophotometer type shimadzo 230, in quartz cells of (2 and 10 mm)optical path . The cells were flashed with nitrogen gas and filled with U(III) solution then closed tightly with a para-film. Absorbance of U(III) was measured at the range 522-740 nm.

Results and discussion:

Table 1. Presents the concentrations of impurities in stock solution of uranium. Figure 2. Shows the spectra of U (III) and U (IV).Uranium (III) absorbs at 450, 520, 615 and 740 nm with extension coefficients 72, 120, 81, 37 respectively. While the bands located at 430, 495, 550, and 650 nm with lower extension coefficients are assigned for U. The extension coefficients of U(IV) in the absorption region of uranium (III), were calculated ,and it was found that they were less than 10% of the extension coefficient of the of U (III), except for the U(III) peaks of 520 and 740nm ,the extension coefficients of U (IV) were less than 1% . Accordingly, we used the optical densities of U (III) at these two maxima since the U(IV) absorption is almost negligible. Figure 3. shows the relation between lnCo/Ct and oxidation time of U(III) in different HCl concentrations (3 - 7 M) Where Co is the initial concentration of U(III) and Ct is the concentration of U (III) at time t, and T is the half oxidation time . This relation reveals the auto-oxidation of U (III) in different concentrations of hydrochloric acid, which proceeded reasonably to be a first order reaction.

Accordingly:

$C_t = C_o e^{-\lambda t}$

$C_o / C_t = e^{\lambda t}$

$\ln C_o/C_t = \lambda t$

$\lambda = \ln 2 / T$

The rate of oxidation of U (III) increased with increasing hydrochloric acid concentration which was due to chloro-complex formation of U(III) that is more reactive than the simple hydrated ions of U (III).

Table2.Shows the half oxidation time of U (III) at different hydrochloric acid concentrations, which reveals that the half time increases with decreasing hydrochloric acid

concentration .Figure 4. shows the relation between ln Co/Ct and the oxidation time of U (III) in 3M hydrochloric acid in the presence of 2 mmole of each impurity (Cu^{+1}, Cr^{+3} , Ni^{+2} ,Fe^{+2}). The rate of oxidation of U (III) was dramatically increased compared to the rate of oxidation in a pure system. One can conclude that the presence of these impurities in U (III) solution act as a catalyst to enhance the oxidation of U(III) since these impurities were added in a very small amounts compared to the U(III) concentration .

Table 3. Shows the half oxidation time of U(III) at 3M hydrochloric acid in presence of 2 mmole of each impurity (Cu^{+1}, Cr^{+3}, Ni^{+2} , Fe^{+2}).At high HCl concentration (7M), it was found that U(III) was extracted by 30%TBP in kerosene as a red bloody color which gave an absorption in the same U(III) region.

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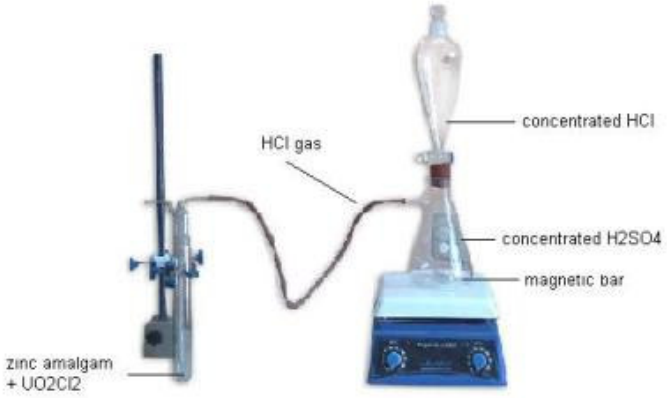

Figure 1. Apparatus for preparation of tivalent uranium

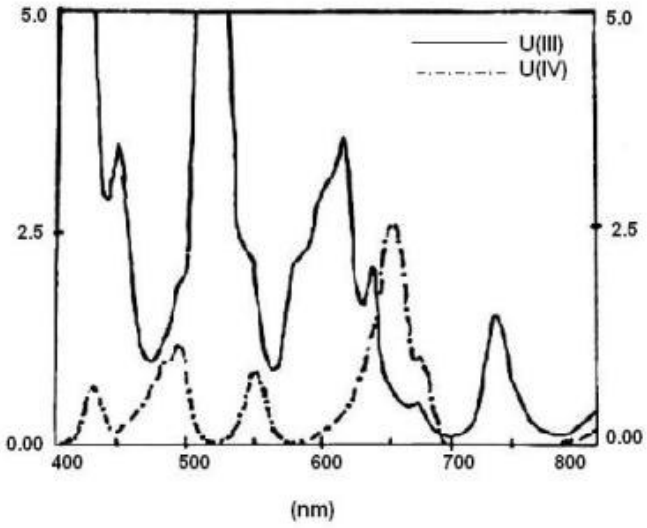

Figure 2. Specra of trivalent and tetravalent uranium

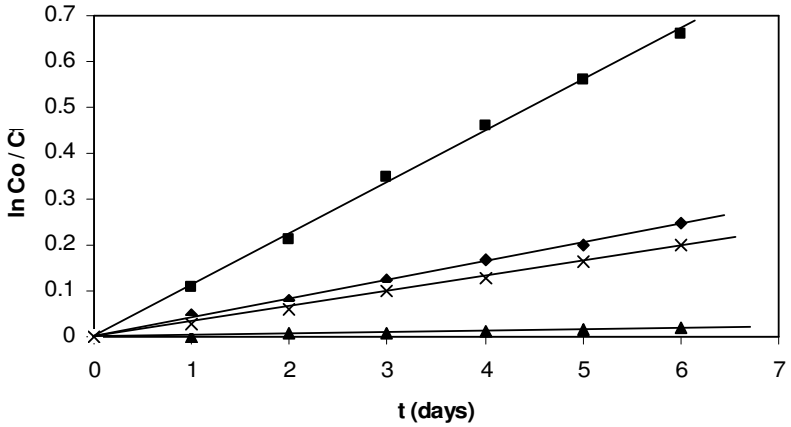

Fig.3.The relation between lnCo/Ct and oxidation time of U(III) in (▲3M , × 4M , ♦5 M and ■7 M) HCl

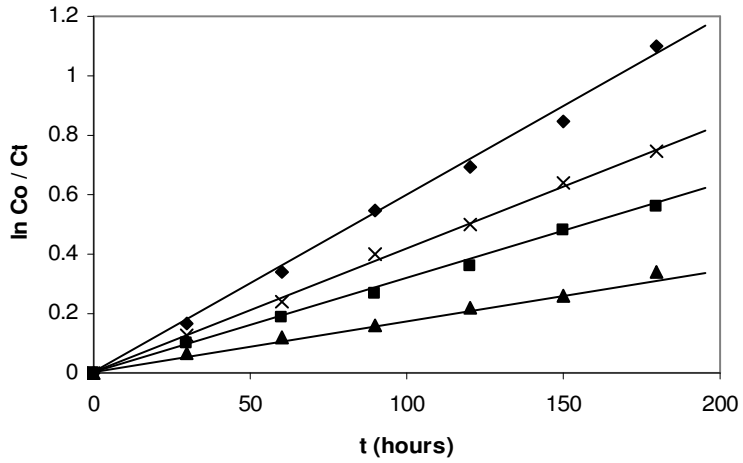

Fig.4 The relation between ln Co/Ct and the oxidation time of U(III) 3M HCl in presence of (2mmole) of each ion impurity (♦ Cu^{+1}, × Fe^{+2}, ■ Ni^{+2} and ▲Cr^{+3})

Table 1. Metal ion concentrations (ppm) measured in stock solution of UO2Cl2.

Metal Impurty	concentration (ppm)
Al	13.7
Co	0.04
Fe	11.5
Ti	0.7
Cr	0.07
Zr	0.8
Cu	0.03
V	0.4
Ca	0.007
Ba	0.12
Mn	0.02
Mo	0.12
Zn	0.01
Se	0.026

Table 2.Calculated half oxidation time of U(III) at different HCl concentrations, U(III)initial = 1.5M

[HCl] M	Calculated T½ (days)
3.0	211
4.0	20.6
5.0	17
7.0	6

Table 3. Calculated half oxidation time of U(III) in 3M HCl in the presence of 2mmole of each metal ion separately.

added metal ions	Calculated T1/2 (hours)
Cu^{+1}	2
Cr^{+3}	6.45
Ni^{+2}	3.73