

Coordination Chemistry

Enhancing Metal Separations by Liquid–Liquid Extraction Using Polar Solvents

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Abstract: The less polar phase of liquid–liquid extraction systems has been studied extensively for improving metal separations; however, the role of the more polar phase has been overlooked for far too long. Herein, we investigate the extraction of metals from a variety of polar solvents and demonstrate that, the influence of polar solvents on metal extraction is so significant that extraction of many metals can be largely tuned, and the metal separations can be significantly enhanced by selecting suitable polar solvents. Furthermore, a mechanism on how the polar solvents affect metal extraction is proposed based on comprehensive characterizations. The method of using suitable polar solvents in liquid–liquid extraction paves a new and versatile way to enhance metal separations.

Liquid–liquid extraction (solvent extraction) is one of the most widely used techniques for the separation and purification of metal ion mixtures. A liquid–liquid extraction system generally consists of two immiscible phases: an organic phase (less polar, LP) containing the extractant(s), diluent(s) and possibly a modifier, and an aqueous phase (more polar, MP) containing the metals to be separated.^[1,2] The less polar phase has been the objective of extensive studies for improving metal separations in many approaches, including developing new extractants, using mixtures of extractants, changing diluents, adding modifiers, and so on.^[2–10] Although these efforts have significantly advanced metal separations, many challenges still remain, such as the low separation factors of neighboring rare-earth elements and the difficulty of extracting lower-valent metals from higher-valent metals.^[5,7,11] In contrast to the ple-

thora of studies on the LP phase, the MP phase has received limited attention. Water has been used as the default polar solvent in the liquid-liquid extraction of metals, whereas numerous other polar solvents have been largely neglected. The use of complexing agents (e.g. diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid, DTPA) in the aqueous solution for enhancing the separation of lanthanides and actinides in TALSPEAK (*Trivalent Actinide Lanthanide Separation with Phosphorus-Reagent Extraction from Aqueous Complexes*) is a modification of the more polar phase, but the process still uses water as a solvent for the more polar phase.^[12,13]

A few preliminary studies explored utilization of some polar organic solvents to replace water in the MP phase for metal extractions; however, no superior metal separations were observed.^[14–18] Recently, extraction of rare earth elements and transition metals from ethylene glycol (EG) solutions showed higher extraction efficiency and higher separation factors compared to the extraction from aqueous solutions.^[19–21] These results clearly indicate that EG affects the extraction of metals differently than water. Nevertheless, how these polar solvents (water and EG) affect metal extraction is not clear yet, and the possibility of using other polar solvents, besides EG, to enhance metal separations remains unknown. Herein, we propose a mechanism on how polar solvents affect metal extraction and demonstrate that metal separations can be dramatically improved by using suitable polar solvents.

We examined first the extraction of transition metals (0.01 M of CoCl₂, NiCl₂ and MnCl₂) from a variety of polar solvents with 10 vol% Aliquat 336 (A336) dissolved in toluene as the LP phase. A336 (Figure S1, Supporting Information) is a commercial extractant with methyltriocylammonium chloride as the main component. Five out ten screened polar solvents (Table S1, Supporting Information), including water, EG, formamide, methanol, and *N*-methylformamide were selected and tested. It is clearly shown that the extraction of metals from different polar solvents differs dramatically (Figure 1). Cyphos IL 101 (trihexyltetradecylphosphonium chloride, abbreviated as C101) was used under the same conditions in comparison to the extraction from aqueous solutions (Figure 1b). C101 extracts Co and Mn more efficiently than A336 under the same LiCl concentration (e.g. 4.0 M LiCl). Interestingly, when EG or formamide is used as a solvent instead of water, the extraction of both Co and Mn by A336 is comparable to the extraction by C101 from aqueous solutions. In other words, changing polar solvents resulted in the same extraction performance as changing extractants. When compared at LiCl saturation, the

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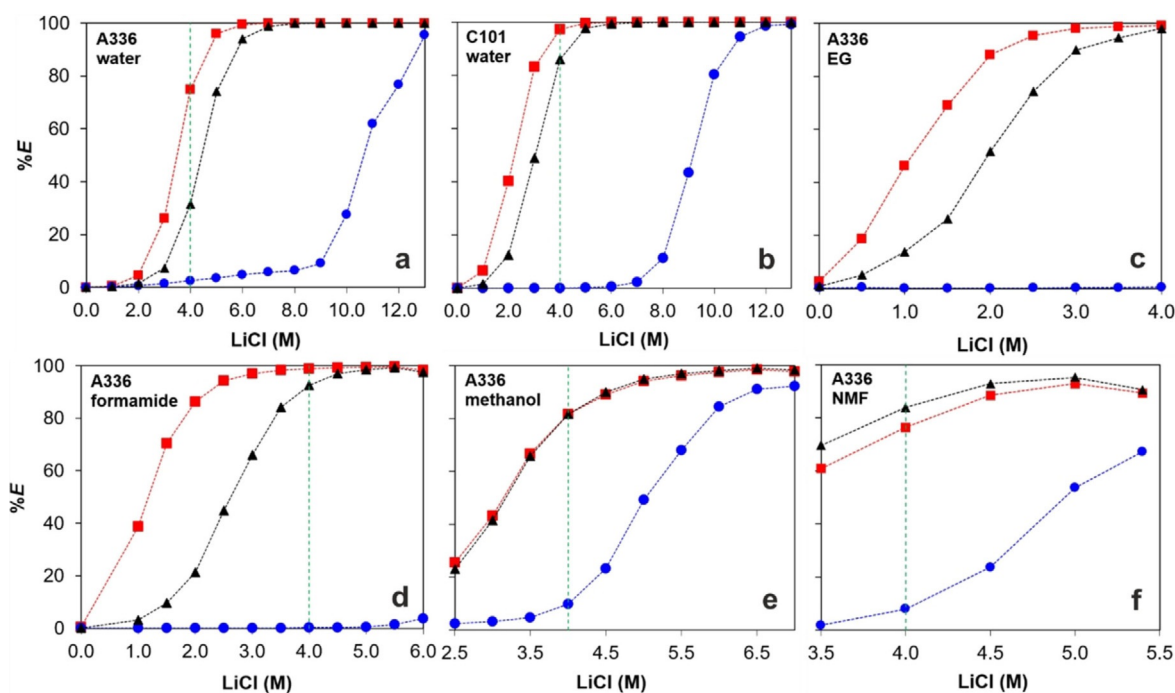
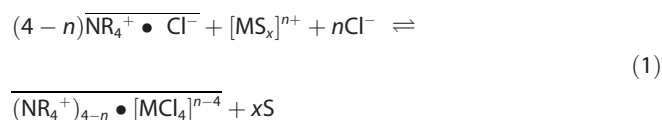


Figure 1. Percentage extraction (%E) of Co (■)/Ni (●)/Mn (▲) by 10 vol% A336 (or 10 vol% C101) in toluene from water (a), water (by C101; b), EG (c), formamide (d), methanol (e), and NMF (f) with LiCl concentration up to saturation in each solvent at room temperature.

extraction of Co and Mn is (almost) complete from all polar solvents except for NMF. Whereas, the extraction of Ni from different polar solvent varies significantly, especially the extraction from EG and formamide is so low that good separation of Co and Mn from Ni can be facilitated.

The extraction mechanism of A336 for transition metals can be written as follows when solvation is included [Eq. (1)].^[22,23]



in which M represents a metal cation with charge n (usually $n=2, 3$), S denotes a solvent molecule, and x is the solvation number. The bar on top indicates that the species reside in the LP phase. In this extraction, anionic chlorometallate complexes $[\text{MCl}_4]^{n-4}$ are formed and bound to ammonium cations in the LP phase.

The extraction reaction involves the breaking of the solvation structure and the formation of the anionic complex $[\text{MCl}_4]^{n-4}$, both of which can be largely affected by polar solvents, as shown by DFT calculations (Figures S2 and S3, Supporting Information). In addition, the different molarities of solvents (Table S1, Supporting Information), the hydrogen-bonding ability of solvent and solvent-solvent interactions play important roles in the metal-ion complex formation.^[24,25] Theoretically it is difficult to concurrently consider all these factors to quantify the effect of polar solvents on the extraction reaction. Fortunately, it is possible to estimate the overall effects experimentally.

The efficiency of $[\text{CoCl}_4]^{2-}$ formation in different polar solvents can be quantified by the absorbance of $[\text{CoCl}_4]^{2-}$, because the octahedral complex $[\text{CoCl}_x(\text{H}_2\text{O})_{6-x}]^{2-x}$ (about 420–580 nm) and the tetrahedral complex $[\text{CoCl}_4]^{2-}$ (about 600–720 nm) have distinct absorption spectra.^[26,27] Surprisingly, the efficiency for $[\text{CoCl}_4]^{2-}$ formation in different polar solvents differs significantly since the concentrations of CoCl_2 and LiCl required to reach the same absorbance (e.g. ≈ 1.1 at 691 nm) vary over a large range (Figure 2 and Figure S4, Supporting Information). The more CoCl_2 and LiCl required to reach a certain absorbance, the less efficient the $[\text{CoCl}_4]^{2-}$ formation. The sequence of the five selected solvents for their efficiency of $[\text{CoCl}_4]^{2-}$ formation is: *N*-methylformamide (NMF) > methanol > formamide > EG > water.

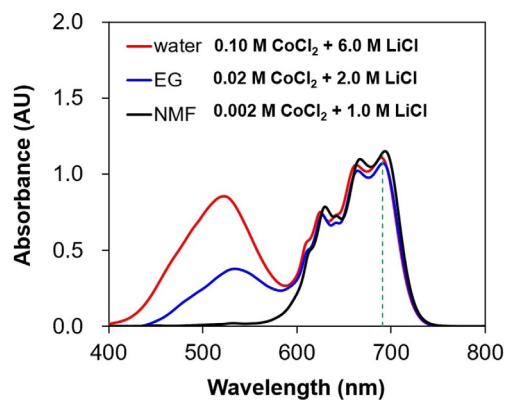


Figure 2. Formation of $[\text{CoCl}_4]^{2-}$ in water, EG, and NMF with various CoCl_2 and LiCl concentrations.

The enhanced extraction of Co and Mn in EG and formamide can be explained by the higher formation efficiency of $[\text{MCl}_4]^{2-}$ ($M = \text{Co}, \text{Mn}$). The Co and Mn extraction from methanol and NMF is lower than from EG and formamide, conflicting with the $[\text{MCl}_4]^{2-}$ formation efficiency. This is because A336 is more soluble in methanol and NMF (Figure S6, Supporting Information).

The extraction of Ni by A336 follows the solvent sequence of $\text{NMF} \approx \text{methanol} > \text{formamide} \approx \text{EG}$, which is consistent with the sequence determined based on $[\text{MCl}_4]^{2-}$ formation efficiency, except for water. The discrepancy of water from the solvent sequence is because Ni can be extracted by another mechanism. Spectrophotometric evidence shows that below 9.0 M LiCl, Ni is extracted by A336 from water partially in the form of $[\text{NiCl}_4]^{2-}$ and partially in the form of $[\text{NiCl}_x(\text{H}_2\text{O})_{6-x}]^{2-x}$ (Figure S7, Supporting Information). The former can be extracted by A336 through forming a neutral compound with the ammonium cation [Eq. (1)], whereas the latter cannot. Nevertheless, $[\text{NiCl}_x(\text{H}_2\text{O})_{6-x}]^{2-x}$ can be dissolved in the LP phase, because A336, as an ionic liquid, is polar and it contains water (Figure S5, Supporting Information). Therefore, the extractability of $[\text{NiCl}_x(\text{H}_2\text{O})_{6-x}]^{2-x}$ to the LP phase depends on its relative solubility between the LP phase and the MP phase. In different polar solvents, Ni has different solvation structures, which would have different relative solubilities between the two immiscible phases due to the intrinsic properties of polar solvents and the different extent of coordination of chloride ions to the metal cations.

Polar solvents affect not only the chlorometallate formation (for Co, Mn, and Ni), but also the speciation of metal ions (for Ni) and the relative solubility of the species in the two immiscible phases. The different evolution of the extraction curves

of Co, Ni, and Mn from water to NMF also show that polar solvents affect the extraction of different metals to different extents, which might be a basis for enhancing metal separations by changing polar solvents.

To validate the hypothesis of enhancing metal separations by polar solvents, La/Ni (as chloride salts) were extracted by A336 from the five selected polar solvents (Figure 3). The separation of these two metals is relevant to the recovery of valuable metals from nickel-metal hydride batteries.^[28] On top of the significant change of Ni extraction curves from water to NMF, the extraction of La also changes substantially, leading to two interesting observations: 1) extraction of Ni and La from water and methanol have almost opposite trend (Figure 3a, d); 2) remarkable separation of Ni from La is achieved with about 80% Ni extraction and La extraction below detection limit (< 0.1 ppm), resulting in an almost infinite separation factor (α) (Figure 3e). It is usually difficult to selectively extract Ni over La, because Ni has a lower affinity to most extractants than La due to a lower charge density, and Ni has a relatively weak ability to form anionic chlorometallate complex compared with other transition metals. The separation factor found here ($\alpha > 1000$) is the highest reported in literature, to the best of our knowledge (more discussions in the Supporting Information, Section 2.9). In addition, water content in methanol also affects the metal extraction significantly (Figure 3f and Figure S9). Overall, extraction of La/Ni can be significantly tuned by simply changing polar solvents and exceptional separation of Ni/La has been achieved using NMF as the polar solvent.

La is not extracted from EG, formamide or NMF, but is efficiently extracted from water and methanol, which requires further study to fully understand the metal extraction mechanism. A number of analytical characterizations have been applied

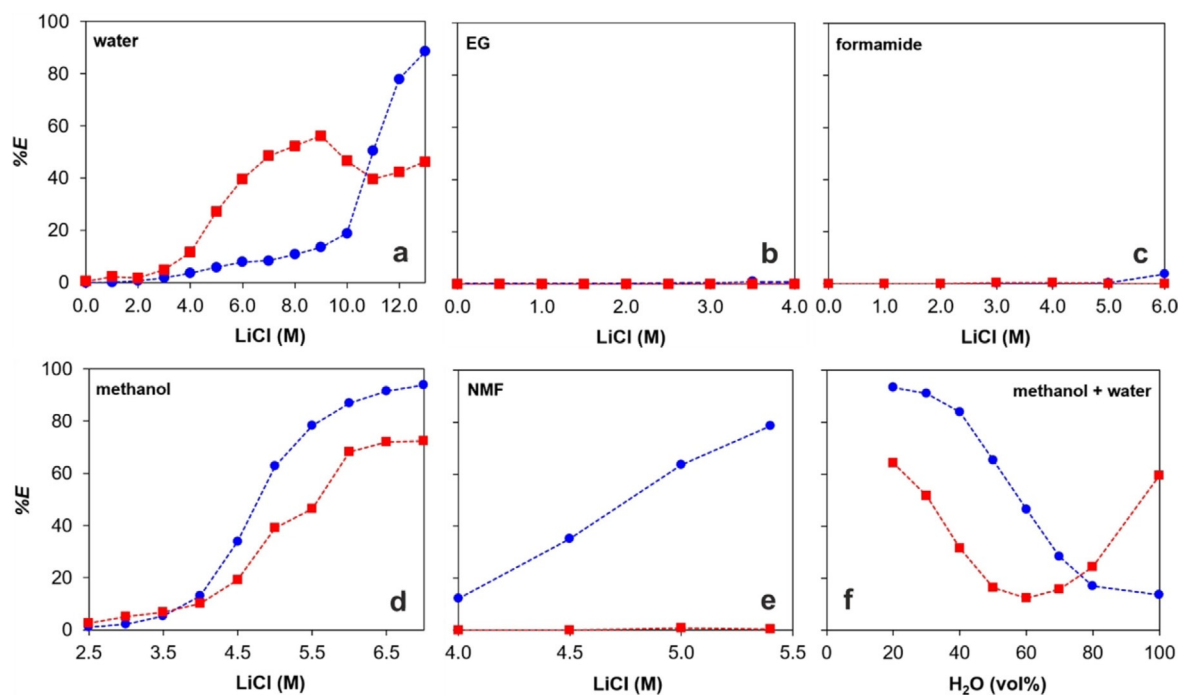


Figure 3. Percentage extraction of La (■)/Ni (●) by A336 in toluene from water (a), EG (b), formamide (c), methanol (d), NMF (e) and water/methanol mixture with 9.0 M LiCl (f).

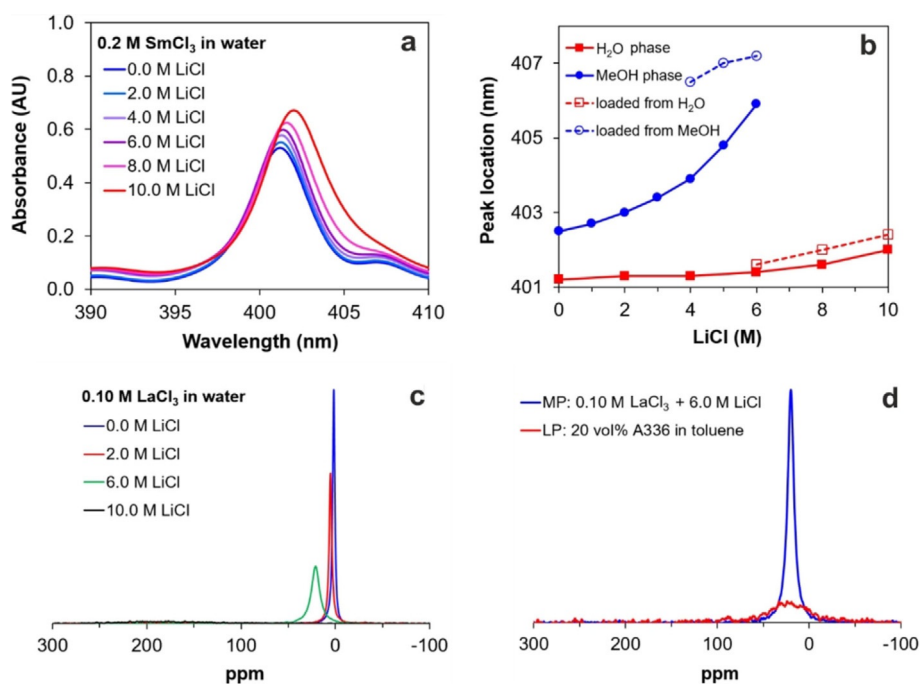


Figure 4. Speciation study for Ln extraction: absorption spectra of Sm in aqueous solutions (a), absorption peak shift of Sm in aqueous and methanolic solutions and the corresponding loaded LP phases (b); ¹³⁹La NMR spectra of La in aqueous solutions (c), ¹³⁹La NMR spectra of the aqueous solution and the LP phase at extraction equilibrium (d).

using different Ln (Lanthanides) as probes to study the speciation, assuming that different Ln are extracted by the same mechanism, considering their similarities in chemical properties. Firstly, UV/Vis absorption spectra of Sm in aqueous solutions and the corresponding loaded LP phases were recorded. The main species of Sm in water is known to be $[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$ at room temperature and atmospheric pressure.^[29] With addition of LiCl and elevation of temperature and pressure, chloride ions may attach to the first coordination sphere, forming $[\text{SmCl}_x]^{3-x}$ ($x=0, 1, 2, 3$ or even higher; water molecules are omitted).^[30,31] The formation of $[\text{SmCl}_x]^{3-x}$ causes redshifts of the absorption spectra and an increase in the absorbance (Figure 4a). The corresponding loaded LP phase show a slightly stronger redshift (Figure 4b and Figure S17, Supporting Information), which is an indication that the Sm species in the LP phase is on average coordinated to more chloride ions than the species in the aqueous solutions. Furthermore, the peak shifts of the loaded LP phases increases with increasing LiCl concentration, indicating that Sm is not extracted as a single species, but as a mixture of $[\text{SmCl}_x]^{3-x}$ ($x=0, 1; x=2$ is less likely due to the low stability of $[\text{SmCl}_2]^+$ in aqueous solutions).^[30,31]

Secondly, ¹³⁹La NMR spectra of La solutions were recorded (Figure 4c). With addition of 2.0 and 6.0 M LiCl to aqueous solutions, the NMR signals broaden and shift downfield, which is due to a lowering of the symmetry of the complex by the binding of chloride ions. Broad ¹³⁹La NMR spectra have been reported for low symmetry La complexes coordinated with a mixture of nitrate and water molecules.^[32,33] Extensive DFT computations performed by Doidge et al.^[34] indicates that La complex with one chloride in the inner-sphere (i.e. $[\text{LaCl}]^{2+}$)

can be formed in aqueous solution although it is very difficult to have two or more chlorides in the inner-sphere. ¹³⁹La NMR spectra were also recorded for the loaded LP phase and the corresponding aqueous raffinate solutions at extraction equilibrium (Figure 4d and Figure S12). On the one hand, the loaded LP phases have the same downfield shift as that of the corresponding aqueous raffinates, meaning that the speciation in the two equilibrium phases are similar. On the other hand, the spectra of the loaded LP phase are less intense and broader, meaning that the La species are probably coordinated to more chloride ions than the corresponding La species in the aqueous solutions.

Similar characterizations were also applied to methanolic solutions and the corresponding LP phases (Figures S13, S16, S18, and S19, Supporting Information). Furthermore, ³⁵Cl NMR spectra (Figure S10 and S11, Supporting Information), EPR spectra (Figure S20 and S21, Supporting Information) and luminescence emission spectra (Figure S22) have been recorded for various Ln probes in both the MP and the LP phases and consistent information has been obtained. In short, the main species of Ln in aqueous chloride solution is Ln^{3+} or $[\text{LnCl}]^{2+}$, depending on the LiCl concentration; the main species of Ln in the methanolic chloride solution is a mixture of $[\text{LnCl}_x]^{3-x}$ ($x=1, 2, 3$). The species in the loaded LP phase is similar to that in the corresponding aqueous or methanolic solutions, but are coordinated to more chloride ions on average.

It is now clear that, the mechanism of La extraction by A336 from water and methanol is similar to the extraction of Ni from water at low LiCl concentration, that is, solvation complexes are dissolved in the LP phase, because a mixture of solvation complexes ($[\text{LnCl}_x]^{3-x}$, $x=1, 2, 3$) were found in both the MP

phase and the LP phase. In retrospect, the arc-shaped curve of La extraction from methanol/water mixtures (Figure 3 f) reflects the change from solvation with methanol to solvation with water, whereas the decrease of Ni extraction with increasing water content is due to the lowering $[\text{NiCl}_4]^{2-}$ formation efficiency. More interestingly, in the separation of La and Ni using NMF as the polar solvent, the effect of polar solvents on enhancing the formation of chlorometallate complexes (for Ni) and on the speciation and relative solubility of species (for La) both played important roles. In principle, the extraction of metals by other types of extractants, besides A336, is also subject to the influence of polar solvents because the effects of polar solvents take place in the more polar phase, independently of the extractants.

In summary, polar solvents play important roles in the formation of chlorometallate complexes and in the speciation of metal cations, hence significantly affecting metal extractions. The effects of polar solvents on the extraction of different metals are of different extent, leading to the enhancement of metal separations by selecting suitable polar solvents. In principle, the method of enhancing metal extractions by polar solvents is applicable to the extraction of various metals using many different kinds of extractants.

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Conflict of interest

The authors declare no conflict of interest.

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