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FORMATION CONSTANTS FOR THE NpO2+ -CARBONATE SYSTEM

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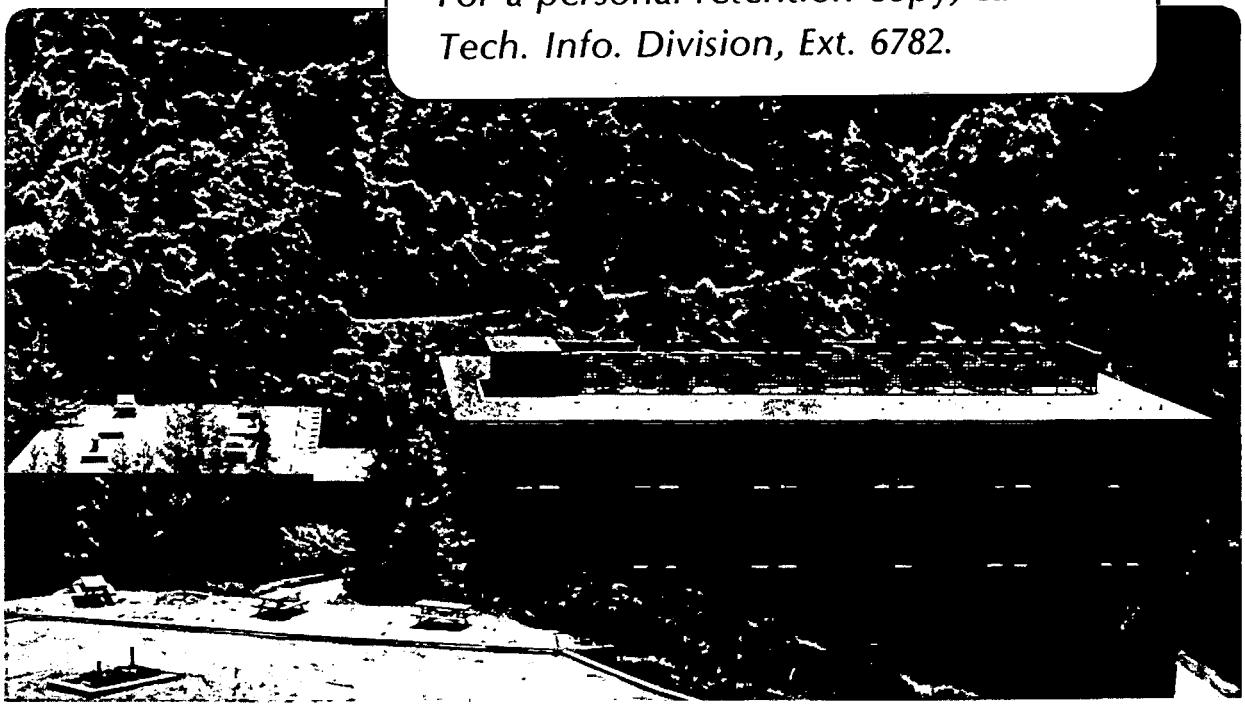

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FORMATION CONSTANTS FOR THE NpO_2^+ - CARBONATE SYSTEM

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Abstract

Formation constants for $NpO_2CO_3^-$ and $NpO_2(CO_3)_3^{5-}$ have been measured at T = 294.2 ± 0.5°K and an ionic strength of 0.05 M ($NaClO_4$) by differential pulse voltammetry. The values of log β_1 and log β_3 are 5.9 ± 0.5 and 16.3 ± 0.5, respectively.

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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). Moskvin 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 $NpO_2CO_3^-$ and $NpO_2(CO_3)_3^{5-}$ 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_{NaHCO_3} = $0\text{-}3.38\times10^{-3}$ 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 5.86×10^{-5} M and 5.89×10^{-5} M respectively.

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

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

gave the following results at T = 294.15 ± 0.5K and an ionic strength of 0.05 M ($NaClO_4$).

1) $NpO_2^+ + CO_3^{2-} = NpO_2CO_3^-$

$\log \beta_{0.9 \pm 0.1} = 5.9 \pm 0.5$

ligand number: $p = 0.9 \pm 0.1$

2) $NpO_2^+ + 3CO_3^{2-} = NpO_2(CO_3)_3^{5-}$

$\log \beta_{2.8 \pm 0.1} = 16.3 \pm 0.5$

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 ($c_{CO_3}{}^{2-}/c_{NpO_2}{}^{+}$) 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 $NpO_2{}^{+}/NpO_2{}^{++}$ couple at total carbonate concentrations greater than 0.01 M, although the ratio of $HCO_3{}^{-}$ to $CO_3{}^{2-}$ changes from $\sim$ 98 at a pH of 8.3 to 0.1 at 11.2. The potential remained constant at 0.252 V (Ag/AgCl) ($E_{1/2}^{calc.}$ = 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, $E_{1/2}^{calc.}$=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 β_1 = 4.7 and log β_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, $NpO_2CO_3{}^{-}$ and $NpO_2(CO_3)_3{}^{5-}$ 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 $NpO_2(CO_3)_3{}^{5-}$ 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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Figure Captions

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

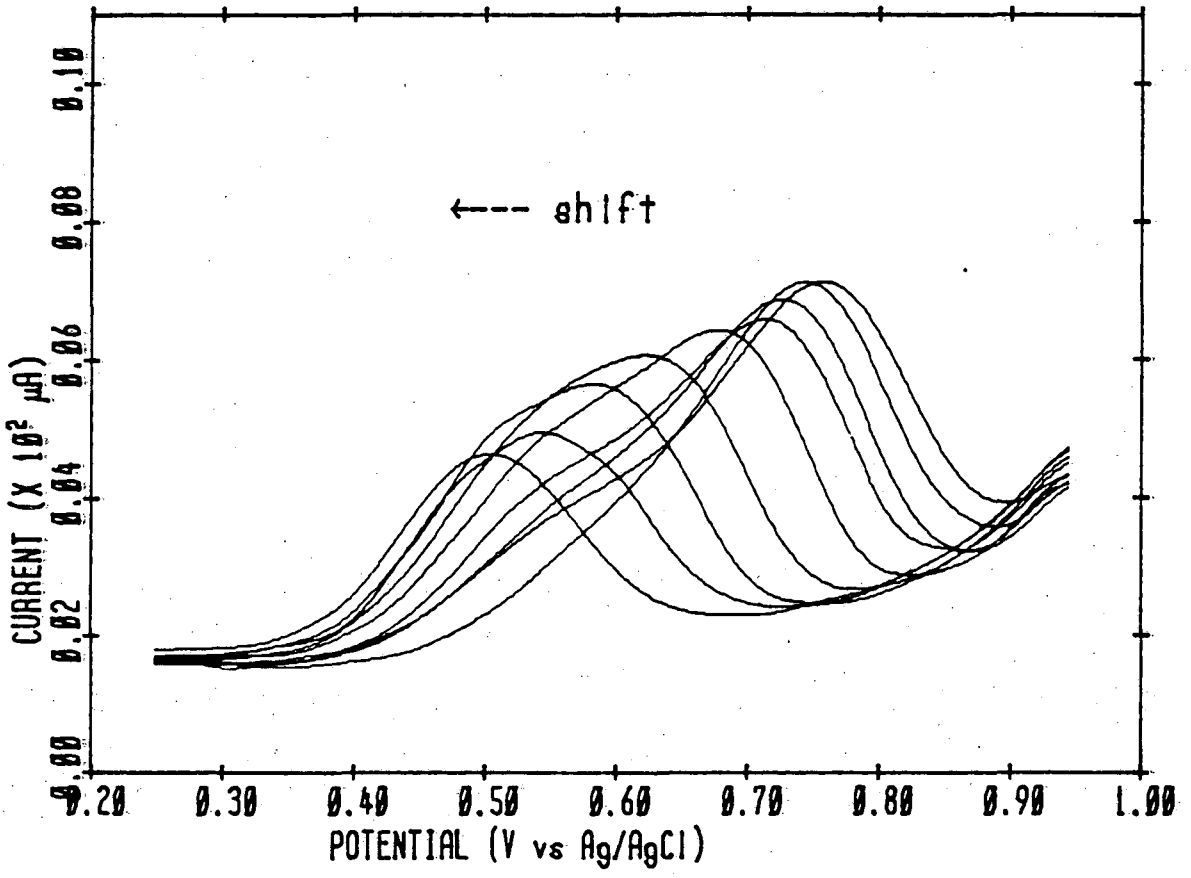

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Figure 1

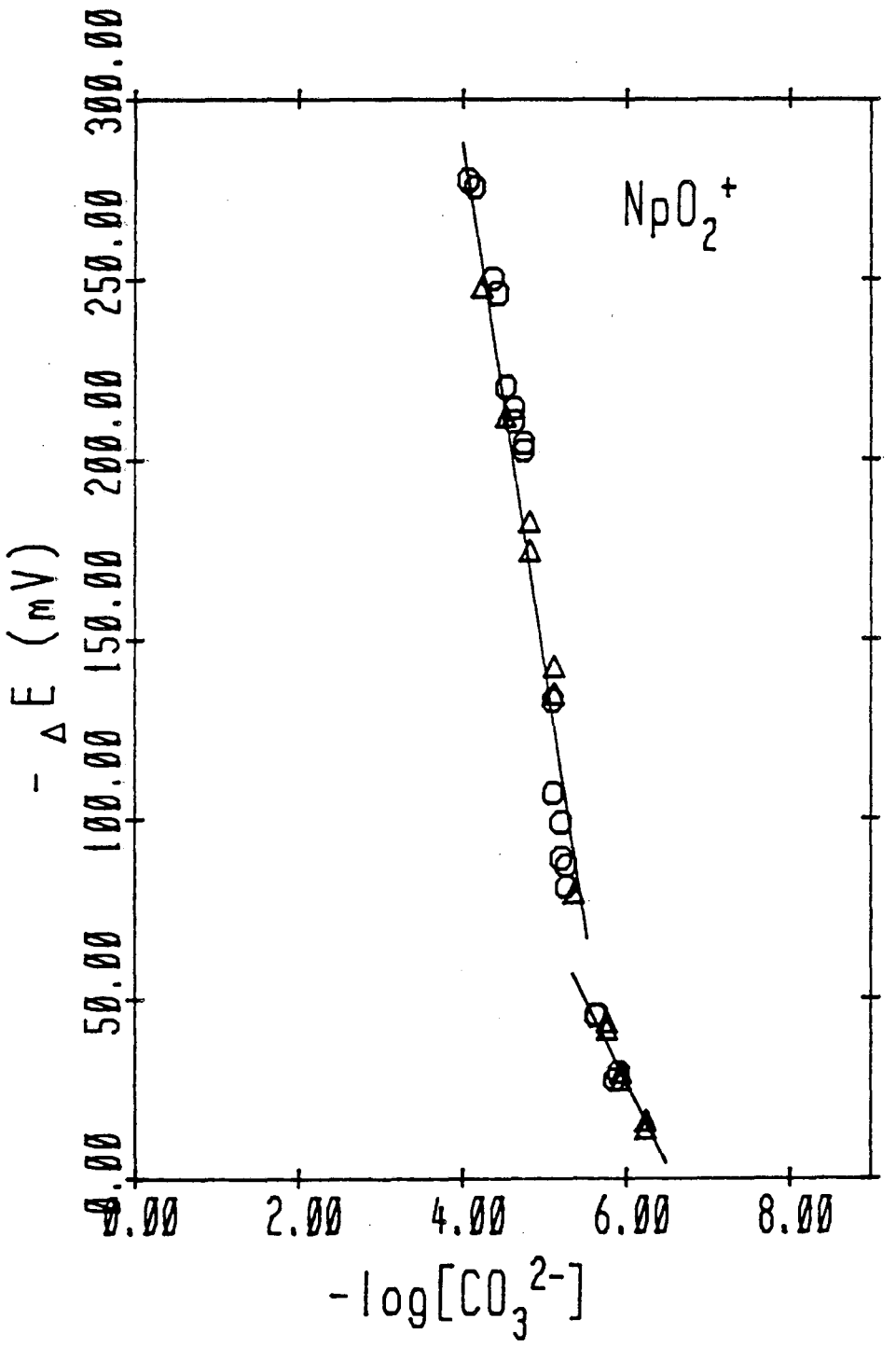

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Figure 2

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