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Importance of weak interactions in the formulation of organic phases for efficient L/L extraction of metals

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ABSTRACT:

Recent experimental studies demonstrate the need to take into account weak interactions in the understanding of solvent extraction processes. This well-established industrial technology now beneficiates of a supramolecular approach, complementary to the traditional analysis based on coordination chemistry. In this article, we focus on the integration of a colloidal approach in the analysis of solvent extraction systems: organic phases employed are complex fluids, in which extracting molecules self-assemble into reverse aggregates. We detail the available analytical tools employed towards characterization of these organic phases, and emphasize the recent results in aggregation driven extraction. All experimental data is discussed in light of theoretical approaches which propose adequate thermodynamic models and shed light on the importance of entropy on the phenomena. Diluent effects or synergism have been successfully rationalized, efficient new formulations based on a physico-chemical analysis have been proposed, and the door is now open for further development at industrial scale.

Keywords: Solvent extraction; separation; aggregation; metals

1. Introduction

Solvent extraction (also called liquid/liquid extraction, abbreviated into L/L extraction) is at the heart of most separation processes in various hydrometallurgical applications, especially in those dedicated to the recycling of metals.[1–4] The aim of this technique is to separate target from non-target ions which are solubilized in an aqueous phase, through liquid−liquid phase transfer of target ions into an organic phase. This is typically achieved by means of extracting molecules, named extractants, designed with a chelating polar group to ensure the metal coordination, and with an apolar part enabling solubility in the organic phase. Historically, industrial processes have been implemented mostly from empirical approaches. Effect of acids, diluents, competitive metals on extraction efficiency were simply tabulated for direct application. For many processes, it appears today that understanding the extraction properties is mandatory for their optimization, or ideally for their prediction. More knowledge and predictive modelling would moreover allow greener recycling process, e.g. which generate reduced effluents and/or with better selectivity.[5]

Traditional approaches based on macroscopic relationships established thanks to the so-called “graphical slope analysis” (GSA, also called “slope method”) have regularly reached their limitations. Based on analysis of extraction isotherms, GSA is employed to determine the stoichiometry of the metallic species extracted in the organic phase. When the extraction process can be described using a simple set of equilibria involving a limited number of metallic species, log-log plots lead to lines with a slope corresponding to stoichiometric coefficients, as long as the experimental conditions are chosen to simplify the extraction behaviour. The validity domain of the method has been widely described, and when taken into account, very satisfactory results are obtained in the case of simple systems, which can be related to well-defined coordination complexes.[6] However, when multiple equilibria need to be taken into account, slope analysis becomes cumbersome, when not impossible to apply, and computer modelling needs to be employed in conjunction with graphical analysis.[7] It was early noticed that slope analysis cannot account for complex extraction mechanisms, especially in the case of mixtures of extractants and synergism, as deviation from expected slope and non-straight lines are observed.[8] Furthermore, application of slope analysis can lead to results of questionable interpretation; mechanisms inconsistencies have been noticed and bias have been reported. For instance, studies of the extraction mechanism of lanthanides(III) by malonamides lead to different metal species according to various sources, with 2 to 3 extracting molecules involved in the metallic cation extraction.[9–11] In the same system, inconsistencies with saturation experiments have been reported, with neodymium(III)[11] as well as palladium(II).[12] Theoretically, the extractant to metal ratio in organic phase at metal saturation corresponds to the ligand to metal ratio of the coordination complex responsible for metal stabilization in the organic phase. However, such assumption is valid only if extraction mechanism is same at low metal loading (employed for GSA) and at high metal loading (for saturation experiments). Finally, diluent effects with the closely related diglycolamides cannot be interpreted by changes in the coordination sphere of the cation without further studies.[13] Recent results demonstrate that evolution of aggregation in the organic phase is mostly responsible for these observations (vide infra, section 3.1), and back the need for detailed analysis involving chemical as well as physicochemical equilibria. The notion of “extended stoichiometry” is thus not adapted and misleading as it suggests that extraction can be summarized in a fixed set of molecular equilibria.

Extractants are amphiphilic molecules, and tend to behave like surfactants, albeit with peculiarities. Since the first hint from Osseo-Asare,[14] the number of annual published papers considering aggregation of extractants has been multiplied by 10. This approach describes organic phases as organized solutions by taking into account long-range interactions as well as classical interactions between nearest neighbours. Indeed, self-assembling properties of surfactants leads to formation of reverse micelles occurring in the oil phase beyond a certain critical concentration. Weak aggregates formed by the extractants need to be understood on different length scales: the atomic scale for metal chelation, the nanoscale for micelle formation, and the micron scale dealing with macroscopic phase behaviour. The nano and supra-molecular scales are perfectly illustrated by the scheme of Guilbaud et al.,[15] showing that the same entity can be studied at molecular scale, as a complex, and at supramolecular scale, as a nano-droplet of polar entities solubilized in an organic phase, or as reverse-micelle like aggregates (Figure 1). Complex, aggregate and micelle definitions are distinguished by considering the water which is extracted in their polar core, and which gradually evolves from frozen to free water states. In parallel, the quantity of water in the organic phase increases from some moelcules to mmol/L macroscopic concentrations.

High extractant concentrations can also bring the possibility of organic phase separations, and occurrence of different complex phases such as the “third phase accident” which leads to viscosity increase and stops mixer-settler operations. To avoid these and to understand interactions one has to study phases, phase diagrams and phase transitions in a systematic way knowing that the classical mass action laws cannot be used without introducing many parameters to describe all simultaneous chemical equilibria involved. Complete understanding of the extraction process requires the establishment of a relationship between distribution law, initially introduced by Nernst, and thermodynamic approach accounting for the different occurring chemical reactions (mass action law), and encompassing thermodynamics of self-assembly.

This paper proposes an overview of the characterization techniques and methods developed in the last decades to describe the organic extraction phases. In a second part, we summarize the main experimental and theoretical approaches taking into account this double scale description to unravel the extraction mechanisms, as well as the contributions of these recent approaches in the understanding of the solvent extraction problems.

2. Experimental approaches towards organic phase characterization

2.1 Coordination at the molecular level

Metal ion coordination remains the basis employed in the description of liquid-liquid extraction, and extracting molecules are usually classified according to their interaction mode with metallic cations. The coordination chemistry principles which underpin the sorting of extracting molecule polar heads have been well described in a recent review.[16] Extracting molecules usually interact with metallic species through bonding in their inner coordination sphere, forming what is generally named a “(coordination) complex”. Interactions in the outer sphere have been described to intervene as well, for example electrostatic of H-bonding interactions, which are favoured by the low polarity of the organic extraction phase. Most of the studies available in the literature on liquid-liquid extraction start with a molecular approach aiming at the description of the species involved at the molecular scale. Parameters such as the amount of acid, extractant, counter ion, etc… are thus studied in order to lead to a proposition of the composition of the molecular complexes. Sometimes, the term “adduct” is employed, and refers to mixed complex, when different nature of molecules (ions, ligands, water…) are necessary to complete the coordination sphere(s) of the extracted cation.

Classical spectroscopic techniques, such as UV-vis, IR, NMR (^{1}H, ^{31}P, ^{13}C…), enable the identification of the different species involved in extraction of the metallic cation.

Stoichiometry of molecular complexes can then be determined using classical approaches involving competition experiments, decay/increase of specific signals, etc… Recent improvements include use of ESI-MS as a tool to identify the presence of specific species, especially mixed adducts. This technique, based on soft ionization, allows the elucidation of metal speciation in organic media through direct transfer into gas phase and generation of charged species without major disruption of the metal-ligand bonds. Thorough analysis and combination of several techniques enable the identification of well-defined species, even in the case of synergistic extraction systems.[17] Structural elucidation of the metallic cation coordination spheres is however more difficult to achieve. Classically, single crystal X-ray diffraction studies bring appreciable data on the coordination environment of the metallic cation extracted in the organic phase. However, this technique relies on physical separation of unique species from a mixture, and the crystallization process may be a thermodynamic sink for several chemical species in equilibrium in the solution. The technique and its limitations have already been widely discussed in the frame of homogeneous catalysis. As a consequence, EXAFS study are also performed – when synchrotron X-ray beam is available - and they bring information such as number of ligands and metal-ligand distances directly on the organic phase, albeit after modelling of the experimental spectra. Such analysis leads to a static view of the coordination sphere. Dynamics of the coordination sphere is also important to describe, as ligand exchanges are sometimes rate determining steps in the overall transfer process. NMR is the most often used technique to this purpose.[18] In our opinion, the key improvement of this decade is the quasi-systematic combination of classical spectroscopic techniques with computational modelling, especially DFT studies. DFT is largely employed in the description of reactions mechanisms involving a metallic center, e.g. homogeneous catalysis. It enables to suppose the occurrence of the most stable species, and to simulate spectra of vibrational spectroscopies. In solvent extraction, DFT has been successfully applied in order to elucidate complex modes of action of extracting molecules.[19,20] Whatever the experimental technique applied, determination of the molecular structures involved still entails some uncertainty.

All these techniques do not take into account the supramolecular ordering of the organometallic complexes formed, nor the hydrophilic-hydrophobic interactions that can lead to the formation of aggregates, especially of the reverse micelle type.

2.2 Experimental methods for weak aggregates characterization

Nowadays, solvent extraction mechanisms are more and more studied by taking into account weak interaction between extracting molecules, involving their self-assembly in amphiphilic aggregates. An aggregation number (Nag) is defined as the number of extracting molecules forming an aggregate. Aggregation phenomena were highlighted for the first time in 1991 by Osseo-Asare, who considered the similarities between the behaviours of surfactant and tributyl phosphate (TBP) used as extractant in the PUREX process.[14] He suggested that the non-stoichiometric extraction of acid or metallic species was due to the formation of reverse micelles, or microemulsion, in the organic diluent due to the aggregation of TBP extractants.

Ben Azouz et al. proposed the first direct structural characterization of these aggregates in 1992, thanks to small angle X ray scattering.[21] Erlinger et al. further furnished a modelling of these SAXS data, which allowed explaining the supramolecular origin of the third phase formation.[22,23] Over recent years, the TBP-alkane system has been reexamined,[24,25] and many organic phases have been studied taking into account the formation of supramolecular species.[26–28] Complete analysis of coupled SAXS and SANS experiments have further been investigated to determine the exact microstructure of reverse aggregates made by extracting molecules. It leads to parameters like aggregation number, polar core volume, attraction between cores, aggregate volume, and average distance between aggregates, as well as diluent penetration in the apolar shells of the aggregates.[29] A recent model derived by Motokawa et al. proposes a hierarchical description of the organic phase which includes both molecular complexes and supramolecular objects, resulting from aggregation of clusters of different sizes.[30]

However, these scattering experiments present in some cases some limitations for the structural description of the solvent extraction organic phases. Being sensitive to electron densities, SAXS scattering intensities are mainly due to the cores of the aggregates. Having sizes in the sub-nanometer range, they produce signal in the high Q range (as the solvent peak), and induce difficult solvent subtraction and fitting. SANS scattering, which mainly depends on the deuterated/non-deuterated parts of the samples, provides full aggregates scattering, which is usually easier to model. Full aggregates however present the drawback to be possibly fitted with different core sizes. These limitations have been exposed by Pecheur et al..[31] Simultaneous SAXS and SANS fitting is safer but tedious.

Coupling SAXS and SANS analysis with molecular dymamics appears today as an innovative and efficient option to completely model and understand the structural aspects of solvent extraction phases. This was initiated by Ferru et al. in 2014,[32] who showed that SAXS data could be completely recalculated from molecular dynamics simulation. It offered key insight into the complex fluid involving weak interactions without any long-range ordering.

Following the approach of considering supramolecular aggregation in solvent extraction, an important parameter that has been extensively characterized on solvent extraction phases is the Critical Aggregation Concentration (CAC). This denomination is preferred to Critical Micellar Concentration (CMC), in order to distinguish the poor ability of the extracting molecules to self-assemble in oil in comparison with classical surfactants in water (direct micelles) or in oil (reverse micelles). Indeed while surfactants form spontaneously micelles of up to hundreds of molecules, extractants form aggregates of 2 to 40 molecules, with a gradual transition between monomeric to aggregated states. Critical micellar and aggregation concentrations are thereby impacted, and lie respectively in the order of 0.001M and 0.1M. CAC was shown to be a thermodynamic parameter of high importance because it characterizes the free energy of aggregates formation. As detailed in the second part of this paper, its determination has been confronted to many solvent extractions problems and mechanistic studies.

As mentioned by Jonsson, Lindman, Homberg,[33] the physical methods for CMC determination of surfactants in aqueous phases include conductivity, solubility, viscosity, light scattering, surface tension (e.g. Wilhelmy slide method), measurement of ion activity, dye incorporation method, gel filtration spectrophotometrically and counter ion magnetic resonance. Concerning solvent extraction phases, the possible techniques to determine CAC are more limited and involve bigger uncertainties due to the high CAC values.

Among the methods exploited in literature, Vapor Pressure Osmometry (VPO) was one of the first method to be used.[31,34–36] VPO enables to determine the solution activity as a function of its solutes concentration. In the case of ideal solutions, VPO signal is proportional to the molality of the solution, and when the concentration of the solution increases, VPO signals show a deviation from ideality at a molality that can be interpreted at first approximation as the critical aggregation concentration.[35] CAC as well as aggregation number can be derived after a cautious data analysis. VPO measurements need to be performed on volatile solvent. Heavy alcanes such as dodecane are often replaced with n-heptane without taking into account the eventual effect of this diluent change on the extraction or aggregation properties. Moreover, vapour pressure stabilization gives rise to extremely long experimental measurements.

As for surfactant, the most commonly applied technique to derive CAC is the surface tension measurement. The drop-shape analysis method is usually applied. For solvent extraction solutions, the interface tension between the organic phase and the aqueous phase is measured by forming a pendant or a spinning drop of organic phase into the aqueous phase. As the presence of extractants adsorbs at this interface and decreases the water-oil interface tension, the CAC can be derived when the interface tension is no more linear with extractant concentration since aggregates are formed (Figure 2a). This method is quite robust, but requires large amount of aqueous phase, and experiments need often to be repeated many times in order to limit the uncertainties.

Another simple and efficient approach to derive CAC consists in exploiting the evolution of SAXS or SANS intensities at low Q for various extractant concentrations. Considering the general expression of scattering, the formation of aggregates is here again characterized by a break of linearity, since the intensity is proportional to the square of the volume of the scatterers that are evolving from monomers to micelle like aggregates with extractant concentration.[37] CAC values and uncertainties obtained with this approach and with surface tension are compared in Figure 2b.

Dynamic Light Scattering (DLS) is also used for the same purpose. Deriving the hydrodynamical radius of the species from the self-diffusion coefficient of the scatterers as a function of the extractant concentration was exploited to determine CAC.[38–40]

In addition to structural information at the molecular level, NMR experiments can give information on supramolecular aggregation properties, principally from self-diffusion coefficient determinations.[41–43] CAC and aggregation numbers can for example be derived to compare and confirm the other techniques such as SAXS and SANS. Furthermore, when a solute distributes between diluent and aggregates, the fraction of solute embedded in the aggregates can be derived provided there is a significant difference in the self-diffusion coefficients between diluent and aggregates.[42,44]

Thanks to these methods, organic phases employed in solvent extraction have been descripted in details at both molecular and supra molecular scales, which enabled in several studies a better understanding of the liquid-liquid extraction mechanisms. This shows the necessity to estimate the interplay between the short-range interactions due to the coordination process, and the long-range interactions responsible for self-organization.

3. Thermodynamic link between weak aggregation and extraction

3.1 Recent examples of aggregation driven extraction

Many papers concerning the study of the key parameters of extraction confirmed the importance of taking into account the aggregation state of extractants in the extraction mechanisms. We give here an overview of the studies exploiting such a supramolecular approach with a special focus on the thermodynamic interpretations of these mechanisms.

The effect of acid that is known to play a consequent role on extraction efficiency, has been investigated with a supramolecular approach. Acid nature usually depends on the targeted application. Nitric media are used for the back end of nuclear cycle, while sulfuric or phosphoric acids are more often applied for the front end. Change of acidity is also commonly exploited in industrial processes to strip out the extracted metallic species. It may appear obvious that acid content and nature acts on the chelation processes, but it was also shown that they strongly impact aggregation properties of the extractants. In 1998, Erlinger et al. demonstrated that the third phase formation originates from the supramolecular aggregation of extractants when high amount of acid is extracted.[45] Several studies confirmed that the acid content influence the aggregation state of the organic phases of extraction.[40,46] As illustrated in Figure 3, for low extractant concentration, higher acid contents induce higher neutrons or X ray intensities at small angles, characteristic of the formation of bigger or more aggregates in the organic phase.

Déjugnat et al. further examined the acid effect on aggregation by modifying not only its content but also its nature. He showed that counter ions of the acids play a role on the aggregation and therefore on the third phase appearance according to the Hofmeister series. The more polarizable anions are more inclined to provoke aggregation and therefore the third phase formation.[47] Taking into account that extractants are organized in reverse micelle-like aggregates, the same authors demonstrated that acid extraction can be modelled with a Langmuir isotherm from which a free energy of adsorption was derived. Again according to Hofmeister series, the more polarizable counter ion were revealed to be less extracted.[48] In parallel, aggregation state was shown to be thermodynamically nucleated by the acid, with a minimized aggregation energy in presence of acid. Aggregation formation and properties (CAC, domain of stability, attractive potential between micelles) does greatly depend on the acid content and on the nature of the extracted counter anions of the acid.[40]

Another important parameter of solvent extraction is the diluent in which the extractant are solubilized, or in a similar extent, the apolar chains of the extractant. Many studies aim at limiting or even completely avoiding the use of organic diluents in extraction solvents, because of their volatility, and potential flammability. However replacing a diluent with another one implies strong alterations of extraction properties that cannot be explained with a pure chelation approach. Understanding the diluent effect on liquid-liquid extraction is therefore essential to propose a predictive approach towards greener diluent substitution.

Effect of various aliphatic diluent chains or extractant alkyl chain lengths has been investigated with the supramolecular approach. The most important parameter revealed in this case is the penetration of the diluent in the shell of the aggregates.[29,49] It was shown to provoke strong variation of the bending energy of the reverse micelle-like aggregates, limiting consequently their swelling or perturbing the metal complexation (Figure 4a).[29]

The modulation of weak interactions in the organic phase has also been studied in non-usual systems, i.e. systems not based on a classical aliphatic or aromatic diluent. Malonamides bearing a long perfluoroalkyl chain have been developed in order to modulate independently the strength of both the coordination of the polar moiety and the inter-molecular Van der Waals interactions.[43,50] The perfluoroalkyl chain is hydrophobic, but also oleophobic, and it was observed that the oleophobicity prevails over the tendency of hydrophilic moieties to self-assemble: in the organic phase, in a chlorinated diluent, malonamides with a perfluoroalkyl chain lead to direct aggregates with a fluorous core, whereas classical hydrocarbon malonamides lead to the previously described reverse aggregates with a hydrophilic core (Figure 4b). This difference of supramolecular ordering of the extracting molecules has a great impact on the extraction process: extraction is inefficient with the perfluoroalkyl compounds in comparison with the hydrocarbon compounds, all other parameters remaining equal.[43]

In some cases, the use of a fluorinated malonamide in a perfluorinated diluent led to better extraction performance in comparison with the corresponding hydrocarbon system. It has been recently reported that a fluorous phosphate in fluorinated diluent showed improved extraction of Zr(IV) in comparison with extraction based on tributylphosphate (TBP) in n-octane.[51] In this case, higher stability of the Zr(IV) complex in the fluorous phase is supposed, but structuration of the fluorous phase remains to be determined in future work. No major difference in the Zr(IV) coordination by the phosphate group was noticed.

Knowledge on the role of the diluent, especially its influence on metal coordination, through e.g. precise description of the effect of its dielectric constant, has also to be increased. It is then particularly striking to notice that so far no detailed determination of the dielectric constant of the whole organic phase has been performed to our best knowledge.

Understanding the effect of diluents on aggregation and extraction is also essential when the diluent needs to be replaced by an unconventional diluent such as ionic liquid. ILs are more and more considered as green diluents for solvent extraction, as they prevent economic, ecological and safety problems thanks to higher flash points and lower volatility than the conventional organic solvents.[52] In some cases, they also significantly improve the extraction efficiency.[53] But, these higher performances cannot be fully exploited because of their unpredictability. Understanding the peculiar mechanisms of ILs based extraction systems is therefore essential to render the use of ILs more straightforward and reliable in solvent extraction. Metal extraction in ILs occurs through extraction mechanisms which can differ from those observed in molecular solvents. It was shown for example that some ILs exchange their cation or anion with the metal to extract.[54] However, this behavior is not systematic and not sufficient to explain the unpredictable extraction efficiency in ILs. As for the conventional extraction systems, most of the mechanistic studies rely on the definition of complexes stoichiometry derived from the macroscopic distribution coefficients. More and more descriptions of the complexes microstructure are also proposed in ILs, providing essential information on the extraction mechanisms.[55,56] However, the structure and the role of extractant aggregation are usually completely ignored in the extraction mechanisms. It was shown only recently that some aggregates are actually also formed in ILs.[57] It appears therefore essential to pursue this approach in order to elucidate aggregation influence on the extraction efficiency in ILs.

Taking into account aggregation is also very important when mixtures of extractants are employed. Many processes use synergistic mixtures of extractants to ensure higher separation efficiency and selectivity.[58,59] While broadly exploited and efficient, origin of synergistic extraction is not always fully understood. Supramolecular origin of synergy was investigated in 2012, to bring new insight on its mechanisms. Deriving free energy of micellization thanks to critical aggregation concentration determination, it was shown that aggregation is systematically favoured in case of synergistic extraction.[37,60] Looking further into the origins of synergy, it was however demonstrated that synergistic aggregation is not the prime origin of synergistic extraction, but occurs as a consequence of extraction by a nucleation effect of the acid, and of the extracted metal cation.[31] A thermodynamic approach showed that acid induces synergy through attractive interactions between extracting molecules in the case of mixtures of DMDOHEMA and HDEHP extractants.[60]

These enhanced extraction efficiencies due to aggregation, have further been exploited to formulate an efficient synergistic mixture. The extractant DEHCNPB (butyl-1-[*N*,*N*-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid), known to selectively extract uranium in a phosphoric medium and to poorly aggregate, was associated to a surfactant known to aggregate at low concentration in the organic phases, AOT (sodium bis(2-ethylhexyl) sulfosuccinate). This original synergistic mixture appeared powerful to extract rare earths from phosphoric media.[61] This example suggests therefore that extraction can be optimized by improving aggregation of an extracting system by the addition of a suitable surfactant molecule.

3.2 Rationalization through thermodynamic description

The previous part presented some experimental studies demonstrating that aggregation is essential to take into account to understand solvent extraction mechanisms. Some theoretical approaches have also been proposed with the same objective.

In classical thermodynamics considering the extraction process as a whole, the standard derivation by van’t Hoff used for simple fluids can be used only when all aggregation effects are negligible and when enthalpy itself has no temperature variation. In these two restrictions, all entropy variations could be derived by derivatives of the free energy. This van’t Hoff approach, valid for ideal fluids, is known to be a crude approximation. It is not numerically correct and no more valid when aggregation or electrostatic effects are more than 2-5 kJ/mole. A statistical thermodynamic treatment separating electrostatic, dispersion, self-assembly and solvent effect is necessary, such as in amphiphilic self-assembly: each mechanism has its own entropy.[62]

The thermodynamic approach proposed by Zemb et al.,[63,64] consists in identifying the molecular driving forces of ion transfer between the two immiscible phases.[65] In hydrometallurgy, the molecular approach stipulates that the extraction free energy corresponds only to the complexation of the cation by one or more extractants associated to an entropy of mixing.[16] In the colloidal approach called “ienaics” approach proposed by Zemb et al,[66] a more general view is possible that goes beyond supramolecular complexation considerations. That is why we propose Figure 5 to illustrate this colloidal approach which considers that the driving force for extraction is the reference free energy differences of species exchanging between complex fluids i.e. organic and aqueous phase instead of concentrations and activity coefficients.[64,66] The differences in reference free energy are then directly decomposed in three main underlying mechanisms at colloidal scale which take into account long range interactions[67] as well as the nearest neighbours and thus allow the comprehension and description of the origin of interactions.[68–71]

Figure 5 presents a schematic representation of the liquid-liquid extraction process seen from the point of view of an extracted electrolyte. In this colloidal representation, potential differences between electrolytes are represented as levels of chemical potential, by analogy with classical electronics dealing with electron potential in conductors and semi-conductors.[66] The left side in blue represents the aqueous phase containing multiple ion species whereas the right side is the organic phase (solvent phase) made of monomeric extractants and self-assembled aggregates. A thick green line represents the water-oil interface. Considering the surfactant nature of the extractant, the interface is at least partially covered by the extractants (not shown here) In the absence of extracted species, [72,73] most extractant are present as “monomers” [74] that are represented schematically as well solubilized species in the oil phase. Before extraction, the target as well as non-target species, together with the nitric acid are present as a concentrated electrolyte solution near a charged liquid-liquid interface. [75,76] The transfer process is represented in the zoomed rectangle to the left showing the core of the aggregate with the lanthanide cation, the nitrate anion, water molecules and the extractant head groups.

Figure 5 shows also the four “driving forces” [64,65] that control the partition of electrolytes between the solvent and the aqueous phase. All these forces are derivatives of the free energy and they contain an enthalpic and an entropic contribution. [77–79] Among the four terms, complexation with the first neighbors and electric interactions between extracted ions and the head-groups of the extractant which is well known in organometallic chemistry of supramolecular self-assembly is a strong term typically with an enthalpy of 50 kJ/mol per extracted species that favours the transfer to the oil phase. [26,63,80] This term is counter balanced by weaker quenching terms represented at the right and usually hidden behind “activity coefficients” which are associated with the packing of extractants chains i.e. curvature term, differences in ion concentrations between the two phases, the activity of water etc... It has been shown that the forces quenching the water to oil transfer can be decomposed into three terms that can be evaluated from first principles [64,79]:

- The "bulk" term $\Delta\mu_{Bulk}$, mainly related to the confinement of ions in the very small polar volumes of the oil phase. It is the entropic energy associated with the packing of electrolytes inside the polar core of aggregates. When volumes are ignored this bulk term is sometimes taken into account as a "constant" in a mass action law.
- The "chain" terms $\Delta\mu_{Chain}$ concerns all effects linked to solvent nanostructure reorganization around the extracted and co-extracted species.[81,82] It represents the free energy of the chain whose arrangement is schematically shown in Figure 5b and associated to the variation of the shape and number of the reverse micelles i.e. the modification of the packing parameter of the extractant introduced by Israelachvili which depends strongly on the composition of the micelle. In other words, this free energy is related to the deviation of the actual packing parameter from the preferred one and is expressed using a harmonic approximation. [83]
- Finally, the "droplet" term $\Delta\mu_{Droplet}$ is linked to the presence of a disordered condensed globular aggregate made from the complexing head groups, extracted electrolytes and co-extracted water.[68,69,73,75] It is the free energy of the polar core, which represents the free energy of the water/ion mixture. It can be evaluated by considering that this term is equivalent to the corresponding one in a bulk electrolyte solution of the same concentration. Thus, osmotic measurement is able to give this polar effect.

Finally, the observed distribution coefficient is due to the "remaining" gap in electrolyte free energy of transfer is represented as a green arrow. This term can be positive or negative, respectively in extraction and stripping.

Once all the energetic contributions are defined, one can predict overall extraction efficiency by using mesoscopic models. The pseudo-phase model proposed by Tanford is one of the most widely used thermodynamic models in the case of surfactants self-assembly. It assumes that individual aggregates constitute a distinct phase, which is in thermodynamic equilibrium with the free extractants in the solvent. The key point of this model is that it allows calculating the standard chemical potential of the aggregates. Moreover, in combination with the mass action law as initially proposed by Leontidis and Hatton, and exploited by Spadina et al., the prediction of extraction is possible for any independent variable without fitting reactions constants.[68,69]

This colloidal approach was used to estimate quantitatively the driving forces responsible for extraction. As shown by Zemb et al.,[63,64] considering the motor of complexation only is not sufficient to explain the values of distribution coefficient conventionally obtained in solvent extraction. The authors quantitatively showed that the other terms, which intrinsically consider aggregation, act as more or less efficient inhibitors toward extraction, and balance the thermodynamic equilibrium to produce the effective extraction efficiencies. This thermodynamic approach was also applied to synergistic extraction.[60,84] The different motors and inhibitors of extraction were evaluated to identify the significant parameters of synergy. Among them, aggregation has a significant role via the free energy of aggregation formation, characterized by the concentration of critical aggregation, but also and to a greater extent by the energy of curvature of the aggregates. Synergistic extraction was therefore shown to be mainly controlled by the potential aggregates swelling (due to water or solutes extraction), but also by their compression (through the penetration of the diluent molecules in the shell of the aggregates).[84]

3.3 (De)coupling coordination and aggregation

Experimental and theoretical approaches described before clearly show that both metal coordination and organic phase aggregation play a role in liquid-liquid extraction of metallic cations. Traditionally, the seek for optimized extracting molecules is performed via careful design of the polar head of the molecule, with structure-activity relationship based on detailed analysis of first and second coordination spheres.[16]

Still it is not clear whether both metal coordination and aggregation act as complementary necessary motors for metal extraction, or if one is the consequence of the other, ie if organic phase aggregation is the consequence of metal extraction or vice-versa. Recently, it was established that metal extraction induces supramolecular organization of the organic phase in the case of Eu(III) extraction with DMDOHEMA in n-heptane.[85] The metallic cation was demonstrated to seed the formation of reverse micelles in the organic phase, resulting in increasing distribution coefficients with increasing metal uptake by the organic phase. This non-classical behavior was nicely related to an increasing water uptake in the organic phase at higher metal loading. The metal-induced nano-hydrophilic domains enable then more efficient coordination of the metallic cations, as revealed by the detection of polynuclear Eu(III) aggregates with metal centers probably bridged by nitrate anions. These experimental findings were rationalized through molecular dynamics, and it was found that the supramolecular structural evolution driven by Eu(III) extraction leads to an extraction favored by ca 10 kJ/mol, due to entropic gain (Figure 6a).[85] Another recent study also illustrated that there is no aggregation, without prior metal coordination.[31]

In another experimental approach, also with the same malonamide (DMDOHEMA), but at low metal loading, it was demonstrated that Nd(III) extraction requires supramolecular ordering of the organic phase.[46] This result was obtained after the comparison of two organic phases based on the same extracting molecule, but with different diluents, n-heptane and toluene. The diluent effect was levelled via the comparison with another metallic cation, Pd(II), which extraction was only moderately affected by the diluent: a ca 10-fold increase in Pd/Nd selectivity was observed switching from n-heptane to toluene, when the distribution coefficient of Pd was only slightly lowered (from 4.2 to 2.7). The drop in Nd extraction was linked to the difference in supramolecular ordering of the organic phase, monitored by the X-ray scattering intensities at zero momentum (I_0): it was evidenced that in toluene no ordering of the organic phase occurs. The supramolecular ordering of the organic phase is induced by nitric acid which is also extracted from the aqueous layer into the organic phase.[60] Altogether, these results show that metallic cations are more or less sensitive to aggregation of the organic phase: Pd(II) seems much less sensitive to long-range interaction than Nd(III), and stabilization of Nd(III) in an organized organic phase is favoured by 5 kJ/mol in comparison with Pd(II) (Figure 6b).[86] In other words, Pd(II) extraction seems piloted by coordination chemistry, whereas Lanthanides(III) extraction seems to require further supramolecular ordering.

The different sensitivity of both metallic cations regarding the supramolecular ordering of the organic phase was attributed to a different coordination behavior: Pd(II) leads to stable 1/1 complexes with the extracting molecule, whereas Nd(III) is the object of weaker coordination, revealed by a dynamic exchange in the coordination sphere of the metal.[46] Assuming that the coordination chemistry of Nd(III) and Eu(III) with malonamides is similar, both works lead to the statement that efficient coordination of lanthanide cations in organic phase requires supramolecular ordering of this phase.

The correlated effect of metal on aggregation and extraction has also been examined with synergistic mixtures of extractant. As synergistic mixtures extract better when they aggregate better, the question asked was to identify if the favoured aggregation (lower CAC) were due to the metal extraction or if the metal was more extracted because of the synergistic aggregation. For this reason, Pecheur et al. measured CAC values in absence of metal, acid and water.[31] They showed that aggregates of 5 extractants were reduced to dimers, but no decrease of CAC characteristic of a synergistic aggregation could be obtained anymore. Another study tried to decorrelate the effect of water, acid and of the metal on aggregation and extraction. J. Rey et al. gradually added these ingredients and measured separately the aggregation state of the synergistic system. They showed that while water has no effect, acid is the first ingredient to induce synergy of aggregation by creating an attractive interaction between the two exctractant at a ratio 50/50.[31,60] In presence of metal the synergy remained present but was strongly shifted to the ratio of synergistic extraction (25/75).

All these studies are fully consistent with the fact that it is impossible to de-couple metal coordination and organic phase aggregation. Each system is parameter dependent, and modification of one parameter cannot lead to modification of sole coordination or aggregation, as both are completely intertwined. Trying to find the key parameter responsible for efficient extraction of a given metal is similar to answering the chicken and egg problem. It is of paramount importance to remember that each component of the organic phase has its importance, including acid and water, and that the organic phase is composed of a distribution of mixed supramolecular species (aggregates), in dynamic equilibrium. According to the experimental conditions, different extraction regimes can be evidenced, where one peculiar parameter has a higher weight on the result. Interestingly, as illustrated in Figure 7, it has been recently evidenced that the most efficient formulations correspond to those of higher CAC, as a too high organization in the organic phase can either lead to third phase formation (metal driven aggregation) or strong H^+ competition (H^+ driven aggregation).[69]

4. Conclusion and perspectives for efficient formulation of extracting system

Recent results highlight the key role of weak interactions in the extraction of metallic ions into an organic phase. Along with metal coordination, supramolecular ordering of the organic phase has been demonstrated to be one the key driving forces of the process. As a consequence, detailed understanding of extraction mechanism of a given metal is nowadays performed using tools dedicated to the analysis of supramolecular organization of the organic phase, especially SAXS and SANS. Such comprehensive analyses are important in order to be able to propose efficient and selective formulations, as they may be useful to direct future work dedicated to the optimization of molecular structure of extracting systems. The use of branched aliphatic diluents is nowadays well established when third phase formation has to be avoided, thanks to the understanding of diluent effects in this frame achieved during last decade. More recently, practical applications and set-up of new processes arose during this decade. For instance, the association of a classical extractant with a classical surfactant (AOT) led to synergistic extraction of rare earth from phosphoric media.[61] Processes in which selectivity is driven by controlling the weak interactions have been developed in the frame of precious metals recycling from waste.[87] In this case, the shift from an aliphatic to an aromatic diluent, the choice of the extracting molecule (a malonamide), and the aqueous phase acid concentration in the extraction, scrubbing and stripping steps are the key parameters employed to recover palladium with an excellent selectivity over base metals such as copper and iron. Limits arise as each system is different, and the weight of each parameter (water, acid, metal, diluent…) has to be established in each case. As a general guideline, all the data gathered suggest that water uptake by the organic phase is a good indicator of the importance of aggregation for a given system. Water can only be stabilized in non-polar organic phase through the formation of reverse aggregates. The simple Karl-Fischer titration of a given organic phase can be seen as a pertinent starting analysis.

Another interesting perspective arises from this work. Molecular modeling appears as a more and more useful tool, as well as for understanding and for prediction. DFT at the molecular level and molecular dynamics at the supramolecular level are now sufficiently accurate to account for observed data, and contribute to the interpretation of experimental analyses such as SAXS, SANS, EXAFS. Curiously, the less described parameter is maybe the most important: coordination free energy. DFT does not enable to reach the absolute precision needed to account for the low differences responsible for the selective transfer of a metallic cation. It is indeed very difficult to model the transfer from aqueous to organic media at the molecular level with reasonable calculation durations. And molecular dynamics rely on a set of parameters which have to be fixed beforehand, including the coordination energy. Complementary experimental data is thus needed, and techniques such as calorimetry remain underexploited. Regarding relative effects and comparisons – between two metals or two extractants – there is no major difficulty to predict which system will lead to the best result. And the picture given by computational modelling is of great help, especially now that it is rather a movie which represents at best the fact that the organic phase is a dynamic system, with aggregates of molecules of variable sizes and compositions, only appreciated through a mean distribution thanks to the analyses. Having this dynamics in mind – contrary to the static vision of a pure metal coordination complex or pure reverse micelle of well-defined size – is of paramount importance in order to propose performing systems.

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Figure 1: Depletion of water-in-oil aggregates from poor solvents: Transition from weak aggregates towards reverse micelles (adapted from Guilbaud et al.[15])

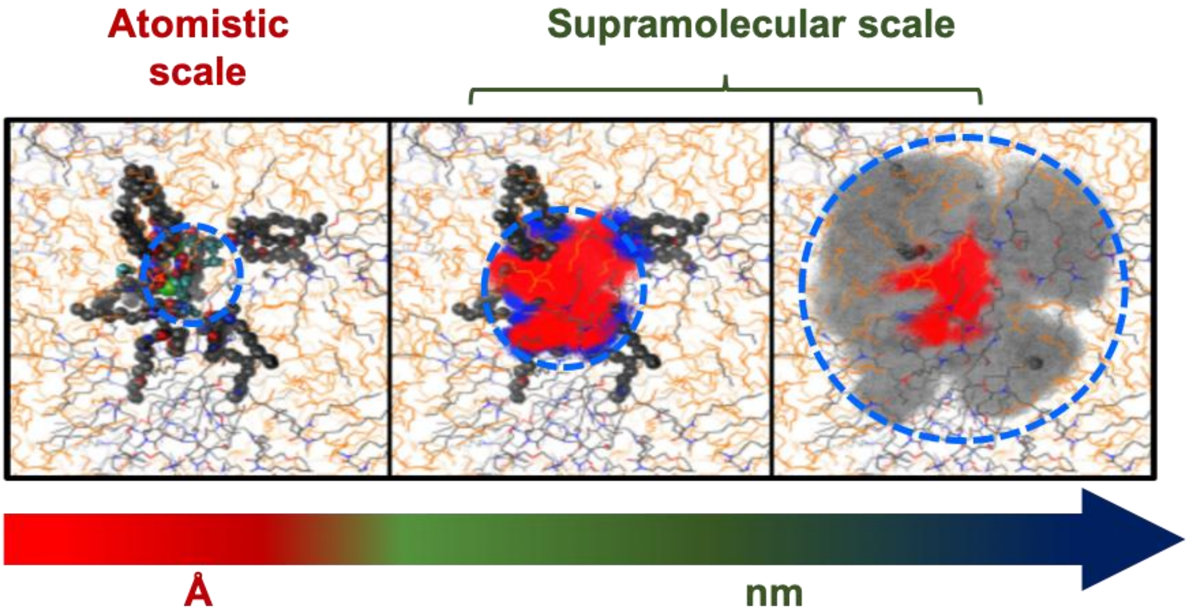


Figure 2: CAC determination from intercial tension measurements between organic and aqueous phases of extraction (a) and comparison of CAC values and unerctainties obtained with tensiometry, SAXS and SANS (b).

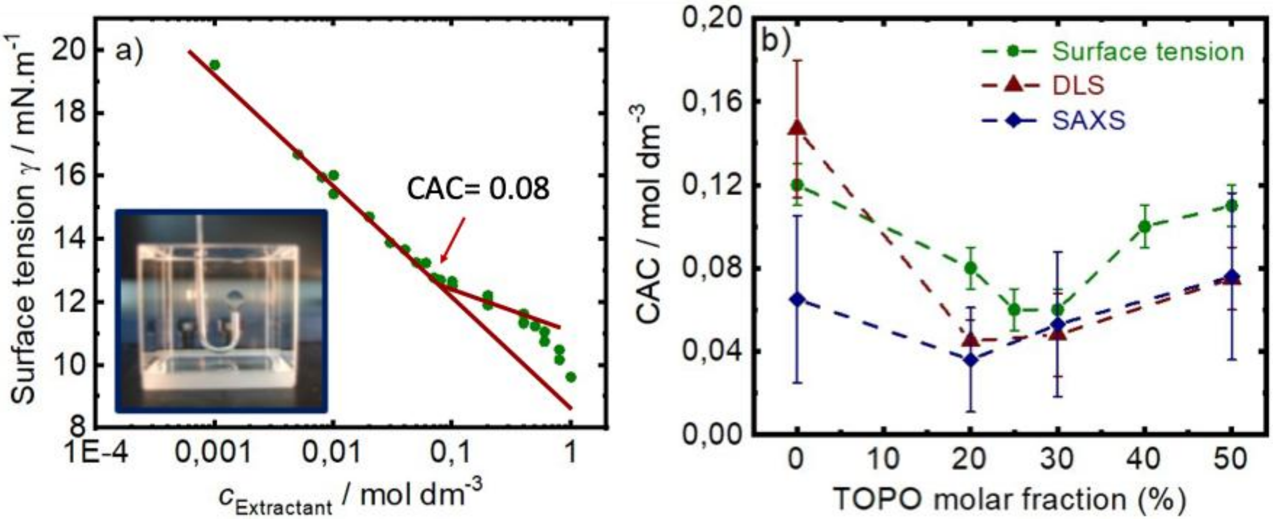


Figure 3: a) SAXS data of extractant DMDOHEMA for increasing HNO_3 concentrations; b) Schematic illustration of aggregation induced by acid concentration.

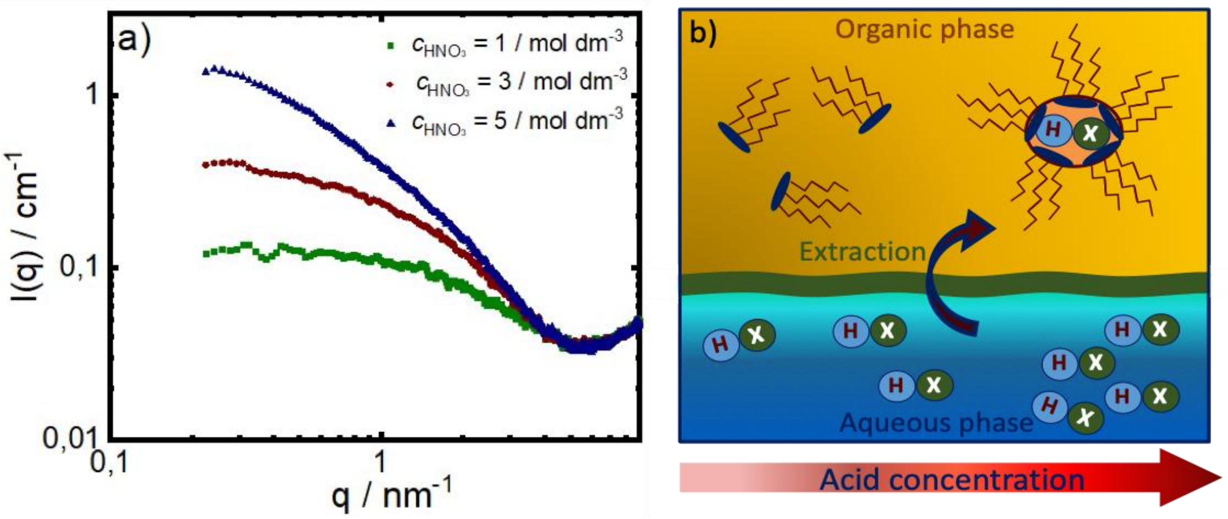


Figure 4: a) Diluent effect of various alkanes on aggregation and selective extraction of the synergistic system HDEHP/TOPO. Selective extraction is also expressed as a double difference of free energy of transfer between U and Fe;[29] b) Effect of hydrogenated and perfluorinated malonamide extractants on their aggregation and extraction yields of Nd and Pd [43].

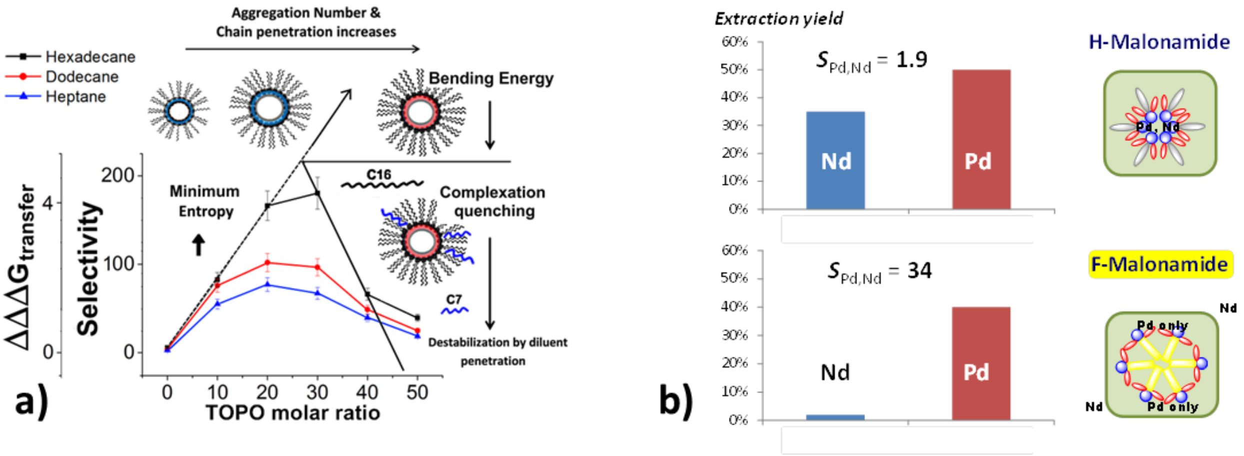


Figure 5: (Left side): Location of the relative chemical potentials of the electrolyte during liquid-liquid extraction: the reference chemical potentials μ_0 are indicated explicitly. The water rich phase is represented in blue and the solvent phase in orange, while the interface or rather the interphase is schematized by a thick green undulating line; (Right side): Graphical free energy balance schematizing the interplay between supramolecular complexation (red arrow), the bulk term associated to mass action law as well as the chain reconfiguration term and the internal energy of the polar cores.

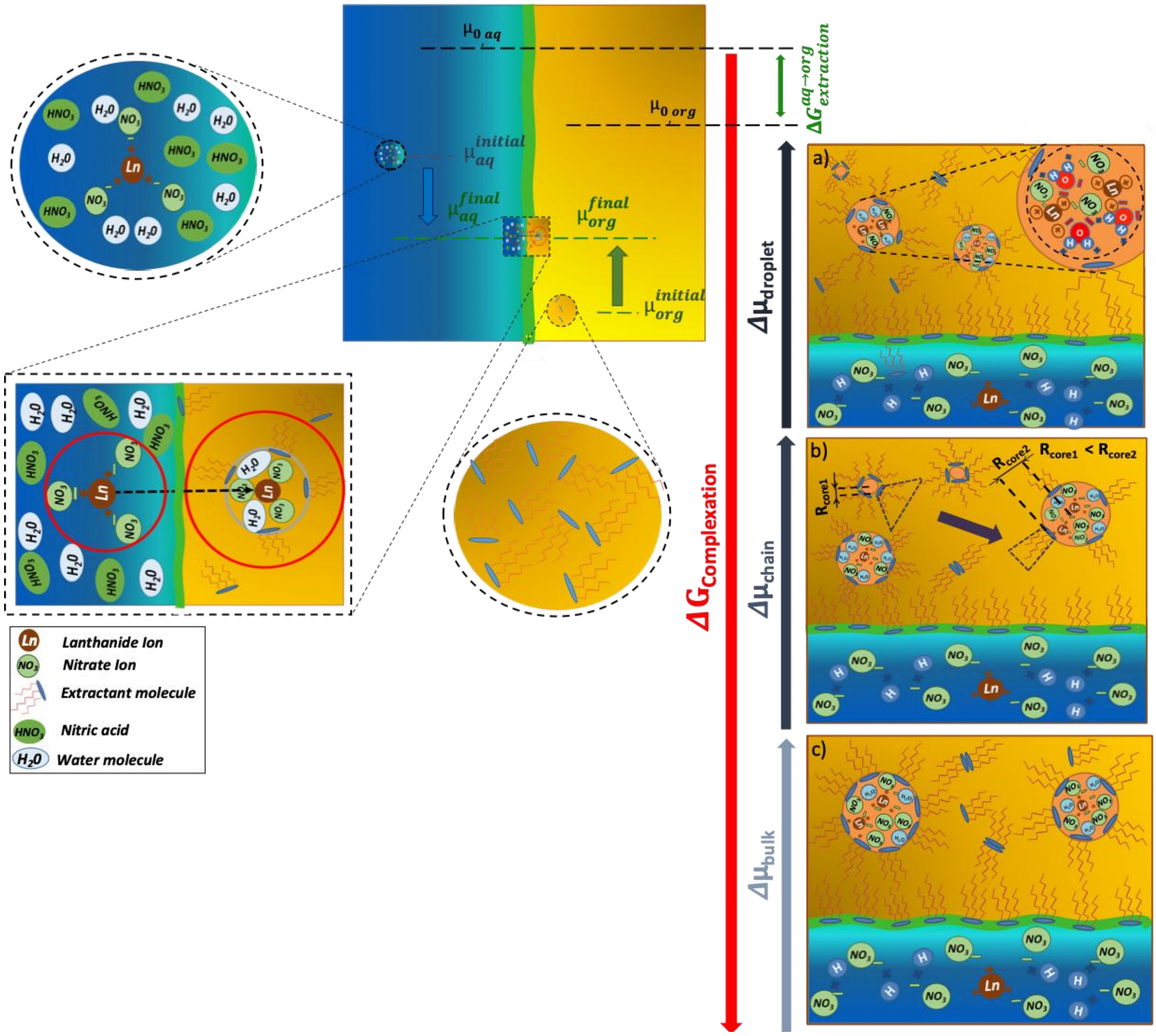


Figure 6: Relative importance of complexation and aggregation as extraction driving forces. a) Case of metallic cation concentration effect, highlighting free energy difference between concentrated (+) and diluted (-) media;[85] b) Case of aggregation state of the organic phase, highlighting free energy double difference between Nd(III) and Pd(II), and weak or high aggregation obtained at high or low aqueous acid concentration respectively.[46]

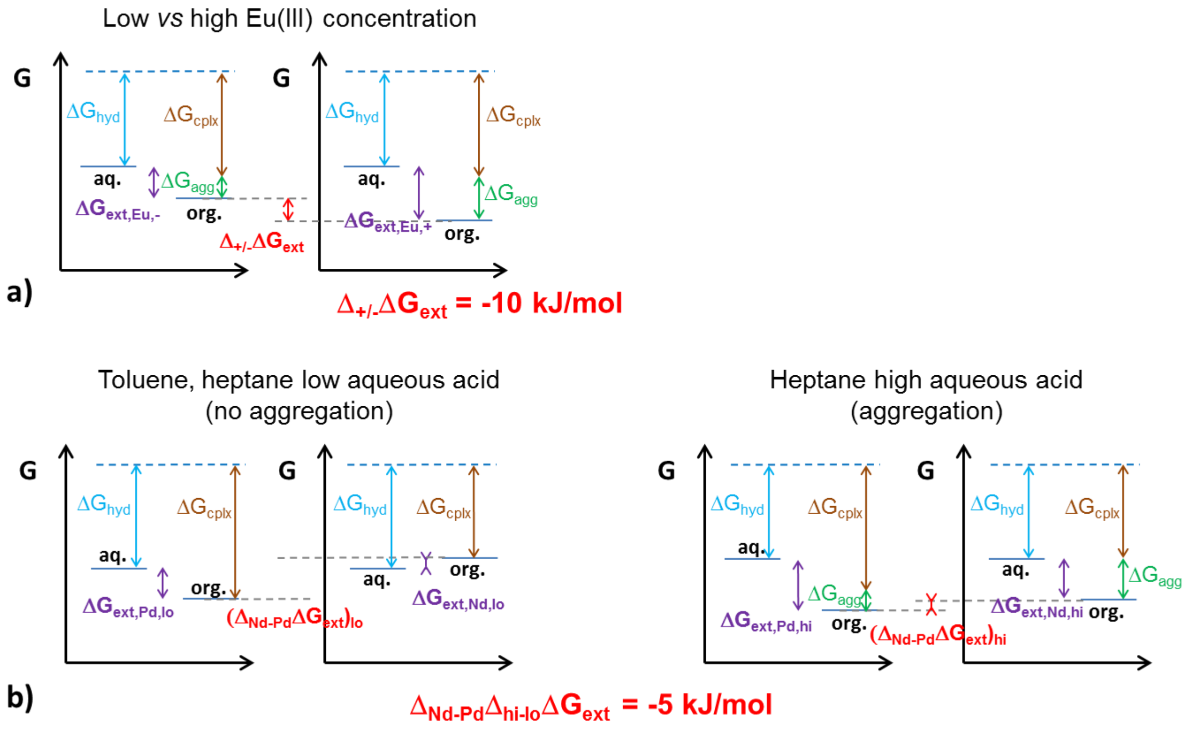
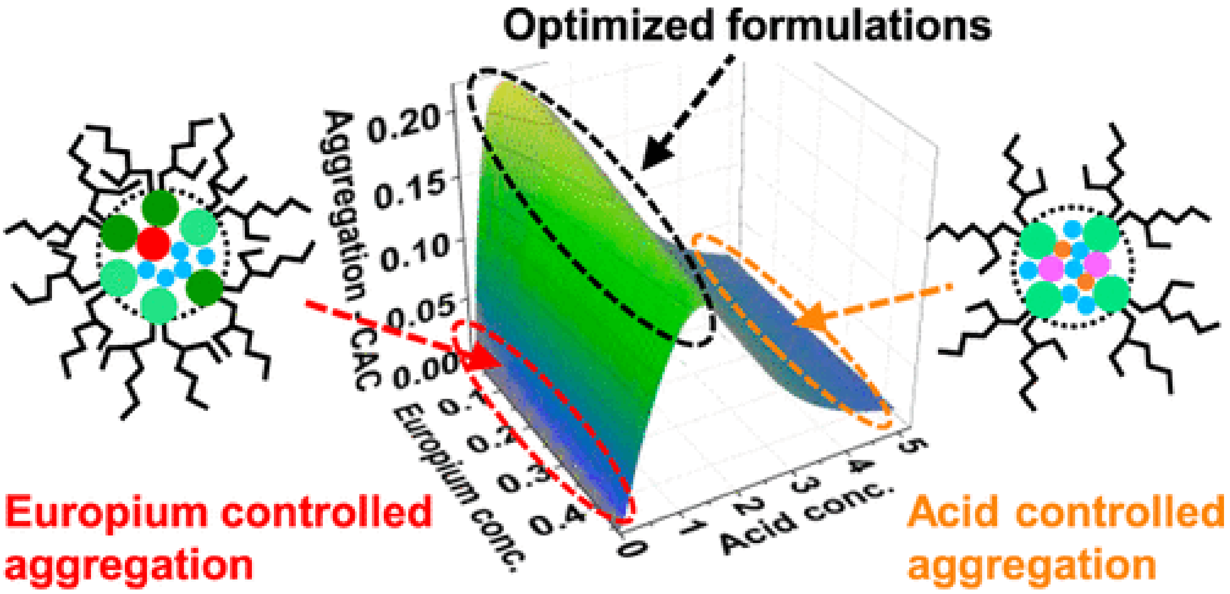


Figure 7: Optimized formulations for extraction of rare earth elements: intermediate between metal-controlled and acid-controlled organization of the organic phase as modelled by Spadina et al..(Figure taken from ref. [69], further permissions related to the material excerpted should be directed to the ACS)



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