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Decreasing viscosity and increasing accessible load by replacing classical diluents with a hydrotrope in liquid–liquid extraction

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Using a generic example, we show that the strategy of replacing a classically used aliphatic diluent with a hydrotrope in liquid–liquid extraction induces higher performance. Liquid–liquid extraction is widely used in hydrometallurgical processes for recycling strategic metals, but it is limited due to the formation of a third phase. Hydrotropes have never been studied as diluents in the context of metal recycling. We show that using hydrotropes as a diluent decreases the viscosity of solutions by more than a factor of ten, even under high load by extracted cations. It also increases the efficiency of extraction for typical ionic extractants such as anionic phosphates or non-ionic amides. The latter also quench all types of third-phase transition that occur when classical diluents are used. The gain in distribution coefficient by a factor of ten comes from the entropy of the solvent phase involved and is not linked to apparent complexation constants. In the case of anionic extractants, the Gibbs energy of transfer depends linearly on the ionic radii of the rare earth considered, which is not true with non-ionic extractants. Moreover, the maximum load possible is increased by a factor of two to three versus alkanes, allowing more compact design and intensification of extraction processes. Based on SAXS and surface tension measurements, the origin of this gain in Gibbs energy of transfer and tunable selectivity in the family of rare earth elements is further identified by three mechanisms: reduction of the term linked to complexation, more than compensated by a synergistic effect of the hydrotrope and the comlexant, and the intra-aggregate entropy of mixing. The result is a systematic increase of distribution coefficient of the order of 50–150 of the distribution coefficients, induced systematically by the replacement of alcanes with hydrotropes as diluents.

KEYWORDS

solvent extraction, phase stability, reverse micelle-like aggregates, small angle scattering, mesoscopic structuring, hydrotropes, ienaics

1 Introduction

Metal recycling processes rely on selective extraction and stripping between aqueous and solvent phases. In chemical engineering literature, the solvent phase contains an extracting "solvent" and a "diluent." In physical chemistry, the diluent is called "solvent." This solvent contains an oil-soluble surfactant that has some affinity for ions—the "extractant." Supra-molecular aggregates made from the electrolytes extracted, the co-extracted water, and a number of complexes are considered stoichiometric complexes when a tentative prediction of hydrometallurgical processes is attempted. The oligomeric aggregates of extractants form objects of colloidal size (>1 nm) that have been termed either "reverse micelles," or weak (w/o) aggregate, and even "clusters" in recent literature; all with the meaning of weak aggregation w/o self-assembly as polydisperse aggregates (Zemb and Kunz, 2016).

When there are less than four molecules located "around" the extracted cation and the amount of co-extracted water is negligible, no "internal volume" can be defined unambiguously. In this case, the most precise concept used in the literature is the concept of multi-scale mononuclear clusters (Motokawa et al., 2019). The presence of free water inside a w/o colloidal aggregate is necessary for obtaining a microemulsion. Methodologies used to study microemulsions have been successful in characterizing and modeling aggregates involved in liquid–liquid extraction (Osseo-Asare, 2002); however, to the best of our knowledge, microemulsions containing a freely moving water core have never been considered or observed in hydrometallurgy linked to rare earth extraction. An extant problem in the field of liquid–liquid optimization is the still unknown effect of bicontinuity between polar and apolar volumes.

This study considers two emblematic and well-studied cases of rare-earth extraction performed by either an anionic extractant Bis(2-ethylhexyl)phosphoric acid (HDEHP) or a solvating extractant, N, N′-dimethyl-N,N′-dioctylhexyl-ethoxymalonamide (DMDOEHMA). All else being equal, we try to investigate the effect of replacing the alkane solvent with a hydrotrope and to identify the advantages and drawbacks of the consequences of that replacement (Zemb and Kunz, 2016).

A "hydrotrope" is a molecule that is able to dissolve high insoluble quantities when present in water above a critical concentration but without forming micelles by themselves. One attraction of using hydrotropes is that they have been known and used for a long time in industry to avoid the formation of liquid crystals in home care, cosmetics, and pharmaceutical applications. Their use has never been described in the context of hydrometallurgy. Hydrotropes are molecules that decrease viscosity when they are used in complex formulations.

Hydrotropes can thus be considered a type of phase "modifier" (El Maangar et al., 2022). As additives, they enhance the solubility of insoluble molecules in a solvent and, at the same time, close the miscibility gap between immiscible solvents. Since hydrotropes close water-solvent miscibility gaps with less than 50% addition by volume, they are of great interest when process safety is a priority, as with the nuclear industry (Zemb and Kunz, 2016). However, the drawback of hydrotropes is that they are soluble in similar quantities in water- and solvent-rich phases, and the hydrotrope must be removed from the mixed fluid after the stripping process. This step can induce high costs that are not economical for low value metal hydrometallurgy. In the case of nuclear fuel recycling or rare earth recovery from waste, the future clearly favors hydrotropes with acceptable flash points; in this domain, hydrotropes that are solids at room temperature are clearly one solution for the future of hydrometallurgy.

In the case of liquid–liquid extraction, the effect of hydrotropes is apparent as a *de facto* modification of apparent extraction reaction constants used to model measurements of species. Replacing solvents by hydrotropes modifies the type of mechanism responsible for extraction. Those are currently classified in one of 17 classes of extracting systems. This 17th class regroups all cases that are paradoxical and cannot be classified in the first 16 (Rydberg et al., 2004).

The threshold for allowing the solubilization of hydrophobic substances in water above the critical aggregation concentration "cac" is illustrated in Figure 1. It can be seen there that the typical values of the solubilization threshold for hydrotropes, such as sodium xylene sulfonate (SXS) or 1-propoxy-2-propanol (PnP), are two orders of magnitude higher than that of classical surfactant sodium dodecyl sulfate (SDS). In the latter case, the solubilization threshold is close to the critical micellar concentration (cmc). Hydrotropes are soluble in water as well as in oil, making the process chart a little bit more complicated than when insoluble branched alkanes are used as diluents (El Maangar et al., 2022). However, all extractants currently used in industry are soluble in hydrotropes, making more efficient processes of extraction and stripping with a formulation based on full or partial replacement of alkanes by hydrotropes possible.

The aim of this study is to determine and explain the observed effect of replacing classical alkanes with hydrotropes within the frame of ieanics theory (Špadina et al., 2019b). Ienaics go beyond the formation of stoichiometric complexes and take into account all molecular forces that combine during the extraction or stripping of electrolytes. The ienaic approach decomposes the Gibbs energy of extraction in "motors", favoring the solvent phase such as

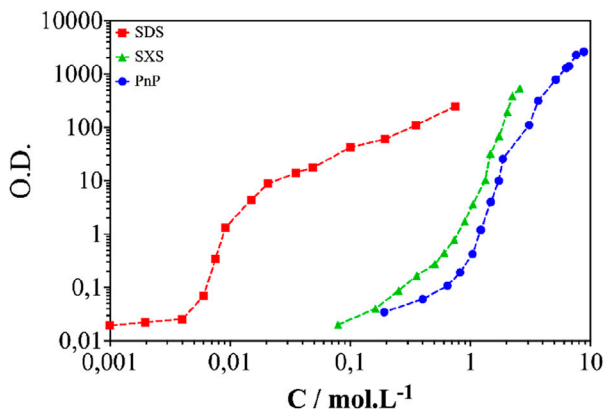

FIGURE 1
Optical densities, proportional to the amount of dissolved Disperse Red 13 dye, as a function of the concentration of sodium dodecylsulfate SDS (■), sodium xylene sulfonate SXS (▲), and 1-propoxy-2-propanol PnP (●) in water (reproduced from El Maangar (2022) with permission).

complexation and entropic effects, and "brakes" that favor the aqueous phase that are linked to solvent organization, the formation of aggregates, or the elastic energy of deformation of the bent molecular film forming an aggregate (Zemb et al., 2015). In the case of weak aggregation, there is little bending effect on the film formed around the core, but the Gibbs energy cost of forming a reverse aggregate is lower, as can be deduced from the high value of the cac (Rey et al., 2017). When the reference state is taken as a solution in the presence of 1M of extractant, the cost in free energy of forming a reverse aggregate is given by RTln (cac).

Even in the absence of a solvent as molecules directly involved in the transfer reaction induced by the complexation of cations by an extractant, we will show the profound influence of replacing the nature of the solvent in terms of viscosity, formation of a stable emulsion via the third phase formation, and spectacular effects on the distribution coefficient of rare earths.

2 Experimental section

2.1 Chemicals

The solvating extractant N,N′-dimethyl-N,N′-dioctylhexyl-ethoxymalonamide (DMDOHEMA) was purchased from Technocomm Ltd. (UK), and the cation exchanger Bis(2-ethylhexyl)phosphoric acid (HDEHP) was purchased from Sigma-Aldrich, both with purities higher than 98%. We purchased 1-propoxy-2-propanol (PnP) from Sigma-Aldrich with a purity higher than 99%. Water was deionized using a Millipore Milli-Q purification system (Merck Millipore, Billerica, MA). All other chemicals where purchased from commercial sources: 70% nitric acid HNO_3 (Sigma Aldrich), lanthanum(III) nitrate hexahydrate $La(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich; purity> 99,99%), neodymium(III) nitrate hexahydrate $Nd(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich; purity> 99,9%), europium(III) nitrate hexahydrate $Eu(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich; purity,> 99,9%), dysprosium(III) nitrate hexahydrate $Dy(NO_3)_3{\cdot}6H2O$ (Sigma Aldrich; purity > 99,9%), ytterbium(III) nitrate hexahydrate $Yb(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich; purity, > 99,9%) and iron(III) nitrate nonahydrate $Fe(NO_3)_3{\cdot}9H_2O$ (Sigma Aldrich; purity, > 99,999%). All chemical products were used without further purification.

2.2 Extraction procedure with hydrotropes

Unlike conventional diluents, the hydrotropic molecule PnP is soluble in water as well as in the diluent or the extractant. This means that when the aqueous and organic phases come into contact, some non-negligible quantity of PnP is transferred between them. Consequently, extractant concentrations in the aqueous phase are similar to those in the organic phase when classical extracting molecular systems are considered for comparison. To isolate the transfer of ions from the transfer of hydrotropes, a pre-equilibration step is performed before any extraction or stripping is performed. This involves introducing a known quantity of PnP into the aqueous phase according to the location of the tie line of the ternary system (Figure 2) in which extraction conditions would be performed. The phase diagrams below are derived from the systematic preparation of 60 samples allowing a location of the miscibility gap, without and with added lanthanide salt. Tie-lines were determined by chemical analysis after phase separation. Hydrotropes usually close the miscibility gap with 20%–50% of hydrotropes. For the two extractants used, PnP is intrinsically a hydrotrope but closes the miscibility gap for concentrations well above 50 wt% (Figure 2). In the of DMDOHEMA, the hydrotrope acts as a common hydrotrope. In the case of HDEHP, PnP acts more as a co-solvent since the miscibility gap is only closed when 80% of PnP is used. The location of the critical point is not modified by the addition of rare earth salts, but the tie-lines are slightly rotated in the phase diagram; this must be considered when the colloidal structures present near the phase boundaries are determined.

2.3 X-ray fluorescence (XRF)

The Gibbs energy of transfer ($\Delta_{tr}G$, Equation 1) per mole transferred from the aqueous to the solvent phase is accessible for each of the points used in the miscibility gap following the expression (Špadina et al., 2021):

$$\Delta_{tr}G = RT\ln \frac{[\text{Cation}]_{\text{aqueous}}}{[\text{Cation}]_{\text{solvent}}}. \quad (1)$$

The optimal value for designing an efficient cascade process is to obtain a yield of 80%–97% of extraction per stage (free energy of transfer between - 3.5 and - 8.7 kJ mol^{-1}). We mark this "ideal domain" with a green zone in the figures reporting the results of extraction experiments.

The precision required in $\Delta_{tr}G$ to understand what is occurring at the molecular scale is higher than most published values, usually when the latter are determined via chromatographic methods. An uncertainty range below $1k_BT$ is nearly impossible to achieve via chromatography because the crucial point is the precision of the traces left in the water phase for efficient extraction and in the oil phase when the Gibbs energy of transfer is positive. Therefore, we performed simultaneous XRF analysis in the metal-rich and metal-poor fluids after extraction to determine REE concentration in aqueous and organic phases with the same analytical method as previously (El Maangar et al., 2020). In order to quantify the elements from the raw spectra, we used a calibration procedure described in Kirsanov et al. (2014) and Maurice et al. (2021). Precise determination of the free energy of transfer needs precise evaluation of the ratio of species between two phases versus time. Relying only on mass balance after chemical analysis of one phase only by chromatography does not provide the accuracy required in free energy of transfer if experiments are to be compared with expectations of parameter-free theories.

2.4 Small-angle X-ray scattering (SAXS)

Small- and wide-angle X-ray scattering experiments were performed on the home-built SAXS camera at ICSM—a home-designed camera sealed with a Mo source (wavelength λ = 0.71 Å). The online detector (MAR Research 345, diameter = 345 mm) allows the simultaneous capture of SAXS and WAXS (distance 0.75 M from the sample). Off-center detection was used to

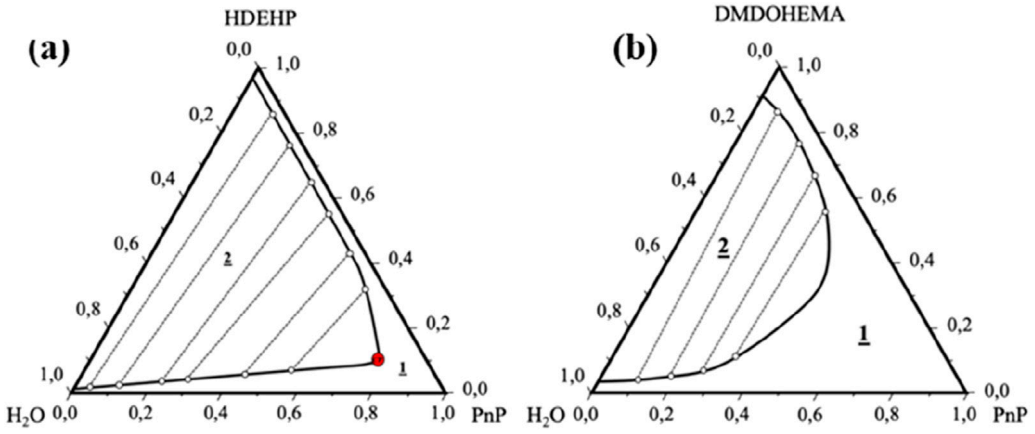

FIGURE 2
Ternary diagram **(A)** H_2O/HDEHP/PnP; **(B)** H_2O/DMDOHEMA/PnP.

improve q-range. The two-dimensional spectra were integrated with FIT2D software. Data were normalized for the electronic background of the detector, transmission measurements, and empty cell subtraction. The typical acquisition time was 1 hour in order to reduce the effect of decay of the latent image stored as excited complexes (Prevost et al., 2016).

2.5 Surface tension measurements

Surface tension measurements were made using a Force Tensiometer–K100 (Kruss GmbH, Hamburg, Germany) with a measurement range of 1–2000 mN m^{-1} and a resolution of 0.001 mN m^{-1}. Different solutions were prepared by mixing organic solutions (HDEHP and DMDOHEMA diluted in PnP and dodecane) and aqueous solutions ([Eu] = 10 mmol.L^{-1} in $C(HNO_3)$ = 0.03 and 3 mol.L^{-1} for HDEHP and DMDOHEMA, respectively). Those solutions were then transferred into a cylindrical measurement cell for 5,000–8,000 rpm centrifugation in order to allow complete phase separation mostly within a few minutes.

3 Results

The efficiency and selectivity of a liquid–liquid extraction process depends not only on the extractants but also on the diluent used, even if the latter has no direct interaction with the extracted ions. The main factors limiting this type of process are usually the kinetics associated with complex formation at the interface between the two phases, such as the formation of a third phase (Poirot et al., 2014; Roberto Danesi et al., 1980; Vasudeva Rao and Kolarik, 1996). On the one hand, the formation of aggregates increases extraction performance such as selectivity, distribution coefficient, and kinetics (Bauer et al., 2012; Moyer, 2010; Roberto Danesi et al., 1980). On the other hand, organic phase structuring could lead to undesirable effects such as emulsion instability, increased viscosity, or the formation of that third phase (Bauduin et al., 2007; Lefrancois et al., 1999; Pathak et al., 2009; Testard et al., 2010; Vasudeva Rao and Kolarik, 1996).

Choosing a suitable diluent is essential for a liquid–liquid extraction process since it is the key to the viscosity and density of the organic phase control. Both terms contribute to better phase separation. However, diluents tend to lead to third-phase formation if the extractant or metal concentration is too high. For example, third-phase formation is more frequent with aliphatic than with aromatic diluents (Osseo-Asare, 2002). Likewise, long-chain alkyl diluents are usually more inclined to form a third phase than short, branched-chain alkyl diluents (Chandrasekar et al., 2016; Chiarizia et al., 2003; Chiarizia et al., 2004; Rao et al., 1993; Vasudeva Rao and Kolarik, 1996). The“ third phase” phenomenon involves the separation of the organic phase into a light phase (a diluted solution of non-aggregated monomers of extractant) and a heavy viscous phase (high extractant, ions and acid concentrated) (Bauduin et al., 2007; Testard et al., 2010). Currently, no diluent used in industrial processes efficiently prevents the formation of this third phase at a high load of extracted metal. Therefore, we investigate the impact of replacing conventional diluents with hydrotropic compounds at different scales on the efficiency and stability of extraction phases.

A systematic comparison between a conventional system (aqueous phase/extractant/diluent) and a hydrotropic system (aqueous phase/extractant/hydrotrope) was made using two extractants as generic examples (HDEHP as model of anionic extractant and DMDOHEMA as model of chelating extractant) well known for rare earth extraction in nitric media (Antonio et al., 2008; Déjugnat et al., 2014; Gannaz et al., 2006; Innocenzi et al., 2015; Jowitt et al., 2018; Masry et al., 2015; Mowafy and Aly, 2002; Muller et al., 2016; Narita et al., 1999; Spjuth et al., 1997; Zhao et al., 2017). HDEHP extracts REEs by ion exchange (acid functions) while DMDOHEMA extracts REEs by forming a solvation shell (complexes or polynuclear neutral aggregates) in the organic phase.

3.1 Determining the Eu loading capacities of HDEHP and DMDOHEMA

The loading capacities of HDEHP and DMDOHEMA were determined by performing extraction tests in a range of initial Eu

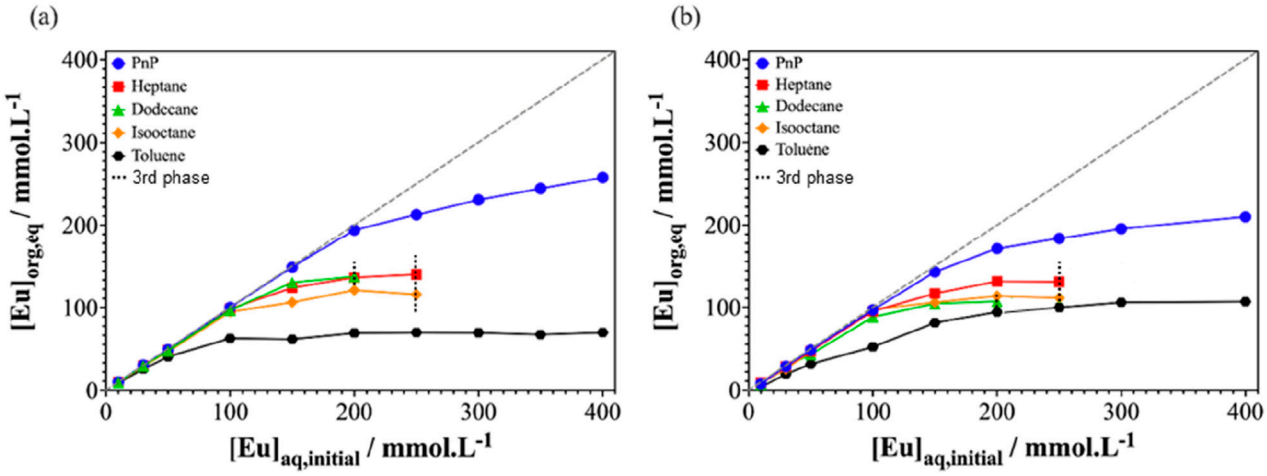

FIGURE 3
Comparison of Eu concentration in the aqueous and organic phases according to the diluent used in nitric acid (0.05 mol.L^{-1}): **(A)** HDEHP (0.6 mol.L^{-1}); **(B)** DMDOHEMA (0.6 mol.L^{-1}).

concentrations from 10 to 400 mmol.L^{-1} in nitric acid (0.05 mol.L^{-1} for HDEHP and 4 mol.L^{-1} for DMDOHEMA). The organic phase is composed of 0.6 mol.L^{-1} of extractant diluted in PnP, dodecane, heptane, isooctane, and toluene. By increasing the initial Eu concentration, a third phase was formed using dodecane, heptane, and isooctane as diluents, but in both toluene and PnP, neither a third phase nor a precipitate were observed (Figure 3).

When toluene was used as the diluent, Eu loading reached a plateau at approximately 100 mmol.L^{-1} for both extractants (Figure 3). No saturation for the PnP was observed, and the Eu loading still increased over the concentration range studied (Figure 3). Therefore, the Eu loading capacity for PnP was at least 400 mmol.L^{-1}, which was twice higher for HDEHP and DMDOHEMA, respectively. Moreover, the replacement of classical solvents in current use by pnp eliminates the phenomenon of third-phase formation, which is an extremely limiting factor in practical applications.

In all cases, extreme care was taken when determining single phase limits; the protocols recommended by Arce et al. (2022) were used at delicate points. Near the critical point, equality in volumes of the tow phase produced just "below" the critical point was the most efficient determination method.

We now compare the behavior of the viscosity of the solutions (Figure 4). Hence, the viscosities of the organic phases before and after Eu extraction were measured for conventional extraction systems (dodecane, heptane, toluene, isooctane) and the hydrotrope PnP. Absolute viscosities are plotted as a function of solute concentration (in this case, the Eu cation). For this purpose, viscosity was normalized by the viscosity of the extractant/diluent mixture before contact with the aqueous phase. As can be seen, the normalized viscosity related to the non-contacted solvent was not equal to 1 at [Eu] = 0 mol.L^{-1}. This demonstrates that the viscosity already increased by one factor after contact with nitric acid. Figure 4 shows that the viscosity of the organic phase depends on the concentration of Eu and the nature of the diluent used. In both cases (HDHEP and DMDOHEMA), viscosity increased with europium concentration for all diluents tested (Figure 4). The most striking observation was that the hydrotrope was nearly as efficient as the toluene in reducing viscosity, even under high load. Reduced viscosity—viscosity under load divided by the viscosity in the absence of metallic load—is a key property in practical applications. Maximum viscosity was achieved when dodecane was used as a diluent, while minimum viscosity was achieved by PnP. Viscosity increased at the same order as the third phase formation (dodecane > isooctane > heptane > toluene > PnP). This suggests the existence of a fundamental link between the formation of the third phase and the viscosity rise. Indeed, by comparing Figures 3 and 4, it is evident that viscosity increases exponentially from 15 to 25 times the non-contacted Eu phase viscosity for diluents forming a third phase—dodecane, isooctane, and heptane. On the other hand, viscosity did not exceed two to four times the value of the non-contacted organic phase for toluene and PnP; for those diluents, no third phase phenomenon was observed.

3.2 Impact of using a hydrotrope as a diluent for REE extraction

Using a hydrotrope decreases viscosity and also quenches the formation of a third phase. What about the extraction efficiency obtained by replacing alkanes in a hydrotrope? To answer this question, extraction tests were carried out in batch mode by contacting the same amount of extractant in the organic phase (0.6 mol.L^{-1} of HDEHP or DMDOHEMA) but diluted by dodecane or by PnP, and an aqueous phase containing La, Nd, Eu, Dy, Er, and Yb (10 mmol.L^{-1} each) diluted in nitric acid (0.05 and 3 mol.L^{-1} when respectively HDEHP and DMDOHEMA).

To our great surprise, both the ionic extractant HDEHP and the solvating extractant DMDOHEMA showed higher extraction efficiencies when PnP was used instead of dodecane. Since hydrotropes were also present in the water phase, the presence of supra-molecular complexation only would produce a decrease in the efficiency of extraction. Therefore, other molecular mechanisms must come into play when hydrotropes are used instead of

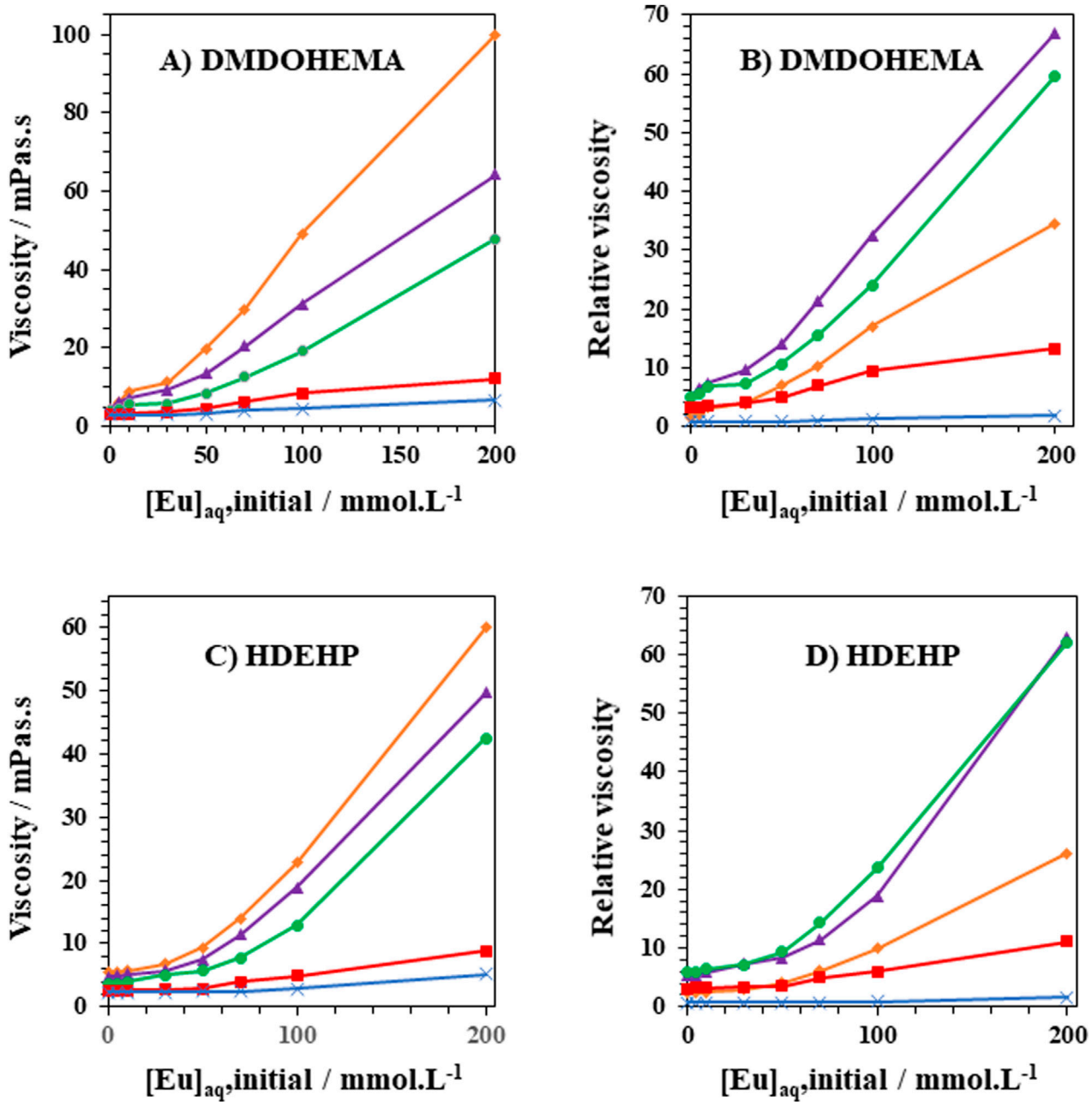

FIGURE 4
(A, C) Viscosity and **(B, D)** relative viscosity of the organic phase as a function of the initial concentration of Eu. The organic phase contains HDHEP (top) or DMDOHEMA (bottom) at a concentration [extractant] = 0.9 M diluted in different diluents and hydrotrope.

branched alkanes. All of these molecular mechanisms have an important entropic contribution. They must be known in ternary systems, for which reasonable approximations have only recently become available (Marčelja, 2017). Synergy between two extracting molecules was investigated by Julien Rey and colleagues and could be there attributed to entropic effects (Rey et al., 2017; Rey et al., 2017).

The quantification of the efficiency implies a precise determination of the Gibbs energy associated with the transfer of one europium from the aqueous to the solvent phase. Transfer of a cation from a water-rich to an extractant-rich phase implies several phenomena: co-extraction of water and partial transfer of the counter-ions but also reorganization of the solvent phase microstructure. The precision required is less than 1 k_BT, implying the measure of the cations present in both phases by X-ray fluorescence. Chromatographic measurement on only one phase did not produce results with the precision required to identify the underlying molecular mechanism involved in the transfer of metals.

In classical treatment, only complexation is considered, and all terms linked to entropy and solvent reorganization are neglected. This is why the classical theory that adjusts apparent complexation

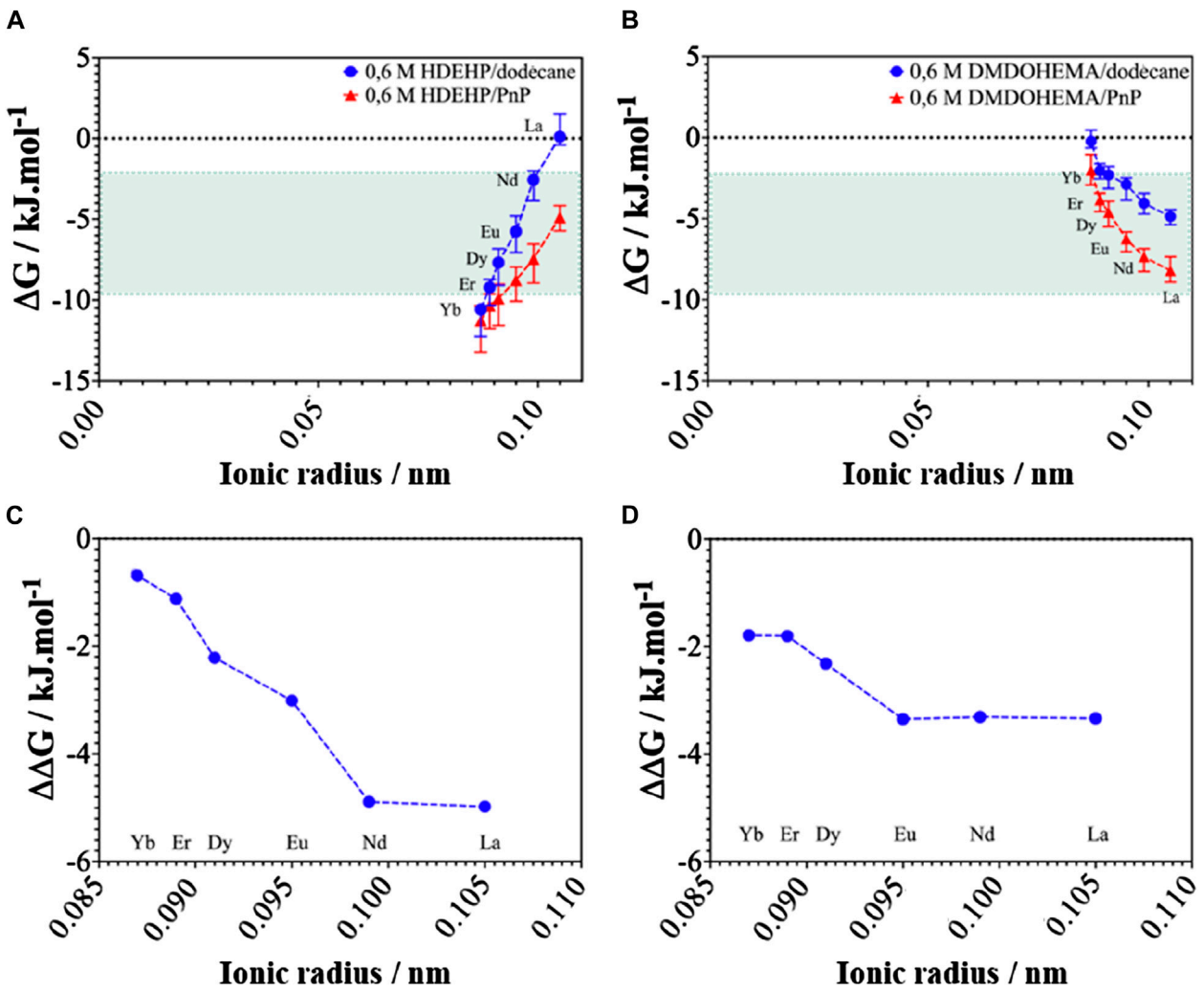

FIGURE 5
Top **(A,B)**: free energy of transfer ΔG from the aqueous to the organic phase for six rare earths (La^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}) as a function of their ionic radius. Bottom **(C,D)**: Difference in transfer free energy (ΔΔG) between the system with dodecane and that based on PnP for the six rare earths and as a function of ionic radius. **(A,C)** Aqueous phase: [REE] = 10 mM each and HNO_3 = 0.05 mol.L^{-1}, in contact with 0.6 M HDEHP diluted in dodecane or in PnP after pre-equilibration of the aqueous phase. **(B,D)** Aqueous phase: [REE] = 10 mM each and HNO_3 = 3 mol.L^{-1}, in contact with 0.6 M DMDOHEMA diluted in dodecane or PnP after pre-equilibration of the aqueous phase.

constantly fails to predict variation of the Gibbs energy of transfer when only the nature of the diluent is changed, all other factors being kept constant (El Maangar et al., 2022). Indeed, the transfer free energy gain ($\Delta\Delta G_{tr}$ = ΔG_{tr}(species A) - ΔG_{tr}(species B)) corresponding to the difference in ΔG between the extractant/dodecane and extractant/PnP systems is 0.5–5 kJ mol^{-1} for HDEHP and 2 and 3.5 kJ mol^{-1} for DMDOHEMA (Figure 5). This variation is equivalent to an increase in distribution coefficient of 1.3–7.5 times the value observed for the classic extractant/dodecane system. Since the molecular affinity of extractants toward REEs is unaffected, the origin of this increase must be a decrease in the cost of reorganization around the metal linked to more configurations with the same efficiency (Špadina et al., 2019b). Moreover, the extracting power of HDEHP increases with the atomic number of the lanthanides. DMDOHEMA shows exactly the opposite behavior, with extraction efficiency increasing with the ionic radius of the REEs (Figure 5). This can be understood by a variation of the chain packing term around the ion: it is easier to swell the polar core with DMDOHMA and more difficult with HDEHP. The chain packing term linked to bending is due to differences in spontaneous and effective packing parameters of the molecular films involved. Quantifying these effects is beyond the scope of this work; a general approach to the cost in enthalpy per molecule of mismatch between spontaneous and effective packing is described in Dufrêche and Zemb (2020).

These three positive results (quenching of the third phase formation, reduction of viscosity, and increasing either the distribution coefficient or the transfer efficiency) pave the way for the use of hydrotropes as a substitute for conventional diluents. In the following paragraphs, we will consider the case of Eu only to check how the formulation parameters, such as acid concentration and optimal concentration of extractant, are impacted by the replacement of classical solvents by hydrotropes.

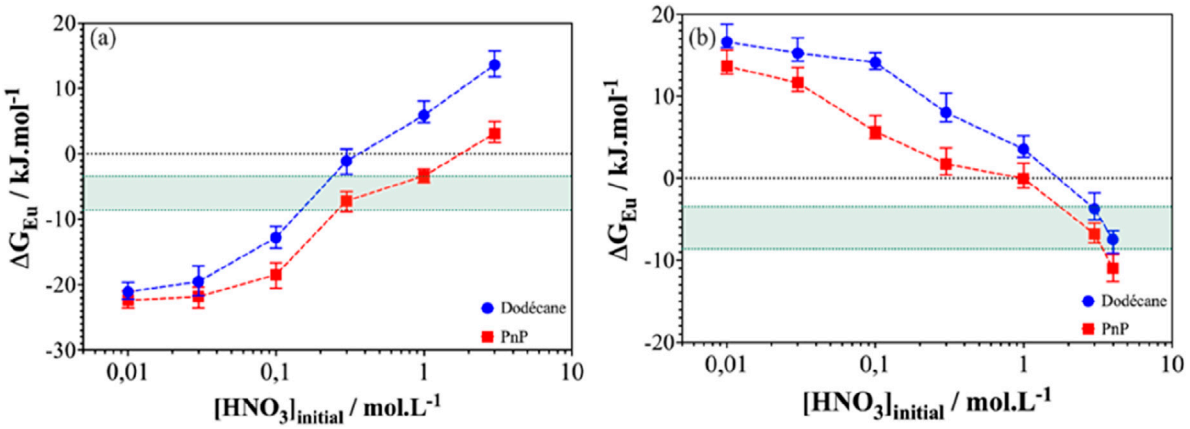

FIGURE 6
Free energy of transfer ΔG from the aqueous to the organic phase regarding aqueous-phase acidity. The aqueous phase contains 10 mmol.L^{-1} of Eu and HNO_3 from 0.01 to 4 mol.L^{-1}. The organic phase contains **(A)** [HDEHP] 0.6 mol.L^{-1} and **(B)** [DMDOHEMA] = 0.6 mol.L^{-1}. The green zone is the zone for which extraction can be performed in an efficient cascade that minimizes effluents.

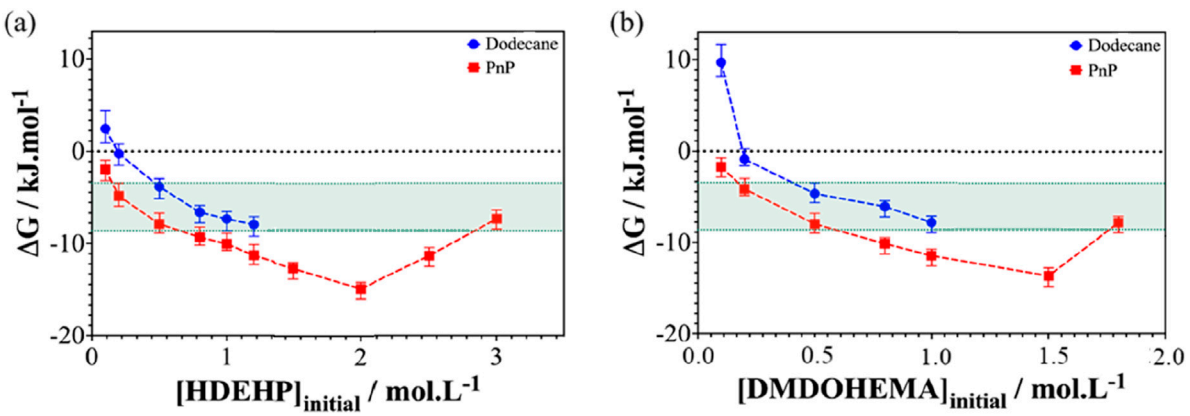

FIGURE 7
Free energy of transfer ΔG from the aqueous to the organic phase regarding the concentration of extractants. The case of dodecane cannot be explored at high concentration because of the occurrence of a third phase. **(A)** The aqueous phase contains 10 mmol.L^{-1} of Eu in HNO_3 0.3 mol.L^{-1}, and the organic phase contains HDEHP diluted in dodecane or PnP. **(B)** The aqueous phase contains 10 mmol.L^{-1} of Eu in HNO_3 3 mol.L^{-1}, and the organic phase contains DMDOHEMA diluted in dodecane or PnP. The green zone is the zone for which extraction can be done in an efficient cascade minimizing effluents.

3.2.1 Effect of nitric acid concentration

The effect of the acidity of the aqueous phase was compared to the two extractants diluted in dodecane or PnP. The aqueous phases are composed of 10 mmol.L^{-1} europium diluted in a nitric acid solution of variable concentration and then contacted with organic phases containing 0.6 mol.L^{-1} of extractant. For each extractant, Eu extraction depends on the nitric acid concentration. At low acidity, Eu extraction with HDEHP is at its highest and decreases proportionally with increasing nitric acid concentration. The opposite occurs when the chelating extractant DMDOHEMA is considered. At low acidity, Eu extraction is minimal and grows with increasing concentration. Figure 6 shows that the global effect of concentration as well as of acid is unchanged. This means that the complexation number—that is, the number of complexants directly linked to the cation—is very similar in the case of hydrotropes and alkanes. The aggregation number is given by SAXS studies performed on absolute scale increases. The aggregation number is the sum of the complexation number and the number of adducts present in a w/o aggregate. Therefore, the number of adducts changes (see Table 2).

Since more molecules are involved in a weak aggregate, the extraction efficiency is improved without any change in the "affinity" of a complexant. If we consider, for example, a typical aggregate comprising eight molecules, four extractants, and four hydrotropes acting as adducts, an intramicellar entropic term as 8!: $(4!)^2$ appears. This purely entropic term represented on its own is RT.ln (70)—10 kJ/mol, about twice the systematic increase in extraction efficiency obtained by replacing alkanes with hydrotropes (Spadina, 2019). In complex fluids with four components or more, the formulation used to obtain a desired mixed weak aggregate that is stable in the bulk solvent is key to

the efficiency of the whole process, more than the search for different complex shapes that are supposed to control supramolecular complexation, as in solids.

If some refinery within the lanthanide series is requested by the application, so that that heavy or light lanthanides are to be extracted from a mixture, the double difference between Gibbs energy of transfer $\Delta\Delta G_{tr}$ must be considered: the element with the most negative Gibbs energy of transfer can in some cases be selectively extracted from the solvent. As revealed in Figure 5, inter-rare-earth selectivity remains unchanged whatever the diluent considered. The bottom line of Figure 5 shows this relative selectivity. HDEHP extracts heavy rare earths better than light ones, while DMDOHEMA extracts light REEs better than heavy ones.

As is evident from Figure 6, the replacement of alkanes by hydrotropes also does not substantially modify the effect of acidity. Chelating ions need high acid concentrations to capture more ions in the short range associated with the mechanism of chelation, while acidic extraction dependent on cation exchange works better with lower ionic strengths, such as in the absence of acids in the aqueous phase. As can be seen in Figure 6, the optimal domain for efficient extraction shown in green is only slightly modified by the replacement of alkane by hydrotropes. On the other hand, by quantitatively comparing extraction data, extraction is significantly better using PnP over the whole acidity range studied for all rare earths and both extractants considered. The free transfer energy increases from 10 to 14.3 kJ mol^{-1} with HDEHP at 0.03 $mol.L^{-1}$ HNO_3 and from 3.7 to 6.7 kJ mol^{-1} with DMDOHEMA at 3 $mol.L^{-1}$ HNO_3, corresponding to a distribution coefficient five and three times larger, respectively. This improvement extends the acidity range for which both extractants are efficient. For example, HDHEP diluted in dodecane no longer extracts (i.e., $\Delta G = 0$) europium from an upper nitric acid limiting concentration of 0.3 $mol.L^{-1}$. By replacing dodecane with PnP, this limiting concentration is increased to 0.7 $mol.L^{-1}$. Similarly for DMDOHEMA, the lower limiting concentration is reduced from 2 to 1 $mol.L^{-1}$.

3.2.2 Effect of the extractant concentration

The influence of HDEHP DMDOHEMA concentration on the free transfer energy was studied by contact during the organic phase with an aqueous solution containing 10 $mmol.L^{-1}$ of Eu in the desired nitric acid concentration (Figure 7). Above a certain extractant concentration (1.2 and 1 $mol.L^{-1}$ for HDEHP and DMDOHEMA, respectively), the organic phase splits into two fluids that can be separated by typically waiting for a few hours or accelerated by soft centrifugation. A third phase appears for both extractants when the diluent is dodecane. Moreover, the distribution coefficients of metals are profoundly modified when different alkanes are used a diluent. In classical supramolecular theory based solely on competition between water-in-oil complexes, large modifications observed in distribution constants versus diluent nature cannot be reconciled with values expected by theories that rely on competing complexes. Using the ienaïc theory, the diluent is similar to molecules which wet or do not wet the polar cores by penetrating the chain brush of the w/o aggregates formed around each extracted cation. This was first modeled by Berthon et al. (2007).

However, when the extractants were diluted in PnP, no third phase was observed in the concentration range studied. At the same time, Eu extraction improved with this particular system. Using PnP not only improves extraction yield, but it also avoids the formation of the third phase, which is considered a major problem in industrial liquid–liquid extraction. Moreover, extraction performance is improved at relatively low extractant concentrations (2 and 1.5 $mol.L^{-1}$ for HDEHP and DMDOHEMA, respectively), enabling the feed-stock of processes to be increased without the risk of a third phase and thus reducing organic effluents and the energy consumption associated with their post-treatment.

In order to understand why this gain in transfer-free energy occurred, extraction tests with PnP alone were performed by contacting an aqueous phase containing six rare earths at a concentration of 10 $mmol.L^{-1}$ each, diluted in nitric acid to 0.05 or 3 $mol.L^{-1}$ with an organic phase containing different concentrations of PnP diluted in dodecane. Experimental results show that PnP does not seem to extract REEs, whatever the nitric acid concentration (Supplementary Figure S1).

The synergistic effect between the extractant and PnP corresponds to a systematic downshift induced by replacing dodecane with hydrotropes. The downward shift observed in Figure 8 is an extraordinarily effective synergetic effect of the order of 5–10 k_bT; 12–25 kJ mol^{-1} between extractant and PnP may be explained by the dominant influence of intra-aggregate gain in the configuration entropy of a mixed aggregate. In the absence of synergy, a straight line would be obtained. We can see on the plot that the synergy is greatest when the mole ratio is close to 0.5 excess mixing entropy of extractant and the hydrotrope is maximal. The high entropy gain associated with solvent phase reorganization here again acts to assist chemical engineer in charge of the design of process charts (Špadina et al., 2019a). Pnp is not an efficient extractant in itself—the points are above the green zone, but the mixing entropy with the extractant as well as the intra-aggregate configurational entropy act together to favor the extractant-rich phases. This effect is much more important than loss due to solubility of the extractant in water.

4 Discussion

4.1 Water–solvent surface tension

In order to better understand the origin of the synergistic effect of hydrotrope-based systems on extraction, surface tension, and small-angle X-ray scattering (SAXS), measurements were made with an aqueous phase containing 10 $mmol.L^{-1}$ Eu.

To obtain an initial evaluation of the difference in terms of aggregation between the classical alkane-based system and the hydrotrope-based system, it was necessary to determine the critical aggregation concentration determination (cac) in both cases. To achieve this, surface tension measurements were carried out between the aqueous and organic phases of each system at different extractant concentrations (Figure 9). The reduction of the surface tension profiles as a function of extractant concentration indicates that the extractant molecules are adsorbed at the interface, indicating the amphiphilic and surfactant behavior of the extractant

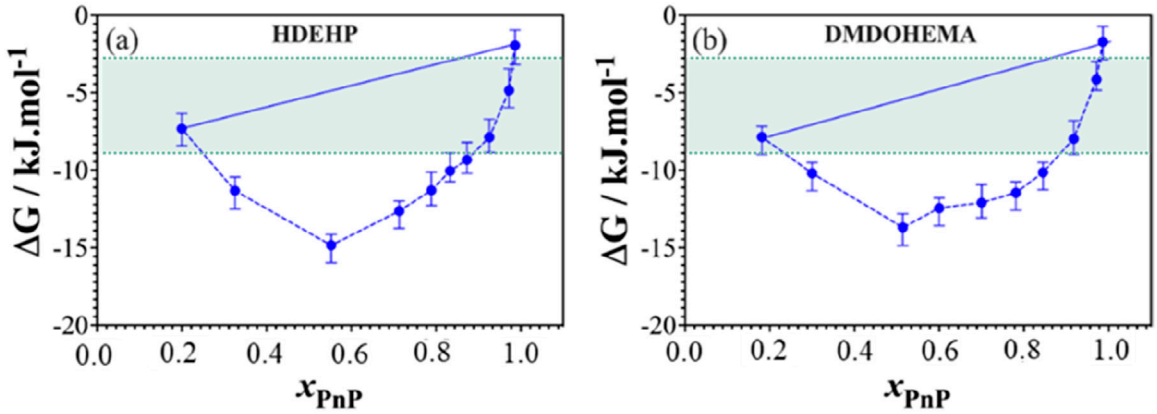

FIGURE 8
Synergy effect between PnP present as a co-surfactant and HDEHP (left) or DMDOHEMA (right) as a function of the mole fraction of PnP. **(A)** The aqueous phase contains [Eu] = 10 mmol.L^{-1}in HNO_3 0.3 mol.L^{-1}, and the organic phase contains different concentrations of HDEHP diluted in PnP. **(B)** The aqueous phase contains [Eu] = 10 mmol.L^{-1} in HNO_3 = 3 mol.L^{-1}, and the organic phase contains different concentrations of DMDOHEMA diluted in PnP. The synergistic point corresponds to x = 0.55 for both extractants. The green zone is the zone for which extraction can be done in an efficient cascade minimizing effluents.

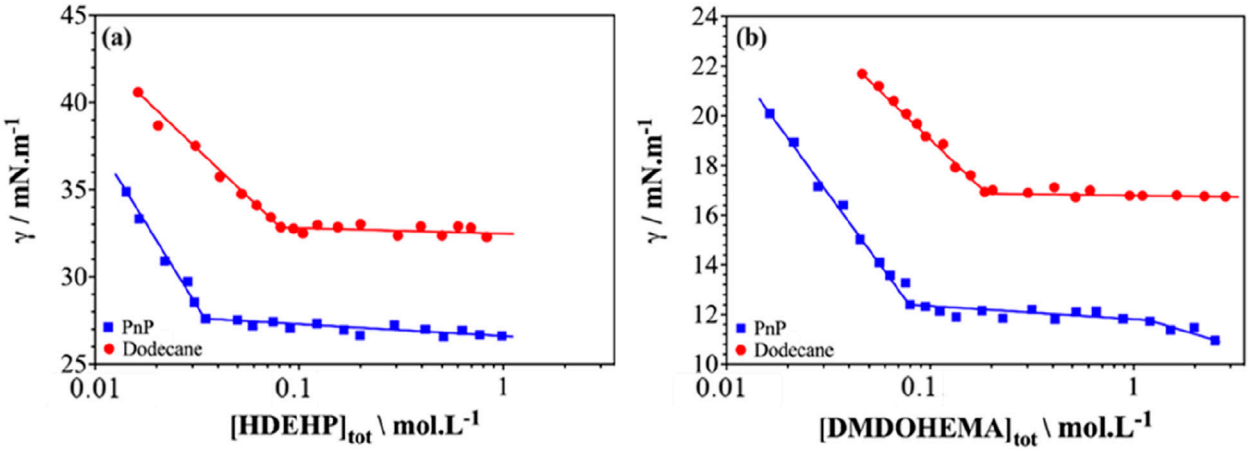

FIGURE 9
Surface tension between aqueous and organic phases as a function of extractant concentration. **(A)** For HDEHP, the aqueous phase contains [Eu] = 10 mmol.L^{-1} and [HNO_3] = 0.3 mol.L^{-1}. **(B)** For DMDOHEMA, the aqueous phase contains [Eu] = 10 mmol.L^{-1} and [HNO_3] = 3 mol.L^{-1}.

molecule. Figure 9 shows that replacing dodecane with PnP reduces the surface tension between the aqueous and organic phases.

This decrease may be due to the weak amphiphilic properties of hydrotropes, which can be adsorbed at the water–oil interface, leading to reduction in the density of the mixture and, thus, the surface tension between the aqueous and organic phases. Moreover, cac values decrease with pnp compared to those with dodecane. The cac decreases from 0.08 to 0.03 mol.L^{-1} for HDEHP and from 0.18 to 0.08 mol.L^{-1} for DMDOHEMA. The Gibbs energy of formation of weak w/o aggregates versus a reference state with 1 mol.L^{-1} of extractant can be evaluated as RT ln(cac) (Tanford, 1973). Aggregates are thus more easily formed in the presence of PnP. The slope of surface tension measurements near the cac are then interpreted as surface area per polar head. At the oil–water interface, the excess surface concentration Γ is then determined from the Gibbs Equation 2 (Berthon et al., 2010; Scoppola et al., 2016):

$$\Gamma = -\frac{1}{RT} \bullet \frac{d(\gamma)}{d(\ln[\text{extractant}])}, \quad (2)$$

where γ is the surface tension (N.m^{-1}), [extractant] is the concentration of extractant in the organic phase (mol.L^{-1}), R is the perfect gas constant (R = 8.314472 J mol^{-1}.K^{-1}), and T is temperature (K). Excess surface concentration Γ can be related to the surface area covered by each extractant σ using the following Equation 3:

$$\sigma = \frac{1}{N_A \bullet \Gamma}, \quad (3)$$

TABLE 1 Surface area σ values per polar head (in Å^2) of the extractants HDEHP and DMDOHEMA diluted in dodecane or in PnP.

	HDHEP	DMDOHEMA
Dodecane	101	140
PnP	70	100

where N_A is Avogadro's constant (N_A = 6.02214.10^{23} mol^{-1}).

Table 1 shows that the surface area per polar head decreases when dodecane is replaced by PnP, which is thus involved in the formation of the interfacial film and, consequently, of the polar core of HDEHP and DMDOHEMA aggregates.

4.2 Microstructures determined by SAXS

Extraction depends on molecular conformations in weak aggregates. Therefore, an in-depth comparison between conventional systems based on alkanes and those based on hydrotropes requires study of the local structures present by small-angle X-ray scattering measurements (and, if possible, by the availability of deuterated solvents' or complexants' small angle neutron scattering—SANS) (Prevost et al., 2016). In order to provide a better understanding of these behaviors, and specifically the effect of PnP on aggregation properties, SWAXS measurements were performed for all organic solutions. These solutions contain 0.6 mol.L^{-1} of HDEHP or DMDOHEMA diluted in dodecane or PnP after contact with an aqueous phase containing 10 mmol.L^{-1} of Eu nitrate diluted in nitric acid (0.1 and 3 mol.L^{-1} for HDEHP and DMDOHEMA, respectively).

Figure 10 shows on linear (a) and logarithmic (b) scales the comparison of the scattering obtained with PnP and with dodecane for the acidic extractant (top) and chelating extractant (bottom). An increase by a factor of two closed to the very small angle, observed in both cases, is linked to the replacement of alkanes by hydrotropes. The scattering at zero angle with fixed concentration is proportional to the volume of the polar core. Therefore, the polar core volume has increased by factors of 2 and 1.6 in the case of HDEHP and DMDOHMEA, respectively. These SWAXS spectra are in agreement with the presence of globular aggregates in organic phases (Anderson et al., 2013; Antonio et al., 2008; Dourdain et al., 2012; Ellis et al., 2013). The effect of depletion attractions is negligible in this case (it would act in the opposite direction). In

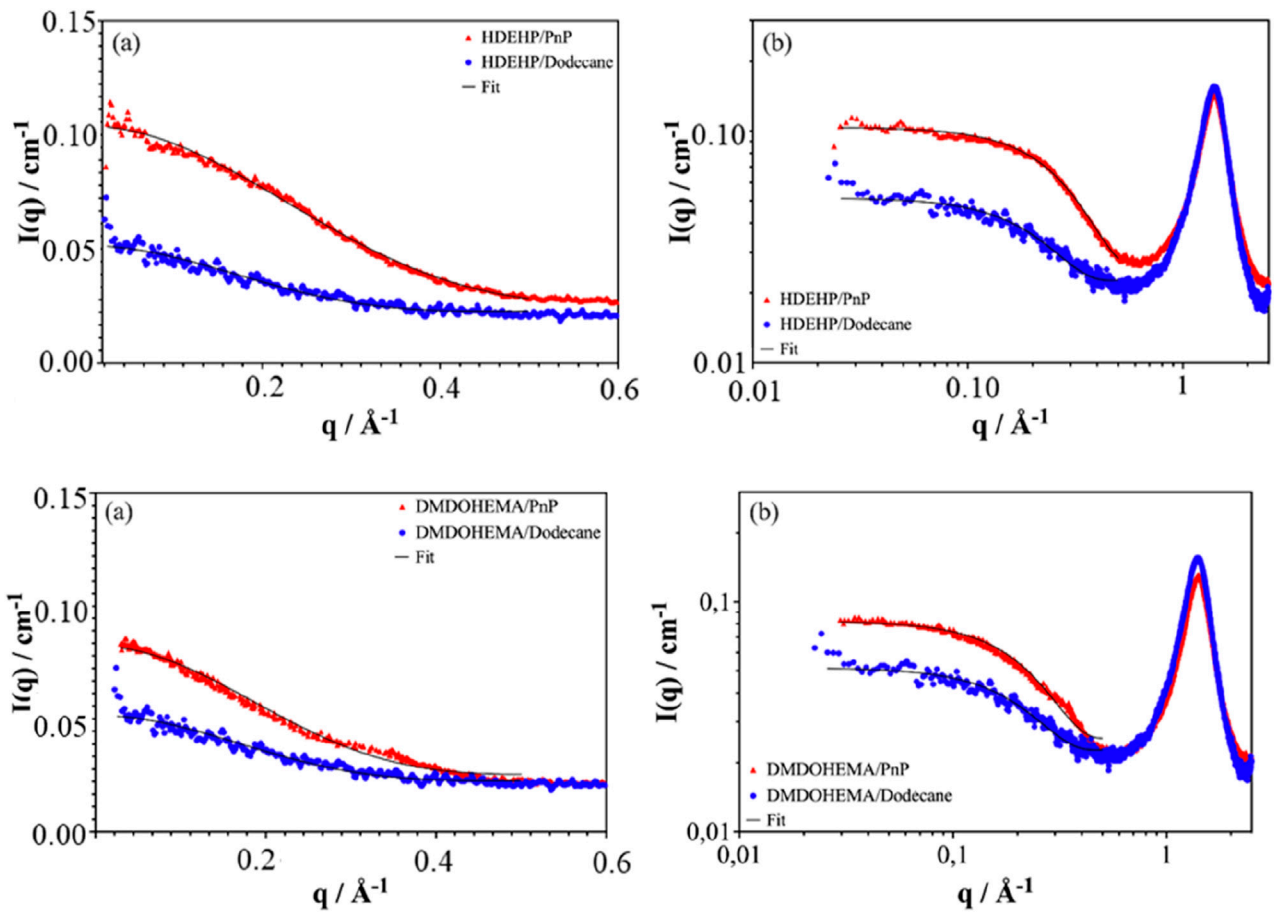

FIGURE 10
Top: experimental and simulated SWAXS spectra for the HDEHP system with conventional diluent (dodecane) and hydrotrope (PnP) **(A)** in linear and **(B)** logarithmic scales. Bottom: experimental and simulated SWAXS spectra for the DMDOHEMA system with conventional diluent (dodecane) and hydrotrope (PnP) **(A)** in linear and **(B)** logarithmic scales.

TABLE 2 Parameters obtained from the fit of SAXS data measured with various extractants and diluents.

Extraction system	HDEHP		DMDOHEMA	
	Dodecane	PnP	Dodecane	PnP
[extractant] [mol.L^{-1}]	0.6	0.6	0.6	0.6
Δρ [10^{-6} Å^{-2}]	1.85	1.95	2.45	2.15
R_{core} [Å]	5.6 ± 0.2	7.5 ± 0.3	6.3 ± 0.2	10.2 ± 0.3
PD	0.27	0.15	0.32	0.2
V_{polar_core} [Å^3]	221	227	280	327
N'_{agg}	3.3	7.7	3.7	13.6
Sticky parameter τ^{-1} [k_BT]	10 ± 0.4	7.1 ± 0.2	9.3 ± 0.3	6.2 ± 0.2

the first order, the area of the polar aggregates is increased by scaling at the 2/3 power of the intensity; the increase of polar/apolar area due to the participation of the hydrotrope is by a factor of 1.6 for the branched HDEHP and 1.4 in the case of DMDOEHMA. To go beyond this approximated estimation based on a globular overall shape of the polar cores made from electrolytes, co-extracted water, and extractant head-groups, a complete fit of the SAXS data has been performed and will be detailed in the following.

By ignoring the monomer-aggregate cross terms in the scattered intensity (Dourdain et al., 2014), the scattering equations for a spherical model were therefore expressed in a first-order approximation, as detailed in the supplementary information (represented in black lines in Figure 10). In this model, a polar core containing the extracted solvates and the polar heads of the extractant molecules is distinguished from the apolar solvent consisting of the alkyl chains of the extractant molecules and the diluent. The basic information obtained from SAXS experiments performed on an absolute scale is the radius of globular cores that are not derived from Guinier gyration radii but from a structure factor–form factor separation described in the Supplementary Information. Note that the presence of bicontinuous cylindrical cores with the same gyration radius cannot be excluded, even if the fit to the experimental curve is good.

Table 2 shows that R_{core} and N_{agg} increase with the presence of PnP for both extractants considered. This is fully coherent with the results for extracted water, acid, and solute concentrations, which are considered to occupy most of the core volume. For both extractants, the polydispersity of the polar core radius decreases with the presence of PnP. This indicates that the sizes of linear aggregates formed with PnP are more monodisperse. In addition, the sticking energy parameter t^{-1} decreases when dodecane is replaced by PnP, meaning that aggregates formed with dodecane are under the influence of stronger attractive interactions between aggregates due to depletion effects (Erlinger et al., 1998). Solvent depletion effects are reduced when a hydrotrope acts as a co-solvent. This quantitatively confirms why the extractant in PnP does not form a third phase. The evolution of these two parameters is consistent with the evolution of SAXS spectra at small angles, where the scattering intensity increases, and the plateau appears when PnP is used as a diluent. An complete description taking into account the sticky potential interaction with the spheres would indicate that the structure factor term variation is also involved. The first-order approximation derived by only fitting the form factor is somehow optimistic: weak complexation of the extracted cation with the alcohol at the head-group cannot be neglected. Hydrotropes act as weakly aggregating species, co-solvent but also as weak extractants, bringing a few k_BT of balance toward the oil phase observed in practice.

4.3 Interpretation using ieanics

Viscosity, surface tension, and diffusion experiments have provided crucial information on the structuring of the organic phase. The ienaic approach first introduced by Zemb et al. (2015) takes into account not only interactions with first neighbors but also the self-assembly of extractant molecules and solvent organization (also Špadina et al., 2021). The transfer Gibbs energy (ΔG_{tr}) is decomposed by considering the combination of driving forces (complexation, aggregation, reorganization of extractor chains, and confinement) regarding the following Equation 4:

$$\Delta_{tr}G = \Delta_{tr}G^{confin} + \Delta_{tr}G^{complex} + \Delta_{tr}G^{chain} + \Delta_{tr}G^{agg} + \Delta_{tr}G^{config.S}. \quad (4)$$

ΔG^{tr} is the transfer of a metallic ion from the aqueous phase to oil, driving the distribution ratio (Equation 5):

$$\Delta_{tr}G = -RT\,\mathrm{In}\frac{[M]_{org}}{[M]_{aq}}. \quad (5)$$

$\Delta_{tr}G^{confin}$ represents the free entropy cost to concentrate the ions and the water molecules in the porous domains of the aggregates and hinders the extraction process. The latter is composed of water molecules and ions and is expected to exhibit properties similar to those of aqueous solutions in bulk. These include cohesive free energy due to local electrostatic inhomogeneities, higher-order ion–ion and ion–interface correlations, van der Waals forces, Keesom interactions, and hydrogen bonding due to coextracted water and counterions in a saturated electrolyte solution (Špadina et al., 2019a). According to equations proposed by Dufrêche and Zemb (2015), the confinement term can be expressed by the following (Equation 6) with Eu as an example:

$$\Delta_{tr}G^{confin} = x\ln\left(\frac{m^{org}_{NO_3^-}\bullet\gamma^{org}_{NO_3^-}}{m^{aq}_{NO_3^-}\bullet\gamma^{aq}_{NO_3^-}}\right) + \ln\left(\frac{m^{org}_{Eu}\bullet\gamma^{org}_{Eu}}{m^{aq}_{Eu}\bullet\gamma^{aq}_{Eu}}\right) + i\ln\left(m^{org}_{ext}\bullet\gamma^{org}_{Ext}\right) + (2x+1)(\varnothing^{org} - \varnothing^{aq}), \quad (6)$$

where x is the stoichiometric coefficient of NO_3^- in the aggregates, m_i is the molality of i (mol.kg$_{solvent}^{-1}$) in equilibrium condition either in organic (org) or aqueous (aq) phase, $\varnothing^{org} - \varnothing^{aq}$ is the difference between the osmotic coefficient in the organic and aqueous phases (approximately equal to 0.5), and γ_i is the activity coefficient of i.

$\Delta_{tr}G^{complex}$ is the free energy of the complexation of extractants toward a metal species representing the difference in complexation energy of a metal ion in aqueous and organic phases; it describes the interaction between the complexed ion and the extractant's head groups. The complexation energy term is difficult to determine using conventional approaches (calorimetry, UV/visible). It corresponds roughly to the free energy in the first sphere of the correlations that can be measured by EXAF. In Špadina et al. (2019b), the complexation term is calculated thus using statistical thermodynamics (Equation 7):

$$\Delta_{tr}G^{complex} = -k_B T \ln N_{complex} - \sum_i N_{i,ext} N_{bond,i,ext} E_{i,ext}, \quad (7)$$

where $N_{complex}$ is the number of microstates associated with the binding of cations to the 2D lattice of sites (a monolayer of extractant head groups), $N_{i,ext}$ is the number of particular cations i in the core bound to the film formed by the extractant, $N_{bond,i,ext}$ is the number of extractants occupied by a cation i (creation of a bond), and $E_{i,ext}$ is the internal energy parameter and represents the energy contribution for each bond created between cation i and the extractant headgroups. We obtain an estimate of the $\Delta_{tr}G^{complex}$ by calculating the difference between the other terms. $\Delta_{tr}G^{chain}$ represents the free energy associated with the curvature of the extractant aliphatic chains that can be described by a packing parameter (Equation 8). The chain term is calculated thus:

$$\Delta_{tr}G^{chain} = \frac{\kappa^{\star}_{ext}}{2}(p - p_0)^2 \text{ per extractant molecules}, \quad (8)$$

where $\kappa^{\star}_{ext}$ represents the extractant film's global curvature constant, p is the effective packing parameter (Equation 10) of the aggregate, and p_0 is the spontaneous packing parameter (Equation 9) of extractant/cation. These parameters are calculated thus:

$$p_0 = 1 + \frac{l_{c,ext}}{R_{core}} + \frac{1}{3}\frac{l^2_{c,ext}}{R^2_{core}}, \quad (9)$$

$$p_{eff} = 1 + \frac{R_{agg} - R_{core}}{R_{core}} + \frac{1}{3}\left(\frac{R_{agg} - R_{core}}{R_{core}}\right)^2. \quad (10)$$

R_{core} et R_{agg} are determined experimentally by SAXS and SANS measurements Table 2).

$\Delta_{tr}G^{agg}$ is the aggregation term that describes the combination of two effects: spontaneous aggregation in a given solvent and the packing of extractant chains. The cost in free energy formation of an aggregate is easily derived from the value of the cac using the following Equation 11:

$$\Delta G_{aggregation} = RT\ln(cac), \quad (11)$$

where cac is the critical aggregation concentration determined by the surface tension measurements (Figure 9). $\Delta_{tr}G^{config.\,S}$ (Equation 13) represents the entropy associated with the polydispersity of the various species i in which the metal is present—every ion is distributed in solubilized species i. If the total number of ions is N and if there are N_i aggregates i, the corresponding number of microstates (Equation 12) is

$$W = \frac{N!}{\prod_i N_i!}. \quad (12)$$

Hence, the corresponding entropy per ion is

$$\Delta_{tr}G^{config.S} = k_B \ln W. \quad (13)$$

Among the molecular mechanisms responsible for the efficiency of extraction, the entropy of configuration around the polar core is most sensitive to the area of the polar core, assuming that four extractants and four hydrotropes in the first layer give $W = 8!/(4!)^2$ configuration—that is, the order of magnitude of "win" in Gibbs free energy observed in practice.

Finally, Figure 11 compares the free energy balance for each extractant (DMDOHEMA and HDEHP) diluted with dodecane and PnP.

Hydrotropic systems have aggregation terms smaller than those with standard diluents. Indeed, a difference in aggregation-free energy ($\Delta\Delta G_{agg}$) (Equation 14) of 2.4 kJ mol^{-1} in the case of HDEHP and 2 kJ mol^{-1} in the case of DMDOHEMA is achieved.

$$\Delta\Delta G_{agg} = RT\ln(\Delta cac). \quad (14)$$

From the cac measured for the two solvents and knowing from scattering that aggregates are similar (average number of molecules per aggregate is four), one obtains a decrease in the aggregate formation entropic term of the order of $5k_bT$ (12.5 kJ mol^{-1}) per cation extracted. The w/o aggregates are easier to form when the solvent is a hydrotrope; this is the origin of the 5 k_BT per ion "win" in transfer efficiency brought in by the exchange of dodecane by the hydrotrope PnP. In terms of distribution coefficient, this represents a factor of exp (5) = 150. The confinement term is linked to a decrease in interfacial curvature by using PnP as a diluent. That decrease is promoted by the formation of mixed aggregates thanks to the easier penetration of PnP than dodecane into the polar core.

The main lessons learned for analyzing structure–function using ienaics (Figure 11) are as follows.

- The free energy of transfer, measured by XRF, is shown as a black arrow and favors the extractant-rich phase. It appears that the gain obtained by replacing a conventional solvent with an hydrotrope occurs for acidic as well as for chelating extractants.
- The chain term shown in orange, linked to the frustration in the curvature energy of the first molecular layer around the cation, is important and should be taken into account in the case of dodecane. Due to the ultra-high flexibility of the molecular film formed when hydrotropes are present, this term becomes negligible in the case of hydrotropes. Those are known to decrease molecular film rigidity. This term is the

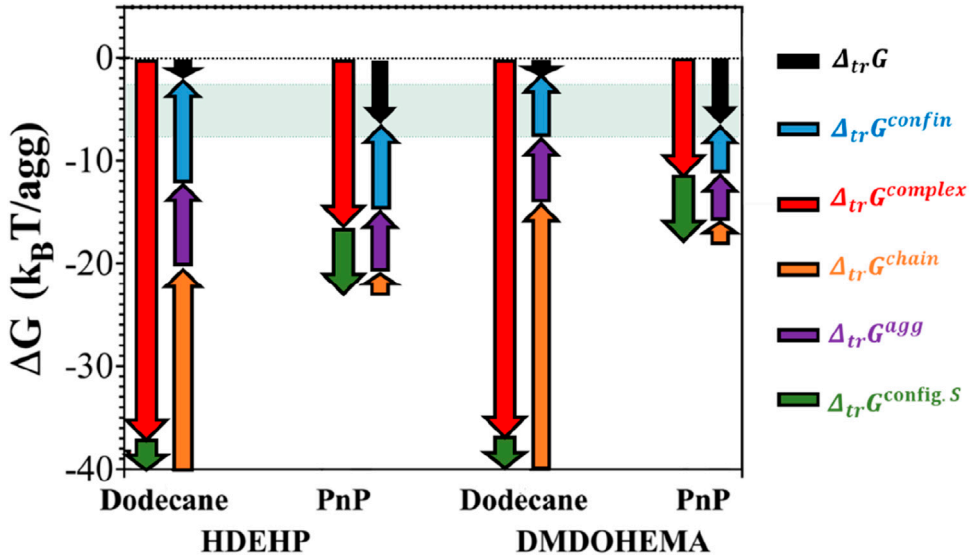

FIGURE 11
Driving forces for L-L extraction with conventional and hydrotropic systems. The main contributions are summarized to illustrate their influence on $\Delta_{tr}G$.

orange arrow pointing upwards and favors the water-rich phase and reduces extraction.

- The confinement term, shown as a blue arrow also pointing upwards, is linked to the assembly of polar species forming the polar cores. This term can be explicitly estimated when the polar cores are considered as super-saturated salt solutions (Špadina et al., 2019b) and is lower in more polar solvents than in alkanes. This term works against extraction and is smaller when hydrotropes are used to formulate the solvent phase.
- The Gibbs energy of the formation of aggregates, derived from surface tension studies and shown as a violet arrow pointing upwards, is greatly reduced by using hydrotropes. Measured values of cac are higher in the case of hydrotropes than of alkanes. This term, quenching extraction by the necessity of regrouping aggregates, is also smaller in the case of hydrotropes.

Finally, the main driving force—the Gibbs energy complexation difference between the solvent and the water phase—cannot be experimentally determined by any other means than joint two-phase mixing calorimetry associated with isothermal calorimetry in a single-phase regime that does not yet seem to have been performed in a system containing rare earths. EXAFS can only determine distances from a metal to the first neighbor, and calorimetric determination linked to extraction of one trivalent cation performed at several temperatures does not yet seem to be available. Once all other terms are evaluated, the complexation Gibbs energies can be estimated, shown as the red arrow pointing downwards. The driving force due to complexation with nearest neighbors is lower in the case of hydrotropes than for alkanes. However, this "loss" in complexation Gibbs energy is more than compensated for by the win in entropic terms, opening the road to a completely new strategy in liquid–liquid extraction, such as described in patents FR2111746 filed on 04/11/2021, EP21306559 filed on 05/11/2021, and EP22306032 filed on 08/07/2022.

Another way of expressing this increase of extraction efficiency is that hydrotropes increase the configurational entropy favoring the solvent phase. Hydrotropes generally have high volatility, which is why ionic hydrotropes are preferred for processes than alkane-based diluents (Kunz et al., 2016; El Maangar et al., 2020). Last but not least, hydrotropes reduce the attractive depletion interaction between aggregates, therefore quenching the formation of a third phase. A third phase when pure hydrotropes are used as solvents is unknown (Diat et al., 2013; Zemb et al., 2015).

The difference of free energy of transfer, mainly due to the easier formation of polar cores, is the origin of the efficiency of hydrotropes "replacing" alkanes as diluents. Hydrotropes allow easier formation of w/o aggregates than alkanes and increase the configurational entropy that favors the solvent phase. Pnp is not only a hydrotrope but also acts as a weak extractant. Here, "weak" means 5–10 k_BT of interaction, smaller than the 30–50 k_BT range estimated at contact for classical extractants. Finally, hydrotropes reduce the attractive depletion interaction between aggregates, thus quenching the formation of a third phase (Zemb et al., 2015). For all these reasons, completely or partially replacing the alkane in formulations by a hydrotrope allows more compact, faster, and safer extraction and stripping in processes. In the strategic case of the waste cycle of the Gen IV nuclear reactors, more radioactive fluids mean minimizing the residence time and increasing selectivities. The use of hydrotropes is potentially core to the new design of sustainable nuclear technology linked to fission induced by fast neutrons.

This more favorable distribution coefficient associated with formulations including hydrotropes can be used to design processes with a lower environmental footprint and a faster transfer reducing size of physical devices, thus reducing the cost of the whole process. Following an extraction step, an elution step of

the organic phase containing the extractant, hydrotrope, and extracted ions could be established to recover the extracted ions in a new aqueous phase solution. Depending on the nature of the extractant, elution can be achieved by modifying the acidity conditions or by adding a complexing agent to the various aqueous phases containing the PnP (after extraction and elution steps). We propose to extract the PnP from aqueous phases in contact with Isane IP 175. Given their respective boiling points (150°C for PnP and 190°C for Isane IP 175), we have chosen fractional distillation as the separation technique. At the end of this step, pure Isane IP 175 can be reused in the hydrotrope elution steps, and recovered PnP will be reintroduced in the hydrotrope content adjustment step. This facilitates a closed-loop process.

Therefore, completely or partially replacing the branched alkanes commonly used in formulations by a hydrotrope will allow more compact, faster, and safer extraction and stripping in processes. In the case of gold and copper extraction, the use of glycine, an amino acid that behaves much like an hydrotrope, has already replaced strong acids in leaching processes in practice (Huan et al., 2023)

In the strategic case of the waste cycle linked to Generation IV nuclear reactors, more radioactive fluids mean minimizing residence time and increasing lanthanide/actinide selectivities. The use of hydrotropes in advanced formulation to replace branched chain alkanes (Bourgeois et al., 2020; El Maangar, A., Duhamet, J., Pellet-Rostaing, S., Zemb, 2023) will certainly be core to the new design of sustainable nuclear generation linked to fission induced by fast neutrons, such as those designed as possible successors of the Phénix reactor that produces electricity generated from 100% plutonium mixed with enrichment cycle waste—natural uranium depleted by the enrichment process—linked to the needs of fourth generation reactors based on fast neutrons and closing the nuclear fuel cycle.

5 Conclusion

We have discussed the molecular origins of the differences obtained by replacing solvents commonly used in hydrometallurgical processes with hydrotropes. The use of the latter removes undesirable third-phase instability. Extraction properties have been systematically quantified along with the conodals in the phase diagrams.

The case of hydrotropy-enhancing solubilization we describe is similar in nature but opposite in structure to local solubilization enhanced by preferential location of one of the components of a binary "solvent" around the solubilizer (Shimizu and Matubayashi, 2024). This preferential solubilization situation, described in the case of curcumin with preferential solubilization around cinnamaldehyde, could be quantified via COSMO-RS as there are no cinnamaldehyde weak aggregates formed in this case (Schmidt et al., 2024). "Local" solubilization and local de-mixing at molecular scale around a solubilizer are different than aggregates of a hydrotrope and critical fluctuations as described here.

In all cases presented in this study, extraction efficiency was surprisingly increased by replacing a diluent with hydrotropes for all acid and extractant concentrations evaluated. The quantities of acid and water coextracted are always greater in the case of PnP, whatever the nature of the extractant considered. However, selectivity decreases in the case of HDEHP while it remains unchanged for DMDOHEMA. Loading capacity and viscosity increases were evaluated for PnP and compared with other conventional diluents. The viscosity of the organic phase increases for both extractants studied, with increasing loading in the order DMDOHEMA < HDEHP—thus with decreasing spontaneous packing parameter. We have established that the viscosity of organic phases increases with decreasing diluent penetration power, in the order PnP > toluene > heptane > isooctane > dodecane. The appearance of the third phase follows the same trend. A direct link has been established between the formation of the third phase, the limited loading capacity, and the increase in viscosity. The water–oil surface tension decreases with the replacement of dodecane by PnP. Cac values show the same trend, meaning that aggregation is facilitated by the presence of PnP; one of the brakes on complexation efficiency is thus released. A decrease in surface area per polar head demonstrates that PnP penetrates to the polar core, helping to form polar cores that comprise more molecules. Consequently, the entropy of mixing is increased, enabling more flexible extraction.

Extractant–hydrotrope "synergy" was also studied by SAXS. We have shown that the synergistic behavior observed results in the formation of larger aggregates capable of extracting more metals from the organic phase as well as water and acid. The fundamental reason for this is that the polar core cohesion term in ienaic decomposition is volume-dependent. In conclusion, considering all these experimental observations, the following model of the organic phase is proposed. The structure determining the efficiency of hydrotropic-based ternary systems compared with conventional diluent is mainly composed of larger mixed inverse aggregates consisting of extractant and PnP per aggregate. Within these aggregates, a larger polar volume is available not only to complexify the first few neighbors with one or two extractants but also to increase the configuration entropy of the extracted species. The use of PnP as a penetrating hydrotrope increases the effective packing parameter of the extractants.

This first picture was then precisely described by ienaic decomposition, which helps explain the interesting increase in efficiency in the presence of PnP. Ienaic decomposition of the free energy of transfer has enabled identification of the molecular forces behind this efficiency. We have shown that replacing conventional diluents with hydrotropes promotes the formation of inverse aggregates as well as the curvature of the extractant film. The curvature constant in the presence of PnP was deduced from the thermodynamic balance. The value of the latter is lower than that of dodecane, meaning that swollen extractant films are more easily formed. Extraction efficiency with hydrotropic-based systems thus appears to be the combination of a favored complexation energy of the cation and a favored bending energy of the aggregate, increasing the free energy of transfer. These simple assumptions explain all the results of the qualitative characterizations as well as the quantitative properties of the synergistic system, provided that the transfer energies of the co-extracted water and acid are also considered. We have highlighted the importance of entropic effects and long-range interactions competing with the free energy of complexation

for efficient liquid–liquid extraction with hydrotropes. To understand the mechanisms of extraction with hydrotropic-based ternary systems, this general approach considers the presence of the extractant, the co-extracted water, and the co-extracted acid. In the systems studied, ions and electrolytes in equilibrium in complex organic fluids interact not only by complexation or solvation with first neighbors or via inner or outer sphere interactions but also via long-range forces classified in electrostatic, Van der Waals, solvation, and steric/entropic terms. These identified mechanisms will enable advanced formulations using hydrotropes instead of conventional solvents, paving the way for sustainable extraction processes that minimize effluents and overall costs.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

AE: data curation, formal analysis, investigation, methodology, and writing–original draft. TZ: conceptualization, funding acquisition, project administration, resources, software, supervision, visualization, and writing–review and editing. CF: formal analysis, investigation, visualization, and writing–original draft. JD: conceptualization, supervision, visualization, and writing–review and editing. J-FD: conceptualization, methodology, validation, visualization, and writing–review and editing. SP-R: software, supervision, validation, visualization, and writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fceng.2024.1476214/full#supplementary-material

References

Anderson, T. L., Braatz, A., Ellis, R. J., Antonio, M. R., and Nilsson, M. (2013). Synergistic extraction of Dysprosium and aggregate formation in solvent extraction systems combining TBP and HDBP. *Solvent Extr. Ion Exch.* 31 (6), 617–633. doi:10.1080/07366299.2013.787023

Antonio, M. R., Chiarizia, R., Gannaz, B., Berthon, L., Zorz, N., Hill, C., et al. (2008). Aggregation in solvent extraction systems containing a malonamide, a dialkylphosphoric acid and their mixtures. *Sep. Sci. Technol.* 43 (9–10), 2572–2605. doi:10.1080/01496390802121537

Arce, A., Arce, A., Jr, and Rodriguez, O. (2022). Revising concepts on Liquid–Liquid extraction: data treatment and data reliability. *J. Chem. Eng. Data* 67, 286–296. doi:10.1021/acs.jced.1c00778

Bauduin, P., Testard, F., Berthon, L., and Zemb, T. (2007). Relation between the hydrophile/hydrophobe ratio of malonamide extractants and the stability of the organic phase: investigation at high extractant concentrations. *Phys. Chem. Chem. Phys.* 9 (28), 3776. doi:10.1039/b701479a

Bauer, C., Bauduin, P., Dufrêche, J. F., Zemb, T., and Diat, O. (2012). Liquid/liquid metal extraction: phase diagram topology resulting from molecular interactions between extractant, ion, oil and water. *Eur. Phys. J. Special Top.* 213 (1), 225–241. doi:10.1140/epjst/e2012-01673-4

Berthon, L., Martinet, L., Testard, F., Madic, C., and Zemb, T. (2007). Solvent penetration and sterical stabilization of reverse aggregates based on the DIAMEX process extracting molecules: consequences for the third phase formation. *Solvent Extr. Ion Exch.* 25 (5), 545–576. doi:10.1080/07366290701512576

Berthon, L., Testard, F., Martinet, L., Zemb, T., and Madic, C. (2010). Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: consequences for phase stability. *Comptes Rendus Chim.* 13 (10), 1326–1334. doi:10.1016/j.crci.2010.03.024

Bourgeois, D., El Maangar, A., and Dourdain, S. (2020). Importance of weak interactions in the formulation of organic phases for efficient liquid/liquid extraction of metals. *Curr. Opin. Colloid and Interface Sci.* 46, 36–51. doi:10.1016/j.cocis.2020.03.004

Chandrasekar, A., Suresh, A., Sivaraman, N., and Aswal, V. K. (2016). Trends in small angle neutron scattering of actinide–trialkyl phosphate complexes: a molecular insight into third phase formation. *RSC Adv.* 6 (95), 92905–92916. doi:10.1039/C6RA20175J

Chiarizia, R., Jensen, M. P., Borkowski, M., Ferraro, J. R., Thiyagarajan, P., and Littrell, K. C. (2003). Third phase formation revisited: the U(VI), HNO 3 –tbp, n -dodecane system. *Solvent Extr. Ion Exch.* 21 (1), 1–27. doi:10.1081/SEI-120017545

Chiarizia, R., Jensen, M. P., Borkowski, M., Thiyagarajan, P., and Littrell, K. C. (2004). Interpretation of third phase formation in the Th(IV)–HNO $_3$, tbp– *n* -octane system with baxter’s “sticky spheres” model. *Solvent Extr. Ion Exch.* 22 (3), 325–351. doi:10.1081/SEI-120030394

Déjugnat, C., Berthon, L., Dubois, V., Meridiano, Y., Dourdain, S., Guillaumont, D., et al. (2014). Liquid-liquid extraction of acids and water by a malonamide: I-anion specific effects on the polar core microstructure of the aggregated malonamide. *Solvent Extr. Ion Exch.* 32 (6), 601–619. doi:10.1080/07366299.2014.940229

Diat, O., Klossek, M. L., Touraud, D., Deme, B., Grillo, I., Kunz, W., et al. (2013). Octanol-rich and water-rich domains in dynamic equilibrium in the pre-ouzo region of ternary systems containing a hydrotrope. *J. Appl. Crystallogr.* 46 (6), 1665–1669. doi:10.1107/S002188981302606X

Dourdain, S., Déjugnat, C., Berthon, L., Dubois, V., Pellet-Rostaing, S., Dufrêche, J.-F., et al. (2014). Liquid-liquid extraction of acids by a malonamide: II-anion specific effects in the aggregate-enhanced extraction isotherms. *Solvent Extr. Ion Exch.* 32 (6), 620–636. doi:10.1080/07366299.2014.924311

Dourdain, S., Hofmeister, I., Pecheur, O., Dufrêche, J.-F., Turgis, R., Leydier, A., et al. (2012). Synergism by coassembly at the origin of ion selectivity in liquid–liquid extraction. *Langmuir* 28 (31), 11319–11328. doi:10.1021/la301733r

Dufrêche, J.-F., and Zemb, T. (2015). Effect of long-range interactions on ion equilibria in liquid–liquid extraction. *Chem. Phys. Lett.* 622, 45–49. doi:10.1016/j.cplett.2014.11.028

Dufrêche, J. F., and Zemb, T. (2020). Bending: from thin interfaces to molecular films in microemulsions. *Emulsions Microemulsions* 49, 133–147. doi:10.1016/j.cocis.2020.06.001

Ellis, R. J., Anderson, T. L., Antonio, M. R., Braatz, A., and Nilsson, M. (2013). A SAXS study of aggregation in the synergistic TBP–HDBP solvent extraction system. *J. Phys. Chem. B* 117 (19), 5916–5924. doi:10.1021/jp401025e

El Maangar, A. (2022). L'extraction raisonnée de métaux stratégiques par des hydrotropes. Available at: http://www.theses.fr/2022UMONS004.

El Maangar, A., Duhamet, J., Pellet-Rostaing, S., and Zemb, T. (2023). Process for liquid/liquid extraction of rare earths or actinides via synergistic combination of a co-solvent hydrotrope with anonic or chelating extractants.

El Maangar, A., Prévost, S., Dourdain, S., and Zemb, T. (2022). Molecular mechanisms induced by phase modifiers used in hydrometallurgy: consequences on transfer efficiency and process safety. *Comptes Rendus. Chim.* 25 (G1), 341–360. doi:10.5802/crchim.205

El Maangar, A., Theisen, J., Penisson, C., Zemb, T., and Gabriel, J.-C. P. (2020). A microfluidic study of synergic liquid–liquid extraction of rare earth elements. *Phys. Chem. Chem. Phys.* 22 (10), 5449–5462. doi:10.1039/C9CP06569E

Erlinger, C., Gazeau, D., Zemb, T., Madic, C., Lefrançois, L., Hebrant, M., et al. (1998). Effect of nitric acid extraction on phase behavior, microstructure and interactions between primary aggregates in the system dimethyldibutyltetradecylmalonamide (dmdbtdma)/n-dodecane/water: a phase analysis and small angle x-ray scattering (saxs) characterisation study. *Solvent Extr. Ion Exch.* 16 (3), 707–738. doi:10.1080/07366299808934549

Gannaz, B., Antonio, M. R., Chiarizia, R., H, C., and Cote, G. (2006). Structural study of trivalent lanthanide and actinide complexes formed upon solvent extraction. *Dalton Trans.* 38, 4553–4562. doi:10.1039/b609492a

Huan, Li, Deng, Z., Oraby, E., and Eksteen, J. (2023). Amino acids as lixiviants for metals extraction from natural and secondary resources with emphasis on glycine: a literature review. *Hydrometallurgy* 216, 106008. doi:10.1016/j.hydromet.2022.106008

Innocenzi, V., Ferella, F., De Michelis, I., and Vegliò, F. (2015). Treatment of fluid catalytic cracking spent catalysts to recover lanthanum and cerium: comparison between selective precipitation and solvent extraction. *J. Industrial Eng. Chem.* 24, 92–97. doi:10.1016/j.jiec.2014.09.014

Jowitt, S. M., Werner, T. T., Weng, Z., and Mudd, G. M. (2018). Recycling of the rare earth elements. *Curr. Opin. Green Sustain. Chem.* 13, 1–7. doi:10.1016/j.cogsc.2018.02.008

Kirsanov, D., Panchuk, V., Agafonova-Moroz, M., Khaydukova, M., Lumpov, A., Semenov, V., et al. (2014). A sample-effective calibration design for multiple components. *Analyst* 139 (17), 4303–4309. doi:10.1039/C4AN00227J

Kunz, W., Holmberg, K., and Zemb, T. (2016). Hydrotropes. *Curr. Opin. Colloid and Interface Sci.* 22, 99–107. doi:10.1016/j.cocis.2016.03.005

Lefrancois, L., Belnet, F., Noel, D., and Tondre, C. (1999). An attempt to theoretically predict third-phase formation in the dimethyldibutyltetradecylmalonamide (DMDBTDMA)/Dodecane/Water/Nitric acid extraction system. *Sep. Sci. Technol.* 34 (5), 755–770. doi:10.1080/01496399908951143

Marčelja, S. (2017). Entropy of level-cut random Gaussian structures at different volume fractions. *Phys. Rev. E* 96 (4), 042147–7. doi:10.1103/PhysRevE.96.042147

Masry, B. A., Aly, M. I., Khalifa, N. A., Zikry, A. A. F., Gasser, M. S., and Daoud, J. A. (2015). Liquid-liquid extraction and separation of Pr (III), Nd (III), Sm (III) from nitric acid medium by CYANEX 923 in kerosene. *Arab J. Nucl. Sci. Appl.* 48 (3), 1–16.

Maurice, A. A., Theisen, J., Rai, V., Olivier, F., El Maangar, A., Duhamet, J., et al. (2021). First online X-ray fluorescence characterization of liquid-liquid extraction in microfluidics. *Nano Sel.* 3, 425–436. doi:10.1002/nano.202100133

Motokawa, R., Kobayashi, T., Endo, H., Mu, J., Williams, C. D., Masters, A. J., et al. (2019). A telescoping view of solute architectures in a complex fluid system. *ACS Central Sci.* 5 (1), 85–96. doi:10.1021/acscentsci.8b00669

Mowafy, E. A., and Aly, H. F. (2002). Extraction behaviours of nd(iii), eu(iii), la(iii), am(iii), and u(vi) with some substituted malonamides from nitrate medium. *Solvent Extr. Ion Exch.* 20 (2), 177–194. doi:10.1081/SEI-120003020

Moyer, B. A. (2010) "Ion exchange and solvent extraction," in *A Series of Advances*. Boca Raton, FL: CRC Press 19.

Muller, J. M., Berthon, C., Couston, L., Zorz, N., Simonin, J. P., and Berthon, L. (2016). Extraction of lanthanides(III) by a mixture of a malonamide and a dialkyl phosphoric acid. *Solvent Extr. Ion Exch.* 34 (2), 141–160. doi:10.1080/07366299.2015.1135030

Narita, H., Yaita, T., Tamura, K., and Tachimori, S. (1999). Study on the extraction of trivalent lanthanide ions with N,N′-dimethyl-N,N′-diphenyl-malonamide and diglycolamide. *J. Radioanalytical Nucl. Chem.* 239 (2), 381–384. doi:10.1007/BF02349516

Osseo-Asare, K. (2002) "Microemulsions and third phase formation," in *Proceedings of the international solvent extraction conference ISEC*, 118–124.

Pathak, P. N., Kanekar, A. S., Prabhu, D. R., and Manchanda, V. K. (2009). Comparison of hydrometallurgical parameters of N,N -dialkylamides and of tri- n -butylphosphate. *Solvent Extr. Ion Exch.* 27 (5–6), 683–694. doi:10.1080/07366290903113934

Poirot, R., Bourgeois, D., and Meyer, D. (2014). Palladium extraction by a malonamide derivative (DMDOHEMA) from nitrate media: extraction behavior and third phase characterization. *Solvent Extr. Ion Exch.* 32 (5), 529–542. doi:10.1080/07366299.2014.908587

Prevost, S., Lopian, T., Pleines, M., Diat, O., and Zemb, T. (2016). Small-angle scattering and morphologies of ultra-flexible microemulsions. *J. Appl. Crystallogr.* 49 (6), 2063–2072. doi:10.1107/S1600576716016150

Rao, P. R. V., Dhamodaran, R., Srinivasan, T. G., and Mathews, C. K. (1993). The effect of diluent on third phase formation in thorium nitrate - Tbp system: some novel empirical correlations. *Solvent Extr. Ion Exch.* 11 (4), 645–662. doi:10.1080/07366299308918179

Rey, J., Bley, M., Dufrêche, J.-F., Gourdin, S., Pellet-Rostaing, S., Zemb, T., et al. (2017). Thermodynamic description of synergy in solvent extraction: II thermodynamic balance of driving forces implied in synergistic extraction. *Langmuir* 33 (46), 13168–13179. doi:10.1021/acs.langmuir.7b02068

Roberto Danesi, P., Chiarizia, R., and Coleman, C. F. (1980). The kinetics of metal solvent extraction. *C R C Crit. Rev. Anal. Chem.* 10 (1), 1–126. doi:10.1080/10408348008542724

Rydberg, J., Cox, M., Musikas, C., and Choppin, G. R. (2004). *Solvent extraction principles and practice, revised and expanded*. New York, NY: Marcel Dekker, 760.

Schmidt, M., Huber, V., Touraud, D., and Kunz, W. (2024). Aromas: lovely to smell and nice solvents for polyphenols curcumin solubilisation power of fragrances and flavours. *Molecules* 29, 294. doi:10.3390/molecules29020294

Scoppola, E., Watkins, E. B., Campbell, R. A., Konovalov, O., Girard, L., Dufrêche, J.-F., et al. (2016). Solvent extraction: structure of the liquid-liquid interface containing a diamide ligand. *Angew. Chem. Int. Ed.* 55 (32), 9326–9330. doi:10.1002/anie.201603395

Shimizu, S., and Matubayashi, N. (2024). Synergistic solvation as the enhancement of local mixing. *J. Phys. Chem. B* 128, 5713–5826. doi:10.1021/acs.jpcb.4c01582

Spadina, M. (2019). Solvation and ion specificity in complex media. Available at: http://www.theses.fr/2019MONTS020/document.

Špadina, M., Bohinc, K., Zemb, T., and Dufrêche, J.-F. (2019a). Synergistic Solvent Extraction is driven by entropy. *ACS Nano* 13 (12), 13745–13758. doi:10.1021/acsnano.9b07605

Špadina, M., Bohinc, K., Zemb, T. N., and Dufrêche, J.-F. (2019b). Colloidal model for the prediction of the extraction of rare earths assisted by the acidic extractant. *Langmuir* 35, 3215–3230. doi:10.1021/acs.langmuir.8b03846

Špadina, M., Dufrêche, J.-F., Pellet-Rostaing, S., Marčelja, S., and Zemb, T. (2021). Molecular forces in liquid–liquid extraction. *Langmuir,acs.langmuir* 37, 10637–10656. doi:10.1021/acs.langmuir.1c00673

Spjuth, L., Liljenzin, J. O., Skålberg, M., Hudson, M. J., Chan, G. Y. S., Drew, M. G. B., et al. (1997). Extraction of actinides and lanthanides from nitric acid solution by malonamides. *Radiochim. Acta* 78 (s1), 39–46. doi:10.1524/ract.1997.78.special-issue.39

Tanford, C. (1973). *The hydrophobic effect: formation of micelles and biological membranes*. New York: John Wiley and Sons.

Testard, F., Zemb, T., Bauduin, P., and Berthon, L. (2010). ChemInform abstract: third-phase formation in liquid—liquid extraction: a colloidal approach. *ChemInform* 41 (1). doi:10.1002/chin.201001276

Vasudeva Rao, P. R., and Kolarik, Z. (1996). A review of third phase formation in extrcation of actinides by neutral organophsorus extractants. *Solvent Extr. Ion Exch.* 14 (6), 955–993. doi:10.1080/07366299608918378

Zemb, T., Bauer, C., Bauduin, P., Belloni, L., Déjugnat, C., Diat, O., et al. (2015). Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienaics.". *Colloid Polym. Sci.* 293 (1), 1–22. doi:10.1007/s00396-014-3447-x

Zemb, T., and Kunz, W. (2016). Weak aggregation: state of the art, expectations and open questions. *Curr. Opin. Colloid and Interface Sci.* 22, 113–119. doi:10.1016/j.cocis.2016.04.002

Zhao, Z., Qiu, Z., Yang, J., Lu, S., Cao, L., Zhang, W., et al. (2017). Recovery of rare earth elements from spent fluid catalytic cracking catalysts using leaching and solvent extraction techniques. *Hydrometallurgy* 167, 183–188. doi:10.1016/j.hydromet.2016.11.013