

A spectrophotometric study of erbium hydrolysis in near-neutral to alkaline aqueous solutions using *m*-cresol purple from 35 to 75 °C

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Aqueous speciation strongly influences the fractionation, mobilization, and enrichment of the rare earth elements (REE) in natural systems. Important REE species include chloride, fluoride, sulfate, carbonate, and hydroxide complexes [1-3]. The stability of these complexes depends on pH and temperature. The hydrolysis of REE in near-neutral to alkaline solutions is however not well understood. To date, most geochemical modeling studies still use the predicted thermodynamic data extrapolated from low temperature experiments [4].

We present here new experimental results from UV-Vis spectrophotometric studies conducted from 35 to 75 °C to determine the hydrolysis constants of Er at pH of 6.0 to 9.5. The Er hydrolysis constants were determined using the *m*-cresol purple (mCP) method based on the study by Stepanchikova et al. [5] at 25 °C. We investigated the optical properties of mCP and derived a new set of dissociation constant allowing to extend the method to higher temperatures. With addition of variable Er concentrations, the mCP absorbance ratios of basic form (I^{2-}) at 578 nm and acidic form (HI^-) at 434 nm decreased due to proton release from the hydrolysis of Er: $Er^{3+} + nH_2O = Er(OH)_n^{3-n} + nH^+$. The pH measurements using UV-Vis permits deriving the hydrolysis constants of $Er(OH)^{2+}$, $Er(OH)_2^+$, $Er(OH)_3^0$, and $Er(OH)_4^-$. Our experimental results indicate that the average number of OH^- ligand coordinated to Er^{3+} increased from 2.0 to 3.0 at 75 °C instead of 1.5 to 2.5 at 35 °C over pH of 7.5 to 9.0. The measured speciation shows that predominance of $Er(OH)^{2+}$ at pH of 7.0 to 8.0 and $Er(OH)_4^-$ at pH above to 8.5, whereas predicted speciation by Haas et al. [4] results in predominance of $Er(OH)^{2+}$ over pH of 7.4 to 7.8 and $Er(OH)_4^-$ at pH above to 8.0. Furthermore, we observed an increase in $Er(OH)_3^0$ stability over the $Er(OH)^{2+}$ from 35 to 75 °C.

[1] Payne et al. (2023), *Chemical Geology* 617, 121256.

[2] Perry and Gysi (2018), *Geofluids*, 21-26.

[3] Migdisov et al. (2016), *Chemical Geology* 439, 13-42.

[4] Haas et al. (1995), *Geochim. Cosmochim. Acta* 59, 4329-4350.

[5] Stepanchikova and Biteikina (2011), *Russ. J. Coord. Chem.* 37, 64-71.

