

Relative stabilities of Ce(IV) and Ce(III) limiting carbonate complexes at 5 to 50°C in Na⁺ aqueous solutions, an electrochemical study.

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Abstract

The normal potential of the Ce(IV)/Ce(III) redox couple was determined by square wave voltammetry at different temperatures in solutions with a constant ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] \approx 10$ for high ionic strengths (3.29 mol.dm⁻³ at 4.39 mol.dm⁻³): $E_{\text{IV/III}}^{0'}$ varies from 259.5 to 198.0 mV/S.H.E. in the 15-50°C range. Linear variations were found for $E_{\text{IV/III}}^{0'}$ vs. $(RT/F)\ln(m_{\text{CO}_3^{2-}})$, leading to the stoichiometry, $\text{Ce}(\text{CO}_3)_6^{8-}$ for the Ce(IV) limiting complex. But, the slopes of these linear variations were actually found in the range 1.8-1.9, not exactly 2. This was interpreted as dissociation of the Ce(IV) limiting complex following the reaction: $\text{Ce}(\text{CO}_3)_5^{6-} + \text{CO}_3^{2-} \rightarrow \text{Ce}(\text{CO}_3)_6^{8-}$ and as dissociation of the Ce(III) limiting complex following the reaction: $\text{Ce}(\text{CO}_3)_3^{3-} + \text{CO}_3^{2-} \rightarrow \text{Ce}(\text{CO}_3)_4^{5-}$; for which maximum possible values of $\log_{10} K_{\text{IV},6}$ and $\log_{10} K_{\text{III},4}$ were estimated via fitting in the 15-50°C temperature range ($\log_{10} K_{\text{IV},6} = 0.42$ (0.97) and $\log_{10} K_{\text{III},4} = 0.88$ (7.00) at 15°C (50°C)). The normal potential was found to decrease linearly with T , these variations correspond to $T^0 \Delta_r S_{T^0} \approx -46 \text{ kJ.mol}^{-1}$, with $T^0 = 298.15 \text{ K}$ and $\Delta_r H_{T^0} \approx -70 \text{ kJ.mol}^{-1}$. The apparent diffusion coefficient of Ce(IV) was determined by direct current polarography, cyclic voltammetry and square wave voltammetry. It was found to depend on the ionic strength and to be proportional to T .

Keywords: cerium; carbonate complexes; square wave voltammetry; temperature dependence; thermodynamic constants.