

Solubility Product of $\text{Pu}(\text{OH})_{4(\text{am})}$

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For the safety assessment of nuclear waste geological disposal, it is important to know how to calculate the plutonium solubility in reducing conditions. Published values of the solubility product of $\text{Pu}(\text{OH})_{4(\text{am})}$, vary by more than 10 orders of magnitude. It is shown in this paper, that Pu(IV) disproportionation, occurring in moderate acidic medium, can induce wide discrepancy in experimental determinations. Typically, the soluble plutonium species in equilibrium with the solid phase $\text{Pu}(\text{OH})_{4(\text{am})}$ is PuO_2^+ when pH is increased from 0 to 1 by titrating Pu^{4+} acidic solution with NaOH. Only two published works have taken into account this problem in their interpretation, but the extrapolation at the standard state rely only on one experimental value at one ionic strength.

In the present work, the chemical conditions have been chosen to reach a steady state between a Pu(IV) solid phase and PuO_2^{2+} , PuO_2^+ , Pu^{3+} aqueous species in a concentration range high enough to be directly and independently measured by UV/Visible spectrophotometry. The speciation was then controlled. The redox potential of the solution at equilibrium, E, was calculated from the measured $[\text{PuO}_2^{2+}]/[\text{PuO}_2^+]$ ratio and the known formal potential of this couple. $[\text{Pu}^{4+}]$ was then deduced from E, $[\text{Pu}^{3+}]$ and the known $\text{Pu}^{4+}/\text{Pu}^{3+}$ formal potential. In this way, $[\text{Pu}^{4+}]$ is determined without approximation even if side reactions (for instance hydrolysis) cannot be avoided. pH was measured and K_s was then obtained at different ionic strength from 0.1 to 3 M in sodium perchlorate solutions. The experimental values were extrapolated to the standard state ($I = 0$) using the specific interaction theory (S.I.T).