Protonation Behaviour of 1:1 U(IV) EDTA Complex

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Summary: Protonation of 1:1 U(IV) EDTA complex has been studied in aqueous acidic solutions. The experimental results suggest that a state of equilibrium exists between the protonated and unprotonated forms of the complex in solutions below pH 3.0.

Introduction

Krot[1] and Martell[2] have reported the formation of 1:1 complex between U(IV) and EDTA in aqueous solution as described by the equation.

$$U(IV) + H_4EDTA \rightleftharpoons U(IV)\,EDTA + 4\,(H)^+$$

They have also identified the presence of various negatively charged species of the complex beyond pH 3.5, as hydrolysis products of the complex. In this work the behaviour of the complex below pH 3 has been examined.

Experimental

a) Materials

(i) *Preparation of U(IV) solution.* An aqueous U(IV) nitrate solution was obtained by reduction of B.D.H. supplied uranyl nitrate hexa hydrate, dissolved in 0.2M HCl. The uranyl solution was reduced in a 100 ml capacity sintered glass vessel by passing hydrogen at a rate of 400 cc per minute in the presence of platinised alumina as a catalyst. The reduction was complete in 25 minutes[3]. The resulting U(IV) solution was analysed for its U content (0.2M) by precipitation with ammonia, and subsequent ignition to U_3O_8 according to the method of Rodden and Warf[4]. The total uranium concentration thus obtained was compared with the U(IV) concentration determined by analysing the same solution by the method described by Sill and Peterson[5] This comparision showed that essentially all the uranium was present in U(IV) form.

(ii) *Ligand.* Concentrated HCl solution of A.R. disodium salt of EDTA (B.D.H.) was neutralized by ammonia to precipitate the pure anhydrous H_4EDTA solid.

(iii) *Complex* The greyish green 1:1 U(IV) EDTA complex was precipitated by mixing the stoichiometric amounts of the U(IV) and H_4EDTA. The complex was analysed for its U(IV) and C,H and N content. U(IV) analysis was performed by means of a volumetric titration with $K_2Cr_2O_7$ using barium salt of diphenylamine sulphonic acid as an indicator[6]. The other components were analysed by the microanalyst. The analytical results given below support the formula of the complex to be U(IV) EDTA $2H_2O$.

U(IV) EDTA $2H_2O$	%U(IV)	%C	%H	%N
Error	± 1.5	± 0.3	±0.3	±0.3
Calculated	41.01	20.7	3.13	4.82
Analysed	41.78	20.6	3.15	4.80

A definite quantity of the complex was then dissolved in a number of dilute perchloric acid solutions varying in pH (2-3.5), to give about 10^{-3}M solution of the complex. These solutions were then analysed for their U(IV) content by titrating them against standard ceric suphate solution[5] using ferroin as an indicator.

A 5ml sample of each of the solutions was pipetted out and forced through a cation exchange column under nitrogen pressure and the effluent along with washing was analysed for its U(IV) content by ceric sulphate titration as described earlier. Thus, it was possible to determine the percentage of the total U(IV) passing through the column at a particular pH. Another set of solutions of the complex having similar concentrations and pH, having 10^{-2}M sulphate ions added, was prepared and the percentage of U(IV) EDTA passing through the cation exchange column was estimated as before.

(iv) *Cation Exchange Resin* Cation exchange resin, 8% cross linked and less than 200 mesh (B.D.H. Ltd.) was used in the preparation of the columns.

b) pH Measurements

pH Measurements were performed in a 25ml cell under nitrogen atmosphere at a temperature of 20±.10°C. A digital pH meter, Radio meter type P.M. 52, was employed in all of the pH measurements.

Results & Discussion

1:1 U(IV) EDTA complex was investigated in aqueous acidic solutions having the complex concentration ranging between 1:1 to 1.6 x 10^{-3}M. The pH of these solutions was varied between the limits 2.07 to 3.1. These results are shown in Table 1. At pH 2.07; 70% of the complex solution was collected as an effluent following its passage through a cation exchange column under nitrogen pressure.

As the pH of the solution is increased the percentage of the U7(IV) EDTA content of effluent approaches the 100% mark at pH 2.84. These results suggest that below pH 2.84, an equilibrium exists between the protonated and unprotonated forms of the complex. 100% recovery of U(IV) EDTA in the form of effluent from all of the solution of the complex having sulphate ions added, at the similar pH values, indicates that the protonation ceases to exist in the presence of sulphate ions because the species U(IV) EDTA SO_4^{2-} is formed[7]. A closer look on the results of a previous study of Martell reveals that the idea of partial protonation of the complex in solution of pH below 2.84 is worth considering. As it is evident from Table 2, the pH values displayed in the figure 1 of the earlier publication, lie in between the pH values required for the protonated and the unprotonated species of the complex.

Table 1.

U(IV) EDTA (M) x 10^3	pH	Percentage of U(IV) EDTA Collected as effulent.	Percentage of U(IV) EDTA Collected in the Presence of Sulphate ions.
1.5	2.07	70	100
1.1	2.58	89	100
1.3	2.84	100	100
1.6	3.10	100	100

Table 2

	Hydrogen ion concentration for two liberated protons (M)	pH calculated for one free proton	pH calculated for two free protons	pH shown in figure of Ref 2
	$Na_2H_2Y + U(IV) \rightleftharpoons U(IV)Y + 2Na^+ + 2H^+$	$Na_2H_2Y + U(IV) \rightleftharpoons U(IV)H^+Y + 2Na^+ + H^+$	$Na_2H_2Y + U(IV) \rightleftharpoons U(IV)Y + 2Na^+ + 2H^+$	
Curve A	$7.5x2x10^{-4}$	3.12	2.82	2.9
Curve B	$2x2x10^{-4}$	2.69	2.39	2.5
Curve C	$2x5x10^{-3}$	2.3	2.00	2.16

References

1. N.N. Krot, N.P. Ermolaev and A.D. Gel'man, *Russ. J. Inorg. Chemistry*, 7, 1062 (1962).
2. C.H. Carey and A.E. Martell, *J. Amer. Chem. Soc.* **90**, 32 (1968).
3. I.I. Naqvi, Ph.D. Thesis University of Leeds (1974).
4. C.J. Rodden, *Analysis of Essential Nuclear Reactor Materials*, U.S. Atomic Energy Commission (1964).
5. C.W. Sill and H.E. Peterson, *Anal. Chem.*, **24**, 1175 (1952).
6. C.J. Rodden, *Analytical Chemistry of Manhatten Project*, McGraw Hill (1950).
7. D.L. Ehman and D.T. Sawyer, *Inorg. Chem.*, **9**, 204 (1970)