# Characterization of a metal-extracting water-poor microemulsion
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Key technologies towards an environmentally benign economy, such as renewable energy from wind power plants, e-mobility and digitalism have had great success in recent years. One concerning problematic however is that these novel technologies base on the so called rare-earth elements, which up to date are not able to be recycled from electronic waste. Hence, these environmentally friendly inventions are based on a non-renewable resource. As a consequence, the project REE-Cycle has been brought to life, financed by the European Research Council (ERC) in order to challenge scientific problems around the recycling of these elements on a fundamental level.

In order to separate rare earths from undesired by-products, a separation method is required that is selective, adaptive and predictive. Thus, the method of choice in the frame of the ERC-project, is *solvent extraction*: two immiscible liquids (like oil and water) are brought together and properly tuning the conditions allows to transfer a target species from the water phase to the oil phase, as depicted in figure 1. This method is already widely applied in industry to retrieve rare earth elements from raw ores, however application for electronic waste is yet out of grasp. The global aim of the ERC-project is to understand fundamental processes on a molecular level, establish physico-chemical laws and provide novel approaches in order to make recycling of rare earths on an industrial scale economically and ecologically possible.
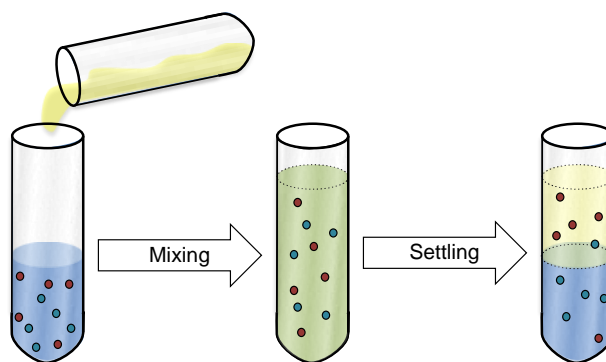
Figure 1 – *Schematic representation of a solvent extraction procedure. Two metal species (red and blue) are solubilized in an aqueous phase. After addition of a formulated organic phase, mixing and settling, a distribution of the two species between the two phases is achieved (red prefers to solubilize in the organic phase, while the blue species stays in the aqueous phase).*

This PhD targets to resolve fundamental questions in solvent extraction of metals, using the so-called *colloidal approach*. Extracting a metal (a very polar entity, normally only soluble in water) into an organic environment is achieved by adding extractant molecules, which form a complex around the metal, thus allowing the solubilisation of the metal into the organic phase. The colloidal approach considers that the driving forces for complex formation is not only the coordination of the metal by the extractant, but also self-assembling properties (as known from surfactant molecules). Thus, the complex is also referred to as *reverse micellar solution* and the solvent extraction system is referred to as a *microemulsion*. This colloidal approach has had great success describing and predicting the extraction properties of extractant molecules, not restricted to the rare earth elements, but every metal species of the

periodic table. Yet, the possibilities to exploit experimental techniques from the colloidal science are by far not at the end, which is the core aspect of this work.

Solvent extraction systems are complex multi-component systems, where the water-phase consists of water, metals in form of salts, acid to solubilize the salts and potentially modifiers. The oil phase consists of an organic solvent, one or several extractant molecules as well as modifiers to adjust the physical properties of the phase, i.e. density and viscosity. A solvent extraction procedure, as demonstrated in figure 1 ought to possess a high selectivity (only the desired target should be transferred into the organic phase), further the transfer should be very fast and the phase separation after contacting the two phases should be fast. However, one of the biggest concerns in solvent extraction is the formation of stable emulsions or even worse, the formation of a third phase: the splitting of the organic phase. The origin of these undesired phases have been postulated in the frame of the colloidal approach, however prediction at which composition the system will enter such an undesired phase has not yet been in the focus of scientific investigations.

In order to solve this fundamental problem, this PhD has been separated into two parts: the first part is interested in a mapping of the phase behaviour, i.e. determining where a solvent extraction system is monophasic, biphasic (as desired), triphasic or forms a stable emulsion. After classification of the different phases as a function of the system's composition, the second objective is to use conductivity, as easy and versatile experimental tool to indicate when a phase transition occurs and what conductivity profile is to be expected in a well functioning extraction.

From an experimental point of view, the multicomponent system is reduced to its four essential components: water, an organic diluent, an extractant and an extractant engaged in complexation of a metal. As extractant, the molecule bis-(2-ethylhexyl)phosphoric acid (*HDEHP*) is used, as it is commercially available and also highly used in industrial applications. The sodium salt *NaDEHP* represents the extractant complexing a metal-cation. The ratio of the two forms of the extractant can be expressed as the *counter-ion ratio Z* between the proton H and the sodium Na. The phase behaviour has been intensively studied in form of *ternary phase diagrams* and as a function of this counter-ion ratio. The resulting prism is depicted in figure 2 with toluene as a "reference solvent".
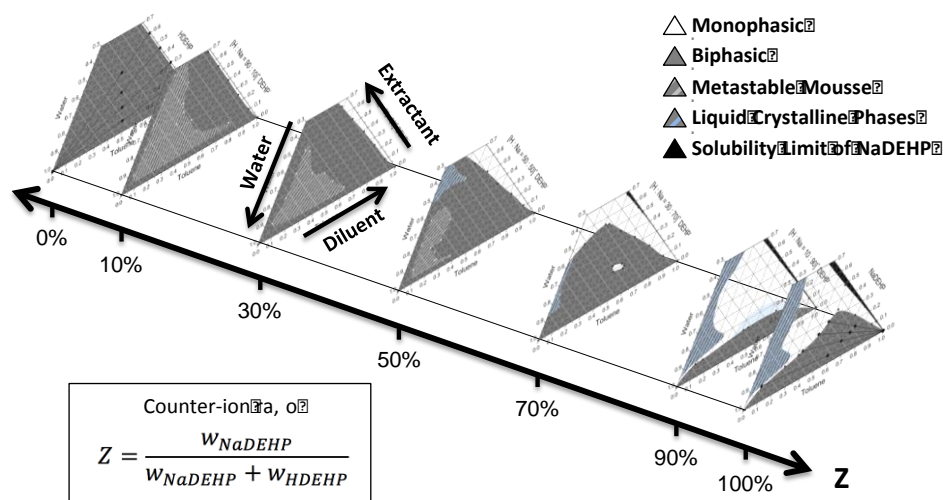
Figure 2 – *First fully developed quaternary phase prism for a solvent extraction system, showing the evolution of the phase behaviour as a function of the counter-ion ratio Z. At 0%, the extractant is fully protonated, at 100% it is fully in the form of a sodium salt. The legend indicates if the system is monophasic, multiphasic or exhibits liquid-crystalline states of matter.*

We wisely chose this "prism-representation", as it allows us comparing the trends as a function of the counter-ion ratio with prisms known from surfactant surfactant science. The

most important results of this evaluation brought to light, that at a counter-ion ratio of Z = 90% the phase diagram exhibits the largest mutual solubility (= monophasic regime). Further, reducing the 3-dimensional representation into 2-dimensional plots allows deducing two crucial aspects: first, the phase separation (transition from monophasic system into a biphasic system, as wanted in a solvent extraction, see figure 1) is due to different origins, either an emulsification failure, where the microemulsion phase (always the organic phase) is not able to solubilize more water, thus excluding the excess water into a second phase. The second origin for phase separation is the phase splitting, where the organic phase splits into a heavy phase due to attractive interactions between the aggregates and a light phase, containing basically only the solvent. The second aspect found, is that these different types of phase separation can be correlated with the concepts of *frustration*, which are explained in details in the manuscript. However, this correlation is completely new and allows to draw a fundamental conclusion where on a map, an extraction is perfectly functioning and where it does not. Additionally, the origin of the third phase can be postulated, as it is a combination of the types of third phase separation and thus enable to establish operation procedures how to avoid these undesirable phases. Finally, the role of the solvent has been in the focus of investigation and toluene is compared to other, often industrially used solvents, as dodecane and isooctane.

In the second part of this work, the conductivity is probed based on the previously determined maps. The focus of interest is primarily the conductivity in monophasic regions close to a phase boundary, comparing the frustrated versus non-frustrated regimes. In general, in frustrated (unwanted) regions, where phase separation is dominated by the phase-splitting, the conductivity is very high, indicating high interaction between complexes as well as a high dynamic on a molecular and nanoscopic scale. In the non-frustrated regime, ideal for solvent extraction, the conductivity is very low, indication on one hand a low interaction between reverse micelles as well as very low dynamics and thus a high stability of the complexes. Consequently, a comprehensive conductivity profile has been determined and shows clear tendencies between regions suitable for solvent extraction and compositions that are unsuited. Hence, conductivity can provide an easy and versatile tool in industrial plants, indicating directly when an undesired phase is approached, as the conductivity is increased drastically. Additionally, what counter-measures shall be undertaken *in-situ* in order to prevent the system from entering an undesired phase can be deduced from the first experimental part.