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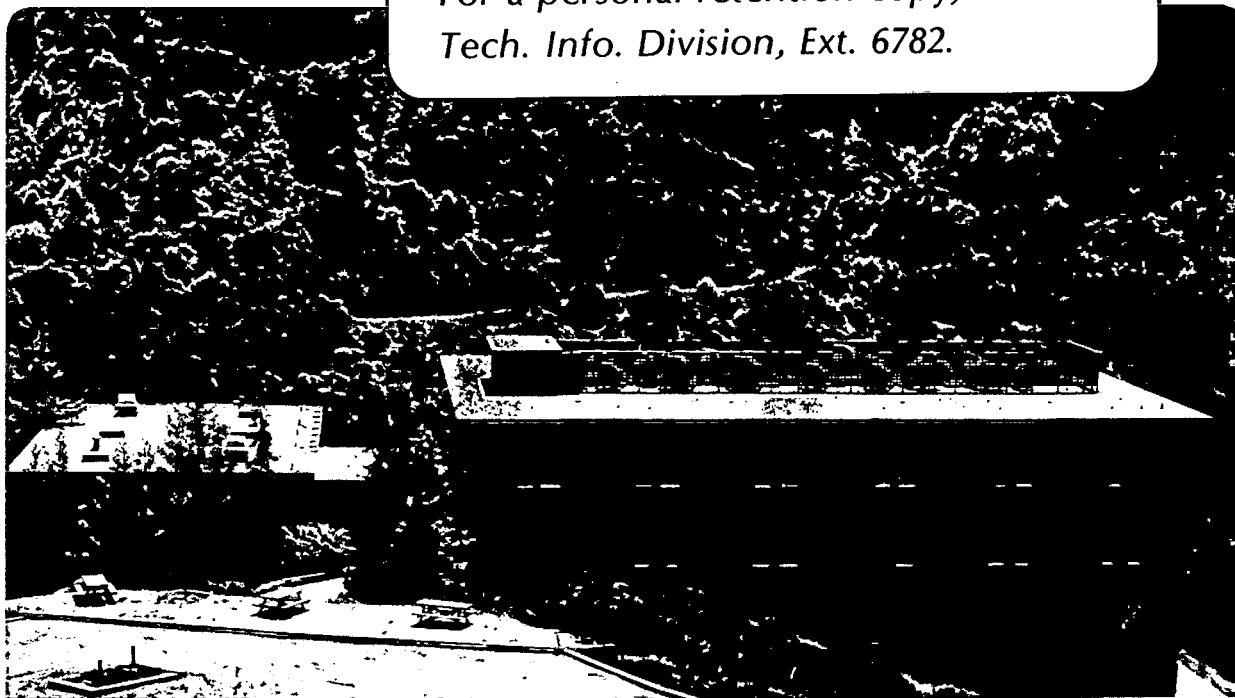
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FORMATION CONSTANTS FOR THE NpO_2^+ - CARBONATE SYSTEM

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Abstract

Formation constants for $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$ have been measured at $T = 294.2 \pm 0.5^\circ\text{K}$ and an ionic strength of 0.05 M (NaClO_4) by differential pulse voltammetry. The values of $\log \beta_1$ and $\log \beta_3$ are 5.9 ± 0.5 and 16.3 ± 0.5 , respectively.

This work was supported by the Assistant Secretary of Nuclear Energy, Office of Commercial Nuclear Waste Management, Commercial Waste Management Program Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Battelle Memorial Institute, Office of Nuclear Waste Isolation (ONWI), Columbus, Ohio under MPO No. E511-05100.

FORMATION CONSTANTS FOR THE NpO_2^+ - CARBONATE SYSTEM

Actinide materials represent a potential long term hazard in the storage of nuclear waste in a geologic repository. Although the NpO_2^+ ion is considered to be an important species in neutral neptunium solutions and carbonate is a common component found in groundwater, no formation constants have been unambiguously determined for this system.^(1,2) Wester and Sullivan⁽³⁾ have studied by electrochemical and spectroscopic methods the NpO_2^+ -bicarbonate system at high metal concentrations (2×10^{-3} M). Moskvina and Poznyakov⁽⁴⁾ have reported formation constants for NpO_2^+ -bicarbonate complexation at a pH of 8.5 by the coprecipitation method. They report the existence of the 1:1 and 1:2 complexes with stability constants of $\log \beta_{11} = 2.15$ and $\log \beta_{12} = 3.66$ respectively. Preliminary results of a differential pulse voltammetric study at glassy carbon electrodes and the measurement of the formation constants of $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$ are reported here.

Addition of NaHCO_3 at pH = 8.33 to 5.64×10^{-4} M Np(V) solutions in 0.05 M NaClO_4 supporting electrolyte resulted in significant potential shifts, but the formation of a white precipitate occurred after equilibrating several hours.⁽⁵⁾ At a neptunium concentration of 5.9×10^{-5} M no precipitation was observed under the same conditions. The peak potential shifted gradually towards more negative values as the NaHCO_3 concentration was increased. (Figure 1, $c_{\text{NaHCO}_3} = 0-3.38 \times 10^{-3}$ M). Two independent experiments were conducted with

both the electrochemical cell and the sodium bicarbonate solutions changed. Figure 1 shows Lingane plots where the triangles and octagons represent the values for the two different experiments with NpO_2^+ - concentrations of $5.86 \times 10^{-5} \text{ M}$ and $5.89 \times 10^{-5} \text{ M}$ respectively.

Linear least square regression fits (Figure 2) to the Lingane equation (Eq. 1)⁽⁶⁾

$$\Delta E_{1/2} = E_{1/2}^{\text{compl}} - E_{1/2}^{\text{free}} = - \frac{RT}{nF} p \ln[L] - \frac{RT}{nF} \ln \beta_p \quad (1)$$

gave the following results at $T = 294.15 \pm 0.5 \text{ K}$ and an ionic strength of 0.05 M (NaClO_4).

- 1) $\text{NpO}_2^+ + \text{CO}_3^{2-} = \text{NpO}_2\text{CO}_3^-$
 $\log \beta_{0.9 \pm 0.1} = 5.9 \pm 0.5$
 ligand number: $p = 0.9 \pm 0.1$

- 2) $\text{NpO}_2^+ + 3\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_3^{5-}$
 $\log \beta_{2.8 \pm 0.1} = 16.3 \pm 0.5$
 ligand number: $p = 2.8 \pm 0.1$

For practical reasons the high complexing ability of NpO_2^+ for carbonate ligands does not permit the use of excess ligand. Though this is required for the evaluation of Equation 1, a linear dependence for all concentrations of the potential shift vs. the

$\log (c_{\text{CO}_3^{2-}}/c_{\text{NpO}_2^+})$ was found indicating the relatively small excess of ligand in this system appears satisfactory for the above analysis.⁽⁷⁾

The experiments were conducted in bicarbonate solutions so it was unclear whether the complexes formed are carbonate or bicarbonate in nature. However, experiments conducted at a pH of 11.2 showed no shifts for the $\text{NpO}_2^+/\text{NpO}_2^{++}$ couple at total carbonate concentrations greater than 0.01 M, although the ratio of HCO_3^- to CO_3^{2-} changes from ~ 98 at a pH of 8.3 to 0.1 at 11.2. The potential remained constant at 0.252 V (Ag/AgCl) ($E_{1/2}^{\text{calc.}} = 0.49$ V vs. NHE). This value is in excellent agreement with the cyclic voltammetry results given by Wester and Sullivan⁽³⁾ ($E_p = 0.221$ V vs. SSCE, $E_{1/2}^{\text{calc.}} = 0.49$ V vs. NHE), who also did not observe any differences in electrochemical and spectroscopic studies of 1M NaHCO_3 and 1M NaCO_3 solutions. Furthermore, plots using the free HCO_3^- concentrations instead of free CO_3^{2-} would result in values for $\log \beta_1 = 4.7$ and $\log \beta_3 = 11.6$, which are strikingly different previously published data.⁽⁴⁾ Our experiments suggest that the predominant species for NpO_2^+ at a pH of 8.33 are the two carbonate species, $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$ which is in agreement with the data for UO_2^+ obtained by Grenthe and reported by Allard.⁽¹⁾

The large formation constant reported for the $\text{NpO}_2(\text{CO}_3)_3^{5-}$ species has important implications if one extrapolates to the UO_2^+ and PuO_2^+ ions. It suggests these species will also be stabilized by carbonate ion and possibly prevent in dilute solution the disproportionation reaction to the UO_2^{++} (PuO_2^{++}) and U^{4+} (Pu^{4+}) states.

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We wish to thank Professor S. Brown and Mr. J. Toman for advice and help with the experimental equipment and providing the computer programs for control and analysis.

This work was supported by the Assistant Secretary of Nuclear Energy, Office of Commercial Nuclear Waste Management, Commercial Waste Management Program Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Battelle Memorial Institute, Office of Nuclear Waste Isolation (ONWI), Columbus, Ohio, under MPO No. E511-05100.

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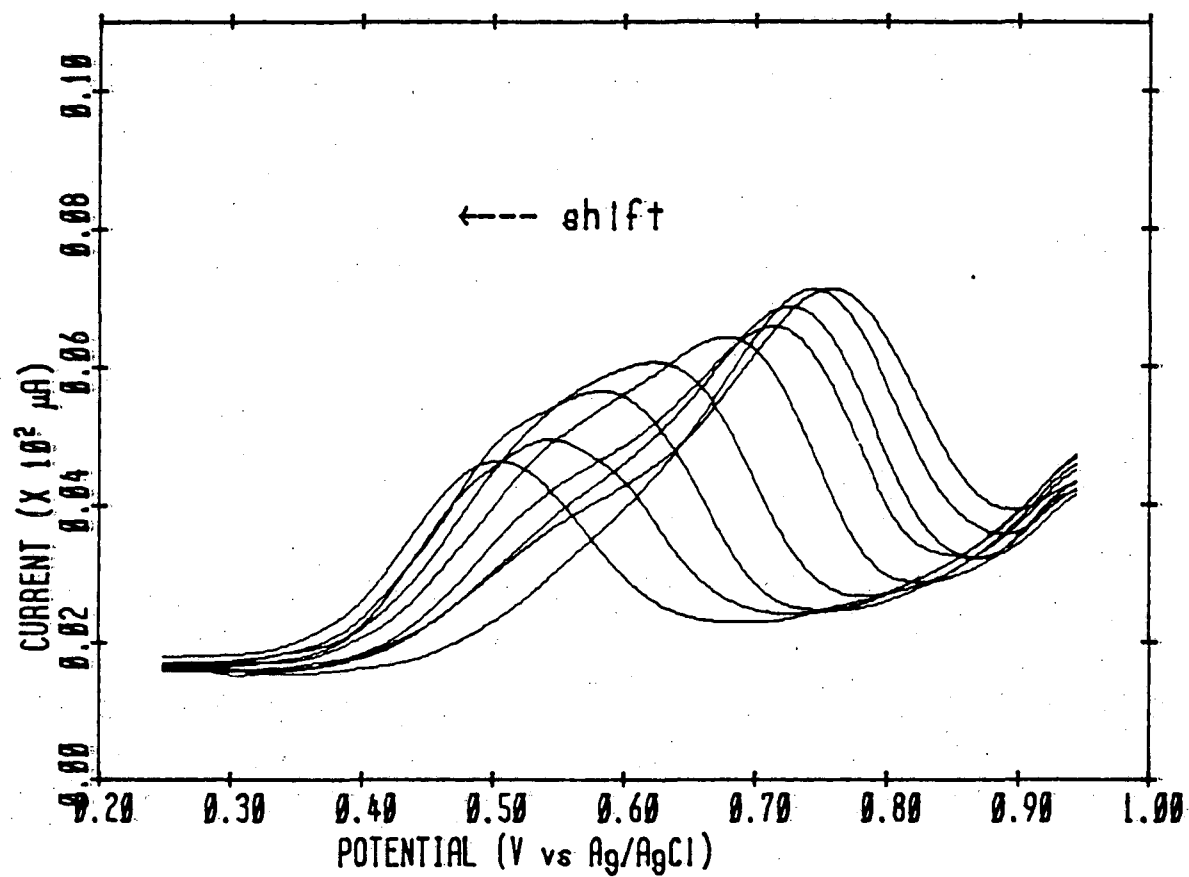
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Figure Captions

Figure 1. Shifts of the Differential Pulse Voltammograms of NpV/NpVI ($c = 5.86 \times 10^{-5}$ M) with Addition of NaHCO_3 ($c = 0-3.38 \times 10^{-3}$ M) at a pH 8.33 in 0.05 M NaClO_4 .

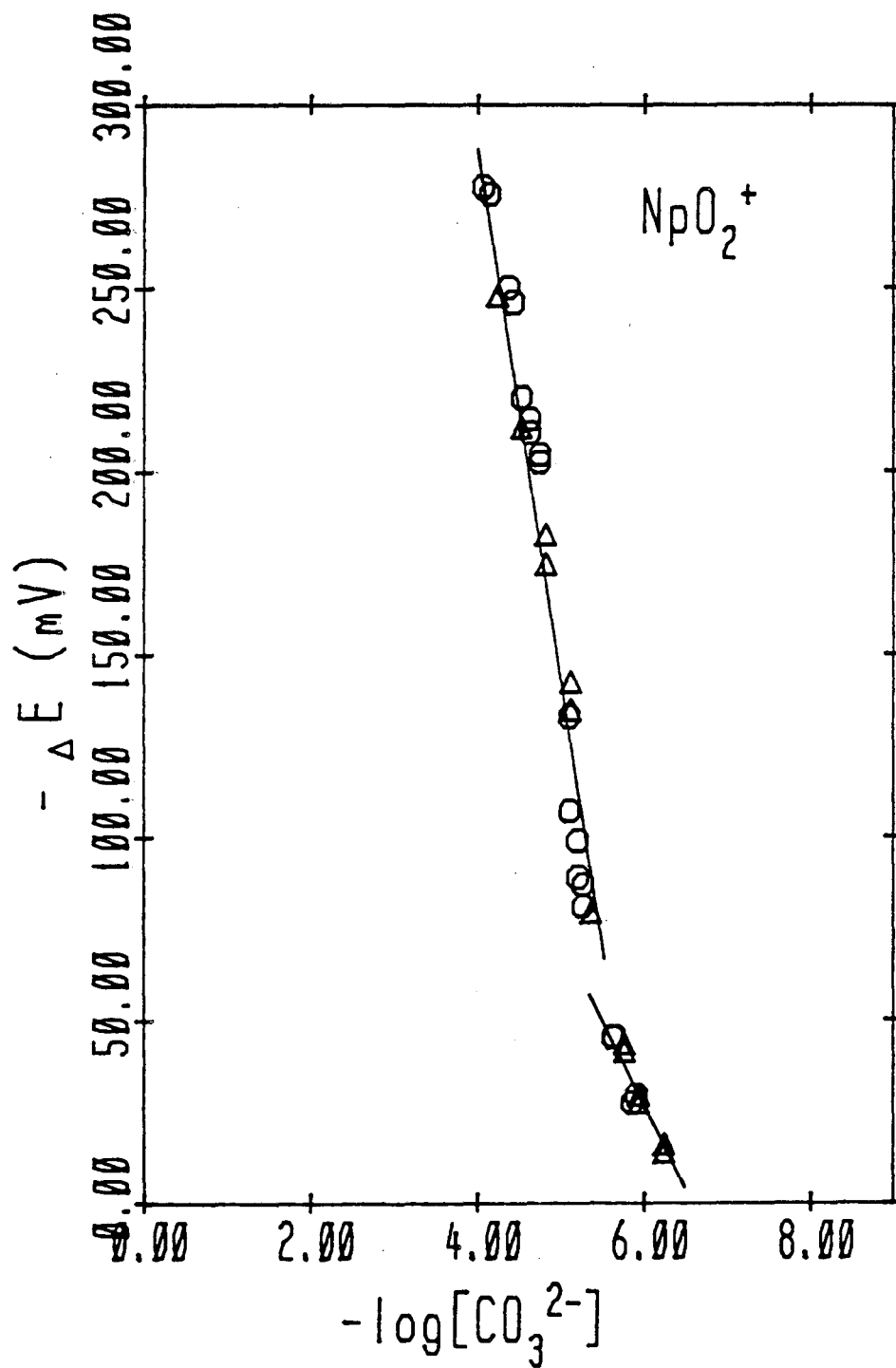
Figure 2. Peak Potential Shifts as a Function of the Free Carbonate Concentration.

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Figure 1



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Figure 2

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