Potentiostatic Measurement of the Diffusion Coefficient of UO_2^{2+} in Carbonate Media

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(Received March 31, 1988)

For more than three decades, an international research program has been in progress to obtain the necessary chemical data for disposal of wastes from nuclear energy used in electric power production, defense, and energy research and development. An important aspect of this research is to understand the chemistry of actinides and other elements falling in the category of waste radionuclides in natural waters. One waste element of interest is uranium, since spent reactor fuel is largely comprised of uranium oxide. Uranium exists in its highest oxidation state in aqueous systems as the dioxouranium(VI), or uranyl ion, UO_2^{2+}, complexed with a variety of different anions. Extensive studies, for example, have been conducted on the chemistry of hydrolyzed uranyl salts precipitated from water [1]. Spectroscopic studies have been made on uranyl sulfates [2], and uranyl carbonate [3]. Additionally, detailed analytical research on the measurement of uranyl ion in aqueous solution has been reported [4, 5], and even discrete, air-stable uranyl hydrolysis dimers have been documented [6].

While much more experimental data are needed to obtain a truly complete picture of the aqueous solution chemistry of UO_2^{2+}, the work described here was limited to measurement of the diffusion coefficient of UO_2^{2+} in carbonate media. Previous research on the carbonate system [3, 7] has shown that the species in 1 M Na_2CO_3 is the tris(carbonato)dioxouranium(VI) ion, or $UO_2(CO_3)_3^{4-}$. In a saturated carbonate solution, the uranyl ion will achieve its maximum equatorial coordination number ('coordinatively saturated') by being surrounded by three bidentate carbonate ligands. Besides the value of the diffusion coefficient reported here, information has been reported previously concerning the reaction kinetics of the uranium(VI)–carbonate system in aqueous carbonate solutions [8].

Theory

The model used to measure the diffusion coefficient of UO_2^{2+} is based on an electrode reaction which is limited by the rate at which an electroactive substance diffuses to the electrode surface. The electrode reaction is formulated as a substance O being reduced by electron transfer at a conductive electrode surface such as mercury according to eqn. (1),

$$O + ne = R \tag{1}$$

where n = number of electrons, e, and R is the reduced form of O. At a spherical electrode, e.g., a mercury drop, Fick's law equation is written in the form of eqn. (2),

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right] \tag{2}$$

In eqn. (2), C = concentration of substance O (mol/l), D = diffusion coefficient of substance O (cm^2/s), assumed constant, t = time (s), and r = radial distance from the mercury drop surface (cm).

Initially, the concentration of substance O, UO_2^{2+}, in this work, is equal to that added to the solution, so that for

$$t = 0, r_0 < r < \infty : C = C^0 \tag{3}$$

where r_0 is the mercury drop electrode radius (cm) and C^0 is the concentration of electroactive substance (mol/l). On beginning the experiment, reaction (1) takes place, and the following boundary conditions apply for semi-infinite spherical diffusion:

$$t > 0, r \longrightarrow \infty : C \longrightarrow C^0 \tag{4}$$

$$t > 0, r = r_0 : C = 0 \tag{5}$$

$$t > 0, r = r_0 : \frac{D\partial C}{\partial r} = \frac{i}{nFA} \tag{6}$$

In eqn. (6), i is the faradaic current (μA), F is the faraday (96585.31 C/mol), and A is the electrode surface area (cm^2). Equation (4) assumes semi-infinite spherical diffusion; eqn. (5) specifies the electrode reaction takes place under conditions in which the applied potential is in the limiting current region, while eqn. (6) equates the material flux at the electrode surface to the faradaic current, i. When there are coupled kinetic reactions, an additional term such as kC is added to eqn. (2). In the absence of coupled homogeneous chemical reactions, the solution to eqn. (2), taking into account the initial and boundary conditions, is

$$i = \frac{nFAC^0D^{1/2}}{(\pi t)^{1/2}} + \frac{nFAC^0D}{r_0} \tag{7}$$

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0020-1693/88/$3.50

According to eqn. (7), a plot of *i versus* $t^{-1/2}$ yields a straight line with a slope of $nFAC^0D^{1/2}/\pi^{1/2}$ and an intercept at $t^{-1/2} = 0$ of $nFAC^0D/r_0$. The diffusion coefficient is then calculated from the slope, or less accurately, the intercept, with $n = 1$.

Experimental

The potentiostatic method, in which the faradaic current is monitored as a function of time under conditions of constant applied potential, was used to measure the diffusion coefficient in deaerated carbonate/bicarbonate solutions. A three electrode system was used in which a potential of −1.300 V was maintained between a stationary mercury drop working electrode and a saturated calomel reference electrode in an unstirred solution. Under these conditions, the electroreduction of UO_2^{2+} is diffusion-controlled when kinetic complications such as coupled chemical reactions are absent. Plots of the faradaic current *versus* $t^{-1/2}$ are linear, and the diffusion coefficient is calculated from the slope of the plot.

All chemicals were of analytical reagent grade and were used without further purification. The solutions were prepared by dissolving uranyl acetate dihydrate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, sodium carbonate and sodium bicarbonate in deionized water which had been distilled from an all quartz container. Before measurements were made, all solutions were deaerated by bubbling water saturated nitrogen into the solution through a fine glass frit for ten minutes. The equipment used was a Princeton Applied Research Model 173 potentiostat/galvanostat coupled with a PAR Model 276 interface. The Model 276 interface was bussed to a Hewlett-Packard Model 85 microcomputer which controlled the experiment and also stored the data. These data were digitized current–time or current–potential curves. Cyclic current–potential data were obtained by using the PAR Model 173/276 electrochemical system. These cyclic curves were important in obtaining qualitative information about the UO_2^{2+} system such as adsorption or other complicated behavior. Besides computer storage, analog recordings were made on a Moseley Model 2D-2 X-Y recorder.

The electrochemical cell was comprised of three electrodes: a three drop mercury (Hg) hanging working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was connected to the cell via a salt bridge containing supporting electrolyte. This bridge served to prevent KCl in the SCE from entering the cell. The potential was maintained automatically between the working and reference electrodes by the potentiostat. The cell assembly was immersed in a water bath which was maintained at 25.0 °C by a Fisher Model 173 circulator. The circulator was turned off during measurements. Triply distilled mercury was collected from a dropping mercury electrode onto a Teflon spoon and hung on the stationary electrode. During experiments, nitrogen gas was passed over the solution in the cell by raising the nitrogen bubbler out of the solution. Replicate results were obtained by using a fresh mercury electrode of constant surface area (0.07936 cm^2). The electrode area was calculated from the weight of 20 drops of mercury and the density of mercury.

A constant potential was applied by stepping from 0 to −1.300 V for thirty seconds during which current–time curves were recorded. Blank *i–t* curves were obtained to correct for background. A typical plot is shown in Fig. 1. The diffusion coefficient of UO_2^{2+} in carbonate media was calculated from plots such as shown in Fig. 2 and found to be $0.30 \pm 0.07 \times 10^{-5}$ cm^2/s in 0.1 M CO_3^{2-} and 0.1 M HCO_3^- buffer, pH = 9.8 at 25 ± 0.2 °C. This compares well with 0.36×10^{-5} cm^2/s measured at 22 °C in 1 M Na_2CO_3 by Casadio and Orlandini [7] using cyclic polarography.

Our cyclic stationary electrode polarograms indicate that the electroreduction of UO_2^{2+} in carbonate media is a complicated process in which sorption of a carbonate species can occur. Also, preliminary results indicate the electrode reaction is complicated by a coupled homogeneous chemical reaction in which UO_2^{2+} reacts with carbonate to

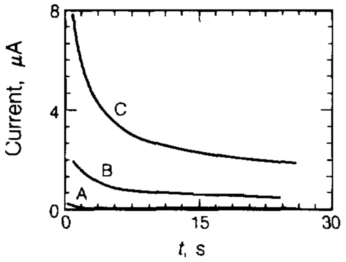

Fig. 1. Faradaic current *vs.* time for electroreduction of U(VI) to U(V) in 0.1 M $NaHCO_3$ and 0.1 M Na_2CO_3 solution; pH 9.8; Hg drop electrode (0.0794 cm^2 area). (A) Blank; (B) 0.0004995 M U(VI); (C) 0.002001 M U(VI).

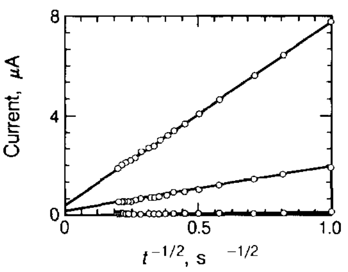

Fig. 2. Plots of faradaic current *vs.* $t^{-1/2}$ using data shown in Fig. 1. (A) Blank; (B) 0.0004995 M U(VI); (C) 0.002001 M U(VI).

form the electroactive species prior to the electron transfer step. Only one electrode reaction occurs, reduction of the U(VI)–carbonate species to a U(V) species [7, 9]. The stationary electrode polarograms also show that the U(VI)/U(V) couple is either non-Nernstian (irreversible electron transfer) [7] or complicated by a coupled, homogeneous chemical reaction which precedes the heterogeneous electrode reaction.

Electrochemistry of the Uranyl Ion in Carbonate Solution

Both cyclic current–potential and potentiostatic current–time curves were obtained for millimolar solution of UO_2^{2+} in carbonate solutions (0.01–1.0 M), in order to study the effect of increasing carbonate concentration. Cyclic stationary electrode polarograms obtained at the two lowest concentrations of carbonate, 0.01 and 0.02 M, showed a complex set of peaks at about −0.50 and −0.70 V *versus* SCE. These peaks appear typical of adsorption pre-waves; however, they could also be small concentrations of electroreducible uranyl carbonates. These small peaks are followed by a larger irreversible peak, just prior to hydrogen evolution. The peaks disappear with larger irreversible peak, just prior to hydrogen evolution. The peaks disappear with increasing carbonate concentration, and the larger, drawnout peak shifts to more positive potentials. The pH changed from 10.6 to 11.0, on addition of CO_3^{2-} (Table I). The data are tentatively interpreted in terms of an hydroxy U(VI) species which complexes with one or more CO_3^{2-} ligands [3] to produce one or more complexes which are more easily reduced than the U(VI) species present in OH^- solutions. However, reduction of the carbonate species is still kinetically complicated, because the anodic peak is far too positive for a Nernstian reaction (Fig. 3). Similar behavior was observed by Wester and Sullivan [9]. We conclude that U(VI)–carbonate in alkaline media is a stable species which is probably not easily reduced to a lower oxidation state in natural waters. From the curve in Fig. 3, one can estimate the standard potential of the U(VI)/U(V) couple in carbonate solution as $E^0 = -1.22$ V *versus* SCE, assuming Nernstian behavior. $E^0 = -0.98$ V *versus* NHE, the Gibbs energy of reaction, $\Delta_r G^0 = 94.56 \pm 0.2$ kJ/mol. Assuming that the UO_2^{2+} ion forms 1:3 complexes with carbonate ligands [3, 10], and using $\Delta_f G^0 [UO_2(CO_3)_3)^{4-}]$, the Gibbs energy of formation for the U(V)–carbonate species is calculated to be -2565.4 ± 10 kJ/mol, corrected to $I = 0$ using the Davies equation [10]. The electrochemical reaction is postulated to be

$$UO_2(CO_3)_3^{4-} + e^- \longrightarrow UO_2(CO_3)_3^{5-} \qquad (8)$$

and the electroactive U(VI)–carbonate species results from a coupled preceding chemical reaction such as

$$(UO_2)_2(OH)_2^{2+} + 6CO_3^{2-} \xrightarrow{k} 2UO_2(CO_3)_3^{4-} + 2OH^- \qquad (9)$$

where the hydrolysis dimer, $(UO_2)_2(OH)_2^{2+}$ [6, 10] is to be taken as representative of one or more hydrolysis products of UO_2^{2+} at pH 10–11. The quantity, k, is the rate constant for eqn. (9).

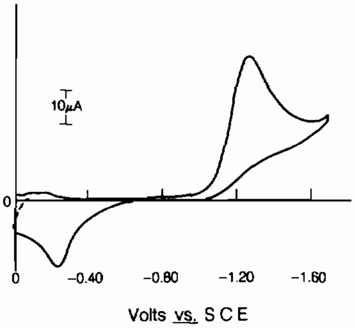

Fig. 3. Cyclic stationary electrode polarogram for 0.00200 M U(VI) in buffer of 0.1 M $NaHCO_3$, 0.1 M Na_2CO_3, pH 9.8. Scan rate is 340 mV/s.

TABLE I. Effect of Increasing Carbonate Concentration on Peak Potentials and Currents for 0.0010 M U(VI)

Concentration	pH	$E_p(c)^a$	$E_p(a)^b$	$i_p(c)^a$	$i_p(a)^b$
0.01	10.6	−1.70	−0.21	16.5	4.6
0.02	10.9	−1.60	−0.19	19.4	4.0
0.05	11.0	−1.43	−0.19	18.8	10.5
0.1	11.1	−1.33	−0.16	19.2	4.1
0.2	11.1	−1.26	−0.23	23.7	12.0
0.5	11.1	−1.17	−0.27	18.6	8.3
1.0	11.0	−1.12	−0.26	17.3	9.3

[a]Cathodic scan. [b]Anodic scan.

Acknowledgements

This work was supported by the Office of Basic Energy Sciences, Division of Geosciences, U.S. Department of Energy, under Contract No. DE-ACO3-76SF00098.

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