Structural and thermodynamic aspects of water–carbonate exchange equilibrium for $M^{III/IV}$–EDTA–carbonate systems.

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Streszczenie

The results of a thermodynamic description of ternary M–EDTA–carbonate (where M = Er(III), Th(IV)) complex formation are presented. The crystal structures of the novel [C(NH2)3]3[Er(EDTA)(CO3)]·H2O (I) and [C(NH2)3]4[Th(EDTA)(CO3)2]·5H2O (II) compounds were determined. The structural and UV-vis-NIR spectroscopic results of crystal I served as the model data to analyze the stoichiometry and stability of the Er(III)–EDTA–carbonate system in aqueous solutions. The formation of the [Er(EDTA)(CO3)]3– complex in solution under different conditions was examined by complementary techniques including temperature dependent UV-vis-NIR and NMR spectroscopy as well as potentiometry. It was established that the affinity of the carbonate for the Er(III)–EDTA chelate is strongly pH dependent. Thus reaction (A) [Er(EDTA)(H2O)2]− + CO32– ⇄ [Er(EDTA)(CO3)]3– + 2H2O is more favoured at near neutral pH, while reaction (B) [Er(EDTA)(OH)(H2O)2]2– + CO32– ⇄ [Er(EDTA)(CO3)]3– + 2H2O + OH− occurs under more basic conditions. The log β values were found to be 3.66 ± 0.07 and 0.20 ± 0.12 for reactions (A) and (B), respectively. The temperature dependence of log β allowed the determination of the enthalpy and entropy changes of both reactions for the first time (ΔH(A) = −2.8 ± 0.8 kJ mol−1, ΔS(A) = 62 ± 3 J mol−1 K−1 and ΔH(B) = 28.1 ± 4.6 kJ mol−1, ΔS(B) = 92 ± 15 J mol−1 K−1). These data indicate that the carbonate anion more readily displaces H2O than the OH− ligand. The obtained results are important not only from the point of view of environmental lanthanide and actinide mobility, but also for designing MRI contrast agents