

6.3 REE separation

A. Geist

The extraction of trivalent lanthanide ions by acidic organophosphorus extracting agents such as di(2-ethylhexyl)phosphoric acid (D2EHPA) is usually described by the following equilibrium, considering the dimerization of D2EHPA in non-polar diluents.



Applying a concentration-based equilibrium model, a slope of 3 is expected for plotting $\lg D_{\text{Ln}(\text{III})}$ over pH . However, slopes of approximately 3.5 are observed when extracting from HNO_3 . This discrepancy is caused by the ionic interaction between Ln^{3+} and NO_3^- . The Specific Ion Interaction Theory (SIT) [13] is one way to account for this interaction.

We have previously been using SIT based equilibrium models for describing solvent extraction systems used for actinide separations. Consequently, such a model was tested for the extraction of Eu(III) into D2EHPA. This model calculates equilibrium distribution ratios as a function of initial concentrations. Activities are used in the aqueous phase, concentrations are used in the organic phase. Ion interaction coefficients of $\alpha(\text{H}^+, \text{NO}_3^-) = 0.07$ and $\alpha(\text{Eu}^{3+}, \text{NO}_3^-) = 0.27$ and an extraction constant of $K = 1500$ are used.

Figure 4 compares experimental and calculated Eu(III) distribution ratios as a function of initial HNO_3 concentration. Excellent agreement is achieved throughout; the small deviations at 0.03 and 2 mol/L HNO_3 are due to experimental uncertainties frequently observed for distribution ratios below 0.001 or above 1000.

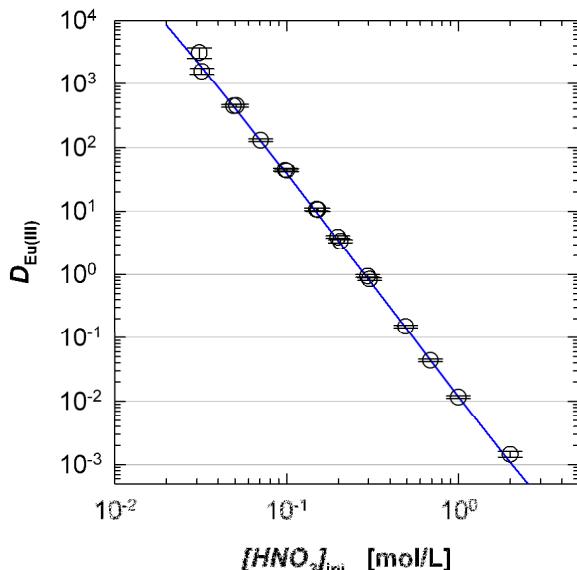


Fig. 4: Extraction of Eu(III) from HNO_3 into D2EHPA. Organic phase, 0.1 mol/L D2EHPA in kerosene. Aqueous phase, 2 kBq/mL $^{152}\text{Eu}(\text{II}) + 50 \text{ mg/L Eu}(\text{III})$ in HNO_3 . A/O = 1, T = 20 °C.

Again, SIT was shown to be useful for describing solvent extraction systems. Further experiments to validate the model under loading conditions (i.e. for metal ion concentrations that result in a significant consumption of the extracting agent) are foreseen.

References

- [1] Kolarik, Z.; Schuler, R.; Müllrich, U. EUR 16958, European Commission, Luxembourg: 1996.
- [2] www.sacess.eu
- [3] www.enviree.eu
- [4] Panak, P. J.; Geist, A., *Chem. Rev.* **2013**, *113* (2), 1199–1236.
- [5] Geist, A.; Müllrich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T., *Solvent Extr. Ion Exch.* **2012**, *30*, 433–444.
- [6] Ruff, C. M.; Müllrich, U.; Geist, A.; Panak, P. J., *Dalton Trans.* **2012**, *41*, 14594–14602.
- [7] Wilden, A.; Modolo, G.; Kaufholz, P.; Sadowski, F.; Lange, S.; Sypula, M.; Magnusson, D.; Müllrich, U.; Geist, A.; Bosbach, D., *Solvent Extr. Ion Exch.* **2015**, *33*, 91–108.
- [8] Carrott, M.; Bell, K.; Brown, J.; Geist, A.; Gregson, C.; Hérès, X.; Maher, C.; Malmbeck, R.; Mason, C.; Modolo, G.; Müllrich, U.; Sarsfield, M.; Wilden, A.; Taylor, R., *Solvent Extr. Ion Exch.* **2014**, *32*, 447–467.
- [9] Macerata, E.; Mossini, E.; Scaravaggi, S.; Mariani, M.; Mele, A.; Panzeri, W.; Boubals, N.; Berthon, L.; Charbonnel, M.-C.; Sansone, F.; Arduini, A.; Casnati, A., *J. Amer. Chem. Soc.* **2016**, *138* (23), 7232–7235.
- [10] Wagner, C.; Mossini, E.; Macerata, E.; Mariani, M.; Arduini, A.; Casnati, A.; Geist, A.; Panak, P. J., *Inorg. Chem.* **2017**, *56* (4), 2135–2144.
- [11] Wagner, C.; Müllrich, U.; Geist, A.; Panak, P. J., *Solvent Extr. Ion Exch.* **2016**, *34* (2), 103–113.
- [12] Wagner, C.; Müllrich, U.; Geist, A.; Panak, P. J., *Dalton Trans.* **2015**, *44* (39), 17143–17151.
- [13] Ciavatta, L., *Ann. Chim. (Rome)* **1980**, *70*, 551–562.