

## Detection of Hydroxo and Carbonato Species of Dioxouranium(VI) in Aqueous Media by Differential Pulse Polarography\*

L MAYA

Chemistry Division, Oak Ridge National Laboratory, P O Box X, Oak Ridge, Tenn. 37830, U.S.A.

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### Introduction

The study of the hydrolysis and carbonate complexation of the uranyl ion near the neutral pH range is hampered by the formation of solids. In the absence of carbonate the onset of solids formation occurs at about pH 4.5. The equilibrium uranium concentration at this pH is about  $10^{-3}$  M, but decreases by two orders of magnitude as a pH of 7.0 is approached and does not significantly increase at higher pH when the source of alkalinity is NaOH [1]. In the presence of carbonate, the uranium solubility is much higher in the alkaline range because soluble species such as  $\text{UO}_2(\text{CO}_3)_3^{4-}$  are formed, while at about neutral pH the solubility is dependent on the ionic strength of the medium. Low ionic strength favors higher solubility, but it is limited to  $10^{-2}$  M [2]. In spite of these difficulties a consistent set of stability constants has been obtained for the hydrolysis and carbonate complexation for both sides of neutral pH. That work was mainly performed by potentiometric titrations and has been critically evaluated by Langmuir [3]. The hydrolysis and carbonate complexation of the uranyl ion near the neutral pH range has been recently investigated [2].

One of the difficulties with speciation schemes for a complex system as derived by computer aided fits is the likelihood of introducing non-existing species or using a set of species when one can account for the data in a given range; therefore, additional physico-chemical means that identify a given set of species serve the useful purpose of further identifying a speciation scheme. In a recent study Toth and Begun [4] were able to correlate Raman spectra of uranyl ion solutions of different pH values with the anticipated hydrolytic species predicted by potentiometric means. Similarly, Raman spectroscopic observations of the carbonate system have allowed us to identify the presence of  $(\text{UO}_2)_2\text{CO}_3(\text{OH}_3^-)$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  [5]. In that study additional confor-

mation was obtained for the last two species by means of  $^{13}\text{C}$  NMR. The present study is an extension of that effort. In this case differential pulse polarography was chosen as a tool to derive complementary information for the system. This technique has the advantage of being highly sensitive, thus extending the limit of detection of uranyl species from  $10^{-2}$  M that can be observed by Raman spectroscopy, to  $10^{-6}$  M or even less. In addition to providing a qualitative means of observing a given species, information is also derived as to the electrochemical behavior of the species, which is also relevant information. This study is part of a wider effort aimed at understanding the behavior of uranium in natural waters.

### Experimental

Uranyl nitrate hexahydrate, Puratonic grade from Alfa Inorganics was used as a primary source of uranium. Sodium uranyl tricarbonate,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ , was prepared according to reference [6].

The instrumentation used included a Model 174A Polarographic Analyzer and a Model 303 Dropping Mercury Electrode both from Princeton Applied Research. Polarograms were obtained at room temperature (24 °C) using, unless otherwise stated, 0.1 M  $\text{NaNO}_3$  as supporting electrolyte and argon for purge and blanketing of the solutions. The electrochemical set-up consisted of a dropping mercury electrode as the working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl reference electrode, which was isolated from the system by a glass membrane. All the potentials given are referred to the saturated calomel electrode (SCE) by adding a correction of 19 mV. Titrations were conducted in the polarographic cell by the stepwise addition of either alkali or acid. After each addition and an 8 min period of bubbling a polarogram was obtained in the differential pulse mode. Under these conditions the typical polarographic waves appear as peaks. This format improves the resolution of superimposed waves.

### Results and Discussion

Preliminary titrations of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  with  $\text{HClO}_4$  and  $\text{UO}_2^{2+}$  with NaOH showed a complex set of peaks which grew or disappeared as the titrant addition progressed. Assignment of the peaks to an electrochemical process involving a definite species was possible by a combination of other physico-chemical tools such as the spectra of the solutions and the predicted composition based on the pH and

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the partial pressure of carbon dioxide in the system. This task was somewhat simplified by running independent polarograms of solutions particularly enriched in a given component.

The potentials for the U(VI)–U(V) reduction of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and  $\text{UO}_2^{2+}$  were established by running polarograms of the initial solution prior to the addition of titrant. All the potentials used to identify a given species refer to the U(VI)–U(V) reduction; that for  $\text{UO}_2^{2+}$  in acidic medium is  $-0.19$  V and closely corresponds to values reported in the literature [7]. Similarly, that for  $\text{UO}_2(\text{CO}_3)_3^{4-}$  takes place at  $-1.26$  V in bicarbonate media, also in agreement with observations reported in the literature [8]. Assignment of the potentials for intermediate species formed in the conversion of  $\text{UO}_2^{2+}$  into  $\text{UO}_2(\text{CO}_3)_3^{4-}$  or *vice versa* is discussed below.

#### Hydrolytic Species

Peaks corresponding to the hydrolytic species  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  were identified in the course of titrations in the absence of carbonate, although these species also form in conjunction with the carbonate species in the carbonate system. The species  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  became evident, at pH 5.35, by the presence of a relatively small peak at  $-0.24$  V. At this point most of the  $\text{UO}_2^{2+}$  had disappeared. On the other hand,  $(\text{UO}_2)_3(\text{OH})_5^+$  started to become evident at pH 4.40 by the presence of a peak at  $-0.53$  V. The intensity of the peak grew considerably in reaching pH 5.35 and by increasing the sensitivity of the instrument it was still evident at pH 6.21, in spite of the fact that most of the uranium had precipitated. These observations are consistent with the anticipated behavior of the system on the basis of the species distribution calculated for this pH range [9]. The presence of species with a higher  $\bar{n}$  number (hydroxyl ligand per uranium) such as  $(\text{UO}_2)_3(\text{OH})_7^-$ , proposed by Sutton [10] or  $(\text{UO}_2)_4(\text{OH})_7^+$  proposed by Sylva *et al.* [11] could not be detected, possibly because they are only minor species.

#### Carbonate Species

The species  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ , (dicarbonate) and  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$  (hem carbonate) were detected in the course of titrations of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  with  $\text{HClO}_4$ . The dicarbonate, recently shown to be a trimer [12], was observed only upon saturation with  $\text{CO}_2$  of partially neutralized solutions. The identity of the peak, observed at  $-0.43$  V, was confirmed by obtaining a polarogram of a solution enriched in this species. The presence of uranyl dicarbonate in this solution was established on the basis of the optical spectrum of this species [13]. This solution was made by the addition of four equivalents of NaOH to a uranyl nitrate solution maintained under 1 atm of  $\text{CO}_2$ . Similarly

the presence of hem carbonate as a peak  $-0.59$  V was observed during the neutralization of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  under relatively low partial pressures of  $\text{CO}_2$ . The interconversion of the species in the system as a function of  $\text{CO}_2$  pressure is illustrated by the polarograms in Fig. 1 and the spectra in Fig. 2. Polarogram A was obtained under argon and shows the presence of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  at  $-1.26$  V and an envelope made by the contribution of dicarbonate, hem carbonate and  $(\text{UO}_2)_3(\text{OH})_5^+$ , while polarogram B obtained under 1 atm  $\text{CO}_2$ , shows the contribution of dicarbonate and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ . The weak broad peak at  $-1.0$  V corresponds to the reduction of U(V) to U(IV) and U(IV) to U(III) which are unresolved under these conditions [7]. The spectra in Fig. 2 also reflect these changes. The enhancement of absorptivity (spectrum A under argon) is due to the presence of hem carbonate and the shift of the peaks at 452 and 439 nm, in B, to 449 and 437 nm in A, respectively is due to the formation of tricarbonate.

The observations in the case of the carbonate species are also consistent with the predictions made of the species distribution calculated for the pH and  $\text{P}_{\text{CO}_2}$  conditions examined.

The fact that the reduction potentials of all the described species differ, evidently reflects changes in complexation strength and possibly suggests that the fate of the reduced U(V) species might be the same for all. The fate of U(V) species obtained by the reduction of  $\text{UO}_2^{2+}$  and also  $\text{UO}_2(\text{CO}_3)_3^{4-}$  is known to involve rapid disproportionation to U(VI) and (IV) [7, 8]. Another expression of this phenomenon is the apparent correlation, although not linear, between the reduction potential of the different species and the  $\nu_1\text{UO}_2$  stretching frequency of each species. These values are given in Table I. The  $\nu_1\text{UO}_2$  frequency in turn shows a linear correlation with the number of ligands bound to the equatorial plane of the uranyl ion [5]. This last correlation indicates a weakening of the axial bonds as the number of ligands in the equatorial plane increases.

In their discussion of the molecular orbital scheme for the uranyl ion McGlynn *et al.* [14] suggest that the contribution of ligand to uranyl bonding involves the interaction of the ligand with the lowest unoccupied orbitals of the uranyl ion  $\phi_u$  and  $\delta_u$ . It appears that considerable electron density is transferred from the equatorial ligands into the uranium atom and that the bond strength to the axial oxygen atoms will decrease due to electrostatic repulsion with increasing bonding strength on the equatorial plane. This explains the Raman spectroscopy results mentioned above. Furthermore, McGlynn *et al.* [14] also discuss the effect of the formal addition of one electron into those orbitals as it occurs in going from  $\text{UO}_2^{2+}$  to  $\text{UO}_2^+$  and into similar orbitals for the other actinyl VI–V couples. Here again the net effect is weakening of the axial bond

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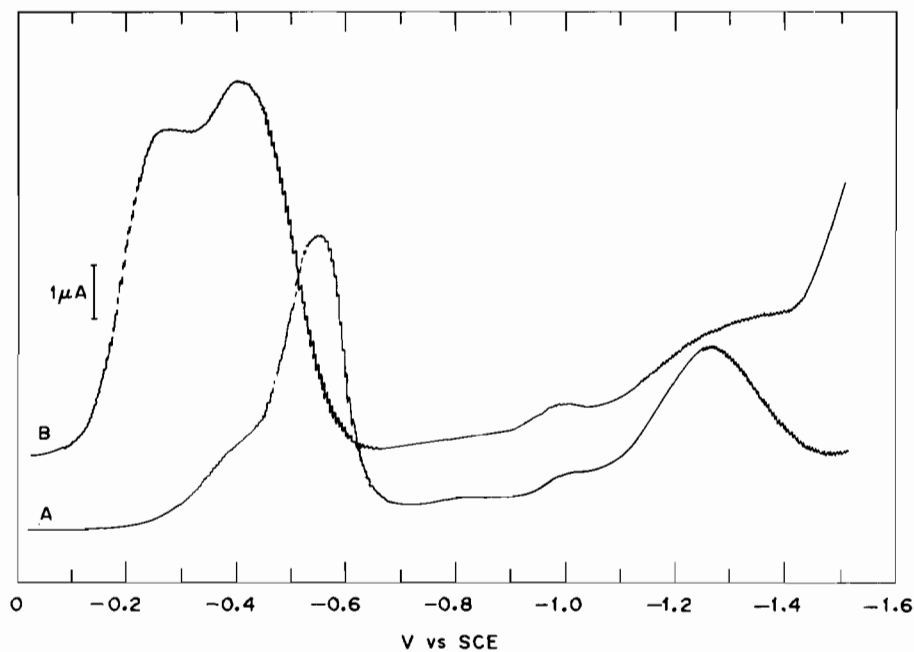


Fig. 1. Differential pulse polarograms partially neutralized  $\text{UO}_2(\text{NO}_3)_2$  solution  $10^{-3} M$  in  $0.1 M \text{NaNO}_3$ . (A) under argon, and (B) under  $\text{CO}_2$ .

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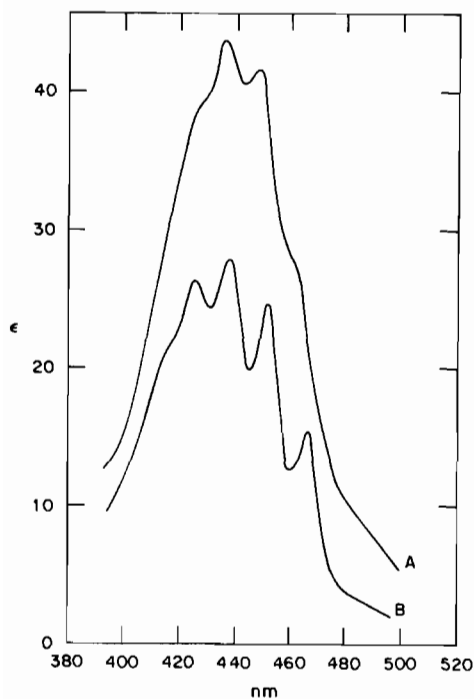


Fig. 2. Spectra of a uranyl dicarbonate solution  $10^{-2} M$ . (A) under argon, and (B) under  $\text{CO}_2$ .

TABLE I. U(VI)/U(V) Reduction Potentials and Symmetric Stretching Frequencies of Dioxouranium VI Species.

	$E^*$ (V)	$\nu_1$ Frequency ( $\text{cm}^{-1}$ )
$\text{UO}_2^{2+}$	-0.19	870
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	-0.24	851
$(\text{UO}_2)_3(\text{CO}_3)_6^+$	-0.43	834
$(\text{UO}_2)_3(\text{OH})_5^+$	-0.53	836
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$	-0.59	834
$\text{UO}_2(\text{CO}_3)_3^{4-}$	-1.26	810
$\text{UO}_2(\text{OH})_4^{2-}$	-0.995	785

\* Versus SCE.

In the case of the species studied in the present work, the effects of electronic density transfer from ligands into the uranium atom and the formal transfer of one electron in the reduction process are compounded, leading to destabilization of the resulting species.

A final experiment was performed after observing the apparent correlation between  $E$  and  $\nu_1\text{UO}_2$  for the species examined. The correlation suggested that

a quite negative potential would be observed for the species  $\text{UO}_2(\text{OH})_4^{2-}$  which has the relatively low  $\nu_1$  frequency of  $785\text{ cm}^{-1}$ . A polarogram of uranyl nitrate  $10^{-3}\text{ M}$  in  $1.0\text{ M}$  tetramethylammonium hydroxide showed a peak at  $-0.995\text{ V}$  indicating a breakdown of the correlation. In this case it was found that the process corresponded to a reversible one electron process. These results are in essential agreement with observations of the behavior of uranyl ion in  $\text{LiOH}$  [15]. Apparently in the highly alkaline solutions the reduced species does not decompose as in the case of all the other species discussed. The formation of a stable hydroxo complex of  $\text{U(V)}$  causes a shift of the reduction potential to a more positive value. A similar shift to a more positive value is observed [8] in the reduction of uranium(VI) in carbonate media ( $0.1\text{--}1.0\text{ M Na}_2\text{CO}_3$ ) which occurs at  $-0.95\text{ V}$ , apparently because of the formation of a stable  $\text{U(V)}$  species.

### Conclusions

The present work demonstrates the usefulness of differential pulse polarography in detecting a complex set of species in aqueous media. This information complements other physicochemical means in establishing the speciation scheme for  $\text{UO}_2^{2+}$ -hydroxo and carbonato complexes.

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