Electrochemical Characterisation of the Ce(IV) limiting carbonate complex

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The stoichiometry and the thermodynamic formation constant of the limiting complex of Ce(IV) were determined at 19.3 ± 1.0°C by using cyclic voltametry technique at a ha nging mercury drop working electrode in concentrated bicarbonate/carbonate medium. The Ce(IV/III) redox potential was measured at pH varying from 9.3 to 10.6 and $[CO_3^{2-}]$ varying from 1.0 to 1.5 M by performing a CO_3^{2-} titration with CO_2 gas. The ionic strength and junction potential effects were taken into account for the potentiometric calibrations and measurements. Quantitative interpretation of the variations of the formal potential $E_{IV/III}$ showed that no polymerisation took place during the redox reaction, and that two CO_3^{2-} ligands, but no OH^- ligand, were exchanged. As the accepted stoichiometry for the limiting complex of Ce(III) is $Ce(CO_3)_4^{5-}$, the Ce(IV) species is $Ce(CO_3)_6^{8-}$. In a 3.06 molal Na^+ carbonate/bicarbonate medium (Ionic strength = 4.33 mol.kg^{-1}), $E^0_{IV/III}$ = 0.161 ± 0.008 V/SHE (in molal units) was measured. This value, combined with the published $Ce(CO_3)_4^{4-}$ formation constant and the (re-evaluated) (Ce^{4+}/Ce^{3+}) standard potential, is used to calculate the $Ce(CO_3)_6^{8-}$ formation constant $\log_{10}(\beta_6^{IV})$ = 42.2± 0.5 (defined in molal concentration except for Ce^{4+} in activity : see table 1) in the same medium. The values of $E^0_{IV/III}$ and $\log_{10}(\beta_6^{IV})$ are ionic strength dependant, e.g. $E^0_{IV/III}$ = 0.182 ± 0.009 V/SHE and $\log_{10}(\beta_6^{IV})$ = 41.8 ± 0.5 in molar units in a 2.67 M $NaClO_4$ medium (Na^+ molality = molal ionic strength = 3.06 mol.kg^{-1}). The possible formation of $Ce(CO_3)_5^{6-}$ is discussed under the experimental conditions used, $\log_{10}(\beta_5^{IV}) \leq 41.8 \pm 0.5$ (in molal units).