

Rare Earth Element Complexes and Ligand Exchange in Solution

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The security of supply of the rare earth elements (REEs) has been identified as ‘critical’ [1]. Given their importance, new and sustainable extraction, processing and recycling methods for REEs must be identified. Since REEs can be mobilised and concentrated in hydrothermal fluids [2] and from easily leachable clays [3], fractionating REEs from solution offers a cheap way to increase their yield from deposits.

In the present study, density functional theory and classical force field molecular dynamics have been applied to investigate the solvation structure and mobility of Nd³⁺, Gd³⁺ and Er³⁺ in water. Ligand exchange reactions involving chloride and organic acids—known to accumulate REEs from solution [4]—were simulated using advanced sampling methods, and complex stability constants were calculated. Analysis of the free energy surfaces for these systems allows us to characterise mechanisms of ligand exchange.

Our results extend the catalogue of thermodynamic data on aqueous REE species and show that REE ion size is crucial for the type of ligand exchange mechanism. We further show that the presence of outer sphere chloride can affect both the mechanism and free energy change associated with ligand exchange. Combined, these simulations provide new information about REE complexation with resulting implications for REE processing.

[1] European Commission, Critical Raw Materials for the EU, EU Commission Enterprise and Industry Report (2010).

[2] C. H. Gammons *et al.* (1996), *Geochim. Cosmochim. Acta* **60**, 4615-4630.

[4] G. A. Moldoveanu and V. G. Pagangelakis (2013), *Hydrometallurgy*, **131-132**, 158-166.

[4] K. W. Goyne *et al.* (2010), *Chem. Geo.* **278**, 1-14.