

Interaction of trivalent cations with MeAl₁₂ type Keggin-compounds

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We present data showing that trivalent lanthanide (Eu³⁺) and actinide (Cm³⁺) ions interact with highly charged cluster cations of ϵ -Keggin type, [AlO₄Al₁₂(OH)₂₄(OH₂)₁₂]⁷⁺, [GaO₄Al₁₂(OH)₂₄(OH₂)₁₂]⁷⁺, and [GeO₄Al₁₂(OH)₂₄(OH₂)₁₂]⁸⁺ (denoted MeAl₁₂, where M = Al, Ga, or Ge) in aqueous solution. Experiments were carried out mainly with time-resolved laser-induced fluorescence spectroscopy (TRLFS) in the pH range 4-7. In the relevant pH-range these polyoxometalates are known to be metastable over long periods of time in the absence of trivalent lanthanide or actinide cations. The results with curium(III) indicate that the formed species strongly resemble curium(III) surface complexes formed on the 001 face of corundum (alpha-Al₂O₃), gibbsite or other aluminium-oxy-hydroxides. The 001 face only exposes doubly coordinated oxygen atoms on its ideal, oxygen-terminated surface. Other faces of alpha-Al₂O₃ exposing singly coordinated sites result in structurally different curium(III) surface complexes [1]. While the 001 face of alpha-Al₂O₃ is negatively charged above pH 4, promoting the uptake and formation of surface complexes with trivalent lanthanide and actinide ions, the formation of analogous species with highly charged (+13) polyoxometalates was a priori unexpected. The interaction is supported by potentiometric titrations, which clearly indicate that the formed species can release more protons before being destabilized, as would be expected with the enhanced positive charge due to the interaction with Eu(III). Structurally the species is interpreted to correspond to binding of the trivalent cation to the six-rings of doubly coordinated (μ_2) aluminol groups, based on analogy to the respective alumina and gibbsite studies [2]. Long-term TRLFS studies involving samples containing Eu(III) indicate that the structure of such species and their concentration relative to the free aqueous Eu³⁺ ion remain stable over periods of months. It is concluded that small polyoxometalates may in principle serve as carriers of pollutants.

References:

[1] Th. Rabung, D. Schild, H. Geckeis, R. Klenze, and Th. Fanghänel, Cm(III) Sorption onto Sapphire (alpha-Al₂O₃) Single Crystals, *J. Phys. Chem. B* 2004, 108, 44, 17160-17165

[2] Kupcik, Tomas (2011) Wechselwirkung von dreiwertigen Lanthaniden und Actiniden mit Aluminiumoxiden und -hydroxiden, Ph.D. thesis, Heidelberg University, 2011.