A high throughput method to determine the selectivity of ion phase transfer in multi-component chemical systems: towards predictive modelling of extraction

J. Theisen[1], J. Rey[1], C. Penisson[1], J. Duhamet[2], O. Diat[1], S.Pellet-Rostaing[1], J.-F.Dufrêche[1], D. Meyer[1], A.Stocco[4], H. Möhwald*[1,3], J.-C. P. Gabriel[3], T. Zemb[1]

[1]Institut de Chimie Séparative de Marcoule 30207 Bagnols-sur-Cèze Cedex, France
[2]CEA, DEN, DTEC, F-30207 Bagnols-sur-Cèze, France
[3]Max-Planck-Institute of Colloids and Interfaces Am Muehlenberg 1, 14476 Potsdam, Germany
[4]Laboratoire Charles Coulomb (L2C), UMR 5221 CNRS-Univ. Montpellier , Montpellier F-34095, France.

*moehwald@mpikg.mpg.de

Liquid-liquid extraction is a crucial process for recycling chemistry. In order to reuse and to avoid mining of rare earths, recycling has often to be performed by separating and purifying the rare earths from iron. This known technology relies on ion equilibria in coexisting phases located between binodal tie-lines in the Winsor II regime of a microemulsion with excess brine. Since the systems contain ten components, the phase diagram in seven dimensions must be projected in tetrahedrons. The selectivity and differences of free energy of transfer can be determined with good reliability and with reasonable time: days instead of months needed by batch methods. Availability of data with variable composition allows to challenge the very few predictive models based on first principles and evaluating the free energy of transfer terms. We show here first results obtained with a microfluidic device allowing continuous exploration of lines in a complex phase diagram. We model the ion and extractant distribution and separation, and compare to expected values from available theories. In special we show that selective ion complexation at an oil/ water interface can be quantified by measuring time and concentrated phase transfer of the ions. This allows to measure free energies of transfer , than can be compared with theories developed for different length scales. With iron as reference selectivities of 2 orders of magnitude can be achieved. The selectivity changes with ion size, pH, and especially surprising is the finding of a strongly temperature dependent selectivity. This is discussed as due to a subtle interplay between entropic and enthalpic contributions, as expected for free energies of transfer with values of only a few kT. The time dependence of phase transfer can be modelled with reasonable assumptions of diffusion coefficients and geometrical parameters of membrane and microfluidic device as shown in the figure . To further speed up the interfacial transfer the application of ultrasound is investigated. By optical measurements it can thus be shown, that this way the interfacial roughness can be increased up to 100 nm, which is expected to strongly enhance phase transfer.

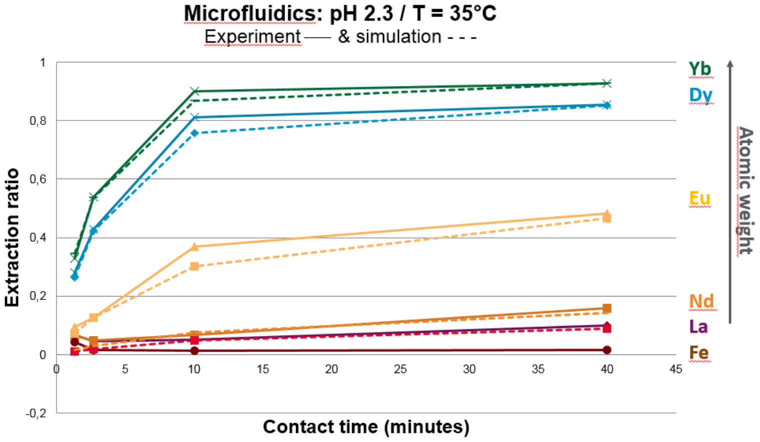

Figure 1: Fraction of ions in oil phase compared to aqueous phase for different rare earth ions versus contact time, comparing measurements and simulation.

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