

Role of Ionic Media in f–f Transitions, Stability, and the Structure of Ln(III) Coordination Compounds

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In this study, it was demonstrated that the composition of the ionic medium in solution may significantly influence not only the complex stability but also the spectroscopic properties of 4f electrons. The following reactions were investigated: $[\text{Er}(\text{EDTA})(\text{H}_2\text{O})_2]^- + \text{OH}^- \rightleftharpoons [\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^{2-} + \text{H}_2\text{O}$ and $[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^{2-} + \text{M}^+ \rightleftharpoons \text{M}[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^-$ (where $\text{M} = \text{Na}, \text{K}, [\text{C}(\text{NH}_2)_3]$ and $[\text{N}(\text{CH}_3)_4]$). To identify this effect, various physical methods were employed, including crystal X-ray diffraction, EDS, high-resolution UV–vis–NIR absorption spectroscopy, ^{89}Y NMR spectroscopy, potentiometry, osmometry, and ICP OES, as well as theoretical approaches such as Specific Ion Interaction Theory and York regression. Finally, it was shown that kosmotropic inorganic cations (Na^+ , K^+) stabilize hydroxy complexes more effectively than bulky chaotropic organic cations ($[\text{C}(\text{NH}_2)_3]^+$ and $[\text{N}(\text{CH}_3)_4]^+$). As a consequence, $\log\beta$ increased from 1.73 ± 0.23 (at zero ionic strength) to 3.5 ± 0.2 at $I = 4 \text{ mol}\cdot\text{kg}^{-1}$ in the presence of KCl. The potassium cations, for which the enthalpy of hydration is lower than that of Na^+ , more readily release water molecules from their nearest coordination sphere and, as a result, may interact more directly with the $[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^{2-}$ complex anion than the other cations under study, forming stable ion pairs of $\text{K}[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^-$. These in turn exhibit spectroscopic features different from those of $[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})]^{2-}$.

Słowa kluczowe

Ions, Anions, Cations, Ligands, Solution chemistry

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