

ABSTRACT: The effects of simulated radiolytic degradation of tri-n-butylphosphate (TBP) on the chemical speciation of cerium were studied by spectrophotometry and electrochemistry of TBP solutions containing increasing amounts of di-n-butyl phosphoric acid (HDBP), a common degradation product of TBP. Tetravalent cerium was found to exchange coordinated nitrate for the dibutyl phosphate anion, forming dinuclear complexes of the formula $(\text{CeOCe})(\text{NO}_3)(6-d)(\text{DBP})_d \cdot 3\text{TBP}$ ($d = 0-3$). Compared to Ce(IV), Ce(III) was complexed less strongly by HDBP in TBP, but HDBP displaced both nitrate and TBP to form the series of mononuclear complexes $\text{Ce}(\text{NO}_3)(3-d)(\text{HDBP} \cdot \text{DBP})_d \cdot (3-d)\text{TBP}$ ($d = 0-3$). Dibutyl phosphate coordination caused large negative shifts in the Ce(IV/III) reduction potential in TBP, indicating a strong stabilization of the tetravalent state. Electrochemical investigation of the reduction of Ce(IV) in TBP revealed it to be a two-electron process in accordance with the dinuclear nature of the organic-phase Ce(IV) complexes. The diffusion coefficients of the $d = 0$ dinuclear Ce(IV)-nitrate-TBP complex and mononuclear Ce(III)-nitrate-TBP complex in TBP equilibrated with 7 M HNO_3 were determined to be $(1.16 \pm 0.06) \times 10^{-7} \text{ cm}^2/\text{s}$ and $(1.9 \pm 0.4) \times 10^{-7} \text{ cm}^2/\text{s}$, respectively, which also is consistent with the larger molecular volume of the dinuclear Ce(IV) complexes.