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COMMUNICATION

Homogeneous liquid-liquid extraction of metal ions with non-fluorinated bis(2-ethylhexyl)phosphate ionic liquids having a lower critical solution temperature in combination with water

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Ionic liquids with an ether-functionalised cation and the bis(2-ethylhexyl)phosphate anion show thermomorph behaviour in water, with a lower critical solution temperature. These ionic liquids are useful for homogeneous liquid-liquid extraction of first period (3d) transition metals.

Ionic liquids (ILs) are solvents that consist entirely of ions.^{1–3} They are distinguished from molten salts by their low melting temperature, arbitrarily set at 100 °C. ILs are often considered as environmentally friendly alternatives for molecular solvents in solvent extraction since they have a negligible vapour pressure.⁴ The physical properties of ILs depend on their structure. Depending on its composition, an ionic liquid is miscible or immiscible with water, leading to a classification into hydrophilic and hydrophobic ionic liquids. Yet, this classification is ambiguous, since the miscibility of some ILs with water is strongly temperature-dependent. In upper critical solution temperature (UCST) systems, the solubility of the IL in water increases with increasing temperature and a homogeneous system is found above a certain point in the cloud point curve, namely above the upper critical solution temperature, the components are miscible in all concentrations. The opposite happens for the lower critical solution temperature (LCST) systems, in which the homogeneous phase is formed with a decrease of temperature. It has been reported that ionic liquids have temperature-dependent miscibility with different molecular solvents.^{5,6,7,8} Ohno and co-workers made seminal contributions to LCST phase changes in ionic liquids.^{9–16} They have prepared ionic liquids derived from amino acids that show LCST-type phase changes with water.¹⁷ IL-water biphasic mixtures are of interest for the separation of molecules by solvent extraction. In 2006, we reported on the IL betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf₂N]) which, mixed with water, shows an UCST at 55

°C.¹⁸ It has been used in the homogeneous liquid-liquid extraction (HLE) of metal ions.^{19–21} The binary mixture of choline bis(trifluoromethylsulfonyl)imide ([Chol][Tf₂N]) and water shows temperature-dependent phase behaviour with an upper critical solution temperature of 72 °C and has been used for the HLE of Nd(III).²² A series of ILs based on Girard's reagents have tunable thermomorphism of the UCST type and were used for HLE of transition metals.²³ In the literature, the LCST behaviour of both glycol ether–water mixtures,²⁴ and functionalised polymers with glycol chains²⁵ were described. The ionic liquid interpretation of the LCST phase behaviour can be comprehended based on the knowledge from polymer studies. Although Ohno and co-workers reported the HLE of LCST ionic liquids for the extraction of proteins,^{26,27} the use of such a LCST system was, until now, never executed for the extraction of metal ions.

In this Communication, ionic liquids having the bis(2-ethylhexyl)phosphate as anion are presented that show lower critical solution temperature phase behaviour. A proof-of-principle extraction of first row transition metals by the ionic liquid [P₄₄₄E₃][DEHP] is the first example of homogeneous liquid-liquid extraction of metal ions with an LCST thermomorph system. The designed ILs are depicted in Figure 1. The synthesis of the ether-functionalised ionic liquids was based on literature procedures.²⁸ After tri-*n*-butylphosphine was reacted with a chloride oligo ethylene precursor, a metathesis reaction was performed in which the chloride anion of the ether-functionalised ILs was exchanged to the bis(2-ethylhexyl)phosphate (DEHP) (Experimental Section).

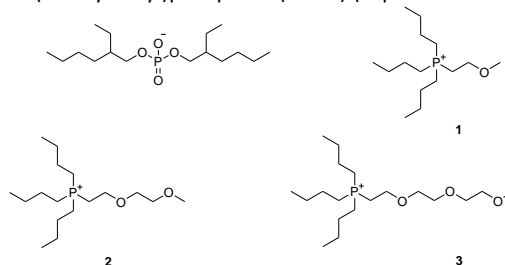


Figure 1. Structures of investigated ILs. Anion: bis(2-ethylhexyl)phosphate ([DEHP]). Cations: 1: tri-*n*-butyl-2-methoxyethylphosphonium ([P₄₄₄E₁]⁺), 2: tri-*n*-butyl-2-(2-methoxyethoxy)ethylphosphonium ([P₄₄₄E₂]⁺), 3: tri-*n*-butyl-2-[2-(2-methoxyethoxy)ethoxy]ethylphosphonium [P₄₄₄E₃]⁺.

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† Electronic Supplementary Information (ESI) available: Experimental details of synthesis and characterisation of ionic liquids, temperature dependence of transmitted intensity, ATR-FTIR, extraction details. See DOI: 10.1039/x0xx00000x

Table 1. Viscosity, water content and phase behaviour of ether-functionalised ILs.

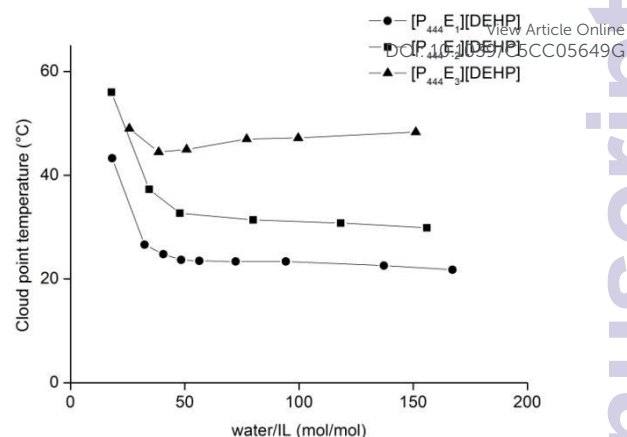
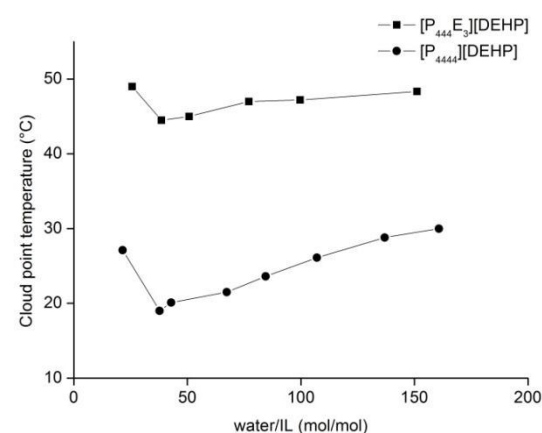
Entry		Viscosity (cP) at 50 °C	Water content (ppm)	Phase behaviour with water
1a	[P ₄₄₄ E ₁]Cl	364	n.d. ^a	miscible ^b
2a	[P ₄₄₄ E ₂]Cl	321	1261	miscible ^b
3a	[P ₄₄₄ E ₃]Cl	172	1259	miscible ^b
1b	[P ₄₄₄ E ₁][DEHP]	94	811	LCST
2b	[P ₄₄₄ E ₂][DEHP]	50	858	LCST
3b	[P ₄₄₄ E ₃][DEHP]	86	790	LCST

^a n.d.: not determined. Solid at room temperature, melting point: 31 °C. ^b Fully miscible with water in the temperature range 0–100 °C.

The physical properties of the DEHP ILs are listed in Table 1. A decrease in viscosity with longer oligo ethylene chain is seen for the chloride ILs (see ESI). Introduction of the bis(2-ethylhexyl) phosphate anion lowers the viscosity. Regarding the phase behaviour of the ionic liquids with water, the structure of the ionic liquid plays a crucial role. Most importantly, the anion drastically changes the miscibility of the ionic liquid with water. All synthesised chloride ionic liquids are fully miscible with water, whilst all the synthesised DEHP ionic liquids show LCST phase behaviour. Also, the role of the cation was investigated. The cloud point temperature was determined for the three different ether-functionalised ILs in a 1:1 wt/wt mixture with water. Complete phase diagrams were constructed via visual observation of the cloud point upon heating the homogeneous mixtures of different compositions (Figure 2). In addition, more accurate but slow transmission measurements were carried out for some of the compounds to verify the visual observations. In this technique, the cloud point temperature was defined as the temperature at which 50% of the initial transmission is reached. Temperatures found are: 34 °C, 38 °C and 44 °C for 1:1 wt/wt binary mixtures with water of [P₄₄₄E₁][DEHP], [P₄₄₄E₂][DEHP] and [P₄₄₄E₃][DEHP], respectively (Figure S1). These temperatures are practical for extraction applications, since increasing the temperature by 10 to 20 °C above room temperature is sufficient for complete phase separation. The cloud point temperature increases with increasing oligo ethylene chains. This can be explained as follows. Mixing of the IL and water will occur when the Gibbs free energy of mixing ΔG_{mix} is negative:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

In case of LCST phase behaviour, ΔS_{mix} is negative. Below the LCST, the two components are fully miscible due to the formed hydrogen bonds between water and the IL, resulting in a hydration shell around the ions. With increasing temperature, this hydrogen bonding is more and more lost until eventually all water molecules from the hydration shell are expelled into the bulk water. A longer oligo ethylene chain in the ionic liquid has more possibilities for hydrogen bonds with water; hence a higher temperature is needed to break them up. The lower cloud point temperature of [P₄₄₄₄][DEHP]:water in comparison with [P₄₄₄E₃][DEHP]:water can be explained in a similar way: [P₄₄₄₄][DEHP] allows for less possible interactions with water, since this IL lacks functional groups (Figure 3).

**Figure 2.** Phase diagrams of the binary mixtures of three ether-functionalised ILs with water.**Figure 3.** Comparison of cloud point temperatures between functionalised ([P₄₄₄E₃][DEHP]) and non-functionalised ([P₄₄₄₄][DEHP]) ionic liquid.

Bis(2-ethylhexyl)phosphoric acid is a well-known extractant in hydrometallurgical processes for the separation of divalent transition metals.^{29–31} Therefore, the bis(2-ethylhexyl) phosphate ILs were tested for homogeneous liquid-liquid extraction of 3d transition metals. The binary mixture of the ionic liquid [P₄₄₄E₃][DEHP] and water was used for the extraction of cobalt(II), copper(II), nickel(II) and zinc(II). The original cloud point of the 1:1 wt/wt mixture was 44 °C. Yet, the presence of salts in the extraction system influences this cloud point temperature. It is known that the alkaline-earth chloride salts induce a lowering of the lower critical solution temperature.³² In this case, with the divalent transition metal ions, the cloud point temperature is reduced significantly. The cloud point temperatures are decreased to approximately 20 °C for contacting the IL with an aqueous solution of approximately 5000 ppm of the metal. The reduction in temperature is beneficial for homogeneous liquid-liquid extraction on a laboratory scale, since the homogeneous region is formed by cooling the mixtures down in an ice bath. However, this lowering of the cloud point temperature can also be disadvantageous since it was observed that no metal concentrations higher than 8000 ppm could be used. The high salt concentration induces a lowering of the cloud point temperature outside the window of cooling by ice water (<0 °C).

Prior to the homogeneous liquid-liquid extraction experiments, the IL was presaturated with water to minimize phase changes. A 1:1 wt/wt binary mixture of the IL and water was made. After homogenisation and subsequent settling of the two phases, it was found that 18 wt% of water dissolved in the IL phase (Karl Fischer titration) and 6 wt% of IL was lost into the water layer (quantitative NMR - see ESI). The influence of the extraction time at 0 °C below LCST on the *percentage extraction* (%E) was investigated first (Figure S2). After 5 min, no significant changes in the %E were observed, so this cooling time was chosen. In order to determine the distribution ratios, four different aqueous solutions of approximately 5000 ppm of the metal (CoCl₂, CuCl₂, NiCl₂ and ZnCl₂) were mixed with the ionic liquid [P₄₄₄E₃][DEHP] in the homogeneous phase. After settling at room temperature for 10 min to form the biphasic system again, the mixtures were centrifuged to ensure full phase separation. Then, the aqueous phases were separated and analysed for their metal content by total reflection X-ray fluorescence (TXRF). The distribution ratios were calculated as:

$$D = \frac{c_{in} - c_{aq}}{c_{aq}} \quad (2)$$

where c_{in} and c_{aq} are the metal concentrations in the initial aqueous phase and the aqueous phase after extraction, respectively. The distribution ratios listed in Table 2 were measured for chloride solutions of the respective metals with initial pH around 3.5. In Figure 4, the three stages of the extraction are presented for copper(II).

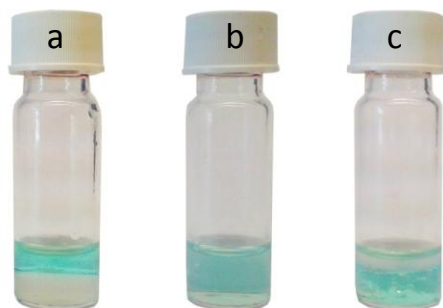


Figure 4. Homogeneous liquid-liquid extraction of Cu(II) with [P₄₄₄E₃][DEHP]/H₂O 1:1 wt/wt mixture (concentration 6866 ppm) a: initial stage, b: homogeneous phase after 5 min in ice bath, c: after settling to room temperature. The upper layer is the aqueous phase; the ionic liquid phase is the bottom layer.

In the Irving-Williams series, the general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is given as Co(II) < Ni(II) < Cu(II) > Zn(II).³³ In case of the extraction with the bis(2-ethylhexyl)phosphate anion, the general order is followed, Co(II) is extracted the least, Zn(II) is extracted better and Cu(II) is the metal ion with the highest distribution ratio (Table 2).

Stripping was performed by adding a 1:1 molar ratio of solid oxalic acid to the isolated IL phase. After shaking at 40 °C for 30 min at 3000 rpm, a sample of the IL phase was analysed with TXRF for its metal content (Table 2). The *percentage stripping* %S is defined as follows:

$$\%S = \frac{c_{ILbs} - c_{ILas}}{c_{ILbs}} \times 100 \% \quad (3)$$

where c_{ILbs} and c_{ILas} are the metal concentration of the ionic liquid phase before and after stripping, respectively. This precipitation stripping technique is advantageous since the metal is removed in one single step. Using oxalic acid as stripping agent, almost all Co(II) and Ni(II) was precipitated as their respective oxalates. The stripping with oxalic acid was still very efficient for Zn(II), more than 90% of the metal was recovered as oxalate. For Cu(II), the solution was still very blue coloured and only 58% of the metal ion was stripped from the organic phase (Figure S4). Apparently, the most extracted ion, Cu(II), is also the most difficult to remove from its complex with the addition of oxalic acid. Instead, the stronger acid H₂SO₄ was used to strip Cu(II). 500 mg of the loaded IL phase was contacted with 500 mg of a 1M H₂SO₄ solution. A light blue precipitate was formed and a percentage stripping of 99% was obtained (Table 2).

It must be noted that the IL cannot be used for a new extraction step directly after stripping, since the anion is now protonated and the chloride IL reformed. Simply by a washing step with an alkaline solution, the DEHP IL is fully restored and ready for another extraction/stripping cycle.

Table 2. Extraction of 1st row transition metals (Co(II), Ni(II), Cu(II), Zn(II)) with [P₄₄₄E₃][DEHP], initial metal concentrations in the aqueous phase (c_i) and metal concentration in the aqueous phase after extraction (c_{aq}), the initial pH of the solutions (pH_{in}), their distribution ratios D and the percentage stripping %S when contacted with solid oxalic acid (for Cu(II), also with H₂SO₄).

Metal ion	c_i	pH_{in}	c_{aq}	D	%S
Co(II)	6866	3.2	1278	4.4	99
Ni(II)	5578	3.4	286	19	99
Cu(II)	4480	3.9	128	34	58/99
Zn(II)	7466	3.0	285	25	91

The coordination of the metal ions by the IL was studied by FTIR spectroscopy. By comparing ATR-FTIR spectra for presaturated IL and the IL loaded with Co(II), an obvious shift to lower wavenumbers was observed for two peaks (Figure S3). The first one: around 1200 cm⁻¹, a small shift in the peak corresponding to a P=O stretch, and around 1600 cm⁻¹, a larger shift in the peak corresponding to the P-O⁻ stretch.³⁴ As expected, this indicates the interaction between the functional group and the metal cation in the extraction.

Also, the selectivity towards other metals was investigated. The extraction of CsCl has a distribution ratio of 4.1, even lower than the worst divalent metal ion tested (Co(II)). Taking into account that indium and some rare earths are listed as critical metals in the EU Report because of their high supply risk,³⁵ and therefore, their recycling demand will increase, these elements were chosen for the study of the selectivity. Unfortunately, these elements form a precipitate when contacted with the ionic liquid. This suggests strong complexation with the bis(2-ethylhexyl)phosphate anion. It is known that the di(2-ethylhexyl)phosphoric acid is an excellent extractant for rare-earth elements and indium.^{36,37} Yet, introducing it as an anion in the ionic liquid leads to formation of an insoluble complex, as was confirmed by TXRF measurements.

In conclusion, we have shown that the introduction of bis(2-ethylhexyl)phosphate as anion in oligo ethylene functionalised phosphonium ionic liquids gives ionic liquids with LCST phase behaviour. The cloud point temperature is tuneable by making modifications in the structure of the ionic liquid. Longer oligo ethylene chains induce higher cloud points. Addition of a metal chloride salt significantly lowers the cloud point temperature. The ionic liquid [P₄₄₄E₃][DEHP] was used in this first example of homogeneous liquid-liquid extraction of metal ions with an LCST thermomorphic system. The extraction capacity towards DEHP ionic liquid is excellent for divalent metal ions.

Experimental section

The synthesis was executed as follows. First, the acidic form of the phosphate was neutralised by a base, as described in the literature,³⁸ by adding a solution of 20 wt% NaOH to bis(2-ethylhexyl)phosphoric acid in ethanol absolute until a neutral pH was reached. The solvent was evaporated and the product was dried in a vacuum oven at 60 °C for 2 h. The phosphate salt (1 mol eq) and the chloride ionic liquid (1.5 mol eq) were dissolved in water and stirred overnight. Dichloromethane was added and the product was extracted to the organic phase and washed with water to remove NaCl and excess IL. The organic phase was isolated and evaporated to yield pure product. Full characterisation can be found in the ESI. In a typical extraction experiment, 500 mg of the presaturated IL is contacted with 500 mg of an aqueous metal solution. The mixtures were cooled in an ice bath for 5 min to reach the homogeneous region. Next, the mixtures are left to settle at room temperature for 10 min. A sample was taken from the aqueous layer and analysed for its metal content by TXRF. For a typical stripping experiment, to 500 mg of the loaded IL, equimolar amounts of oxalic acid were added and shaken for 30 min at room temperature.

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