

TEMPERATURE AND IONIC STRENGTH INFLUENCES ON ACTINIDE(VI)/(V) REDOX POTENTIALS FOR CARBONATE LIMITING COMPLEXES

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For waste disposal or environmental programs, actinide behaviour was studied in our laboratory, especially in two limiting aqueous solutions: acidic and carbonate ones where aqua ions and limiting complexes are formed. Cyclic voltametry technique was first validated with well-known U redox system. SIT was used to account for I influence and this also gave activity coefficient consistent with published data. Taylor's series expansions to the second order were used to account for T influence, and this methodology was validated on published mean activity coefficients of typically HCl and NaCl electrolytes. Redox potentials of actinide couples had previously been measured in non complexing media. The above data treatments give standard values for redox potential E° , for the corresponding entropy ΔS° , enthalpy ΔH° and heat capacity ΔC_p° changes, and also for the corresponding excess values (i.e. the variation of these thermodynamic constants with ionic strength).

This methodology was here used in carbonate media to measure the potential of the redox couple $\text{PuO}_2(\text{CO}_3)_3^{4-}/\text{PuO}_2(\text{CO}_3)_3^{5-}$ from 5 to 70°C and from I = 0.5 to 4.5 M in Na_2CO_3 , NaClO_4 media. Experimental details and full results are given for Pu. Only final results are given for Np. Previous and/or published data for U and Am are discussed. E and ΔS variations with T or I were enough to be measured. The values obtained for the fitted SIT coefficients $\Delta \epsilon$, and for ΔS and ΔC_p are similar for U, Np and Pu redox reactions. Using this analogy for Am missing data is discussed. $\beta_3^{\text{V}}/\beta_3^{\text{VI}}$ formation constant ratio of the carbonate limiting complexes were deduced from the potential shift from complexing to non complexing media for the Actinide(VI)/Actinide(V) redox couples. $\beta_3^{\text{V}}(\text{U}$ and $\text{Pu})$ and $\beta_3^{\text{VI}}(\text{Np})$ were finally proposed using published $\beta_3^{\text{VI}}(\text{U}$ and $\text{Pu})$ and $\beta_3^{\text{V}}(\text{Np})$. These data were then discussed and compared. For Am, this data treatment was rather used to discuss the $\text{AmO}_2^{2+}/\text{AmO}_2^+$ redox potential.