

Ionic-Liquid-Based Acidic Aqueous Biphasic Systems for Simultaneous Leaching and Extraction of Metallic Ions

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Abstract: The first instance of an acidic aqueous biphasic system (AcABS) based on tributyltetradecyl phosphonium chloride ($[P_{44414}][Cl]$) and an acid is here reported. This AcABS exhibits pronounced thermomorphic behavior and is shown to be applicable to the extraction of metal ions from concentrated acidic solutions. Metal ions such as cobalt(II), iron(III), platinum(IV) and nickel(II) are found to partition preferentially to one of the phases of the acidic aqueous biphasic system and it is here shown that it successfully allows the difficult separation of Co^{II} from Ni^{II} , here studied at 24 and 50 °C.

Ionic liquids (ILs) are a well-known class of salts with low melting points and a nanostructured liquid phase. They exhibit unique, often unexpected, physical and chemical properties. In the last two decades these compounds have been applied in all fields of chemistry, including extraction of metal ions from aqueous phases.^[1,2]

The major developments in the use of ILs in solvent extraction of metals can be divided into three main categories: ILs used as the diluting hydrophobic phase in conjunction with a traditional extracting agent, selective extraction of metals through the anion interaction of the IL and task-specific ILs.^[3–5]

Despite the proven potential of ILs as alternatives to volatile organic compounds in liquid–liquid extraction, some significant drawbacks remain. First, the range of hydrophobic ILs is limited, most being based on fluorinated anions such as bis(trifluoromethanesulfonyl)imide, $[Tf_2N^-]$,^[6,7] that are expensive and refractory to biodegradation.^[8] A collateral

problem is that although hydrophobic, these ILs are partly soluble in the acidic aqueous solutions from which the metal ions are to be extracted, which induces a costly undesirable loss.^[6,7,9] Avoiding fluorinated anions is possible by using a simple anion combined with hydrophobic cations, such as trihexyltetradecyl phosphonium chloride. Such ILs, however, exhibit high viscosities, and thus poor transport properties that hinder their industrial applicability.^[10,11] Another type of extracting systems, so-called ionic-liquid-based aqueous biphasic systems (IL-ABS) have been used in the last decade for extracting neutral compounds from an aqueous phase.^[12–15] These systems are based on hydrophilic ILs that, once mixed with a specific inorganic salt in water, yield the formation of two immiscible aqueous phases—a salt-rich and an IL-rich phase, respectively. Few IL-ABS were previously applied to metal ion extraction due to their limited stability at the low pH required to prevent metal hydrolysis.^[16] In addition, in any metal extraction process, acids are used to leach the metal from ores or waste devices.

In this work, we report the development of a new type of ABS, the hereafter called acidic ABS (AcABS), in which the inorganic salt is replaced by the acid used to leach the metals. This new type of systems closes the gap between ABS and metallic ion extraction from acidic phases. An example of the formation of such an AcABS containing high amounts of HCl, of the hydrophilic IL tributyltetradecyl phosphonium chloride ($[P_{44414}][Cl]$) and water is here presented and applied to the partition of four metals, namely Co^{II} , Fe^{III} , Ni^{II} and Pt^{IV} initially dissolved in HCl solutions.

Binodal curves for the system $[P_{44414}][Cl]$ -HCl- H_2O obtained at 24, 36, 45, 50 and 56 °C are reported in Figure 1. Points A to E correspond to mixtures of $[P_{44414}][Cl]$, HCl and water with different compositions, as shown in Figure 1 (see details in the Supporting Information). At a given temperature, the biphasic domain is located at the right of the binodal curve, and, as shown, increases with temperature. This system therefore exhibits a lower critical solution temperature (LCST). This LCST behavior is related to the strong polar/electrostatic interactions between the water and the ions and the unfavorable negative contribution to the entropy of mixing with increasing temperature.^[17] As shown in Figure 1, the concentration of acid required to induce a biphasic system for a $[P_{44414}][Cl]$ concentration of 15 wt % is 20 wt % HCl at 24 °C but decreases significantly with temperature, with only 6 wt % HCl required to induce phase separation at 56 °C. In other words, mixtures C and E are monophasic at 24 °C. When increasing the temperatures of the mixture above 46 °C, two phases are formed.

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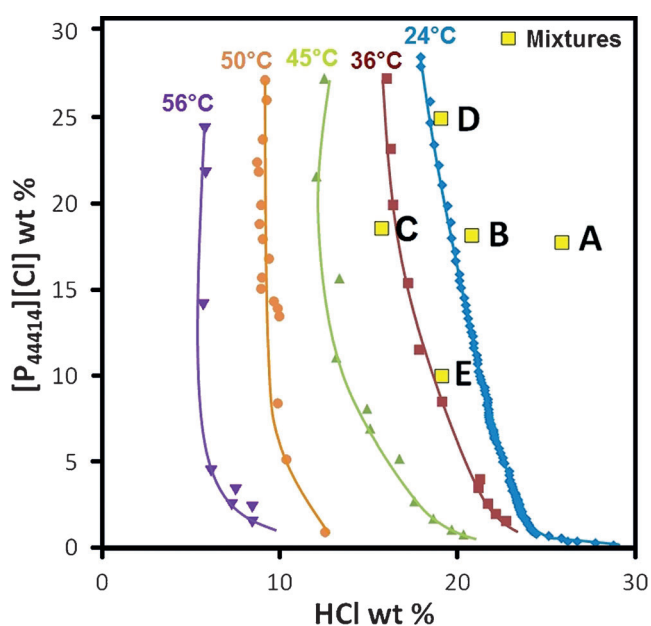


Figure 1. Binodal curves for the system $[P_{44414}][Cl]$ -HCl- H_2O at various temperatures and the composition of mixture points A–E studied. Lines are guides to the eye.

For mixtures exhibiting a phase separation, the compositions of the upper (IL-rich) and lower (HCl-rich) phases are related by tie lines.^[18,19] Since the lower part of the binodal curve is very close to the x -axis this means that the HCl-rich phase contains very little ionic liquid while the upper phase contains essentially all the ionic liquid. Analysis of the water content of the IL-rich phase and of the HCl concentration of the HCl-rich phase (see Table S2) reveals that for a given mixture, the amount of water in the upper phase decreases with temperature (see Table S1).

The ability to separate highly acidic solutions into two phases in presence of an IL by increasing the temperature allows the development of metal recycling processes combining the leaching and extraction of metal ions. The AcABS offer the ability to leach a metal and then partition its ions between two aqueous phases formed upon heating the aqueous leaching liquor. The influence of the temperature on the phase separation of an AcABS is depicted on Figure 2. With increasing temperature, water and HCl are expelled from the upper IL-rich phase which yields a decrease in its volume and the formation of an essentially IL-free lower phase.

Onghena et al.^[16] reported the formation of ABS using $[P_{44414}][Cl]$ and NaCl and their application to the separation of cobalt from nickel. A comparison of the phase diagrams for these systems (compare Figure S2) shows that they have a similar shape and temperature dependency. The phase separation requires a significantly higher concentration of chloride in the case of $[P_{44414}][Cl]$ -HCl- H_2O compared to that required in $[P_{44414}][Cl]$ -NaCl- H_2O . However most metals, for example, platinum and iron, are not stable in solution at the high pH of this system,^[20] while the proposed AcABS allows for the direct “one-pot” extraction of metals from leachates. The highly acidic aqueous solutions used in this AcABS are

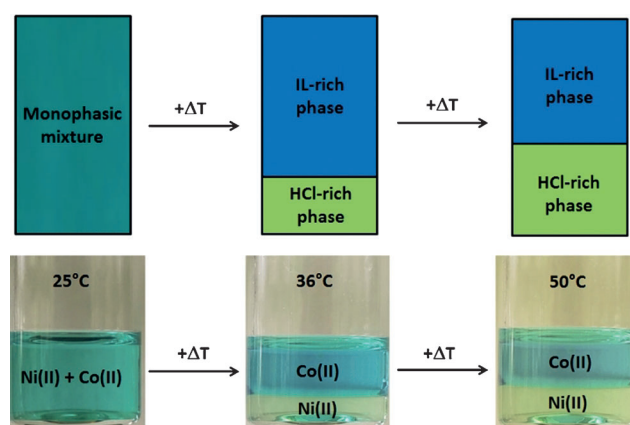


Figure 2. Influence of the temperature on the phase separation. The HCl-rich phase is almost completely depleted in ionic liquid.

representative of the leaching solutions employed in industrial processes to produce metals.

Based on its stability and interesting thermomorphic properties, the described AcABS was applied to the extraction of Fe^{III} , Pt^{IV} , Co^{II} and Ni^{II} ions. To that end, extraction of these ions was studied using mixtures A to E shown in Figure 1 and detailed in the Supporting Information.

As shown in Figure 1, the extraction of metals was achieved using solutions A, B and D at 24°C and all five mixtures at 50°C. Extraction yields for all metals are shown in Figure 3; a comprehensive description is available in the Supporting Information. Snapshots of the extraction at the different mixture points is presented in Figure 4 for Co^{II} and in Figure S4 for Fe^{III} and Pt^{IV} . Figure 3 shows that Fe^{III} and Pt^{IV} are close to quantitatively extracted towards the IL-rich phase for all mixture points, whatever the temperature of the system. Co^{II} is also efficiently extracted from 75 to 97% in mixtures E and C, respectively, at 50°C, whilst the majority of Ni^{II} remains in the HCl-rich phase.

Previous studies have shown that metal ions forming anionic complexes such as $AuCl_4^-$, $IrCl_6^{2-}$, $PtCl_6^{2-}$, $PdCl_4^{2-}$, $RhCl_6^{3-}$, $CoCl_4^{2-}$ ^[21–24,11] are successfully extracted towards hydrophobic ILs by forming a hydrophobic pair between the anionic metal complex and the cation of the ionic liquid. For instance, extraction of $PtCl_6^{2-}$ or $PdBr_4^{2-}$ towards hydro-

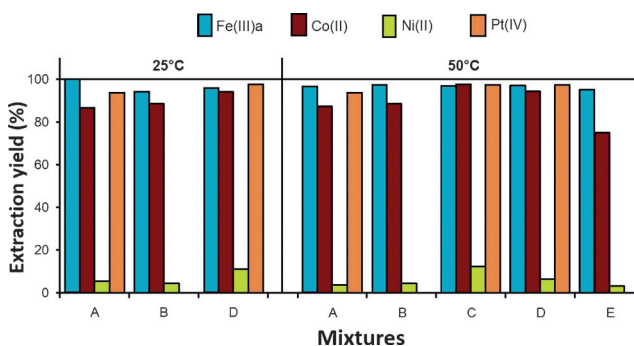


Figure 3. Extraction yields for various metal ions in mixtures A to E at 24 and 50°C. Extraction for Pt^{IV} not carried out using mixtures B and E.

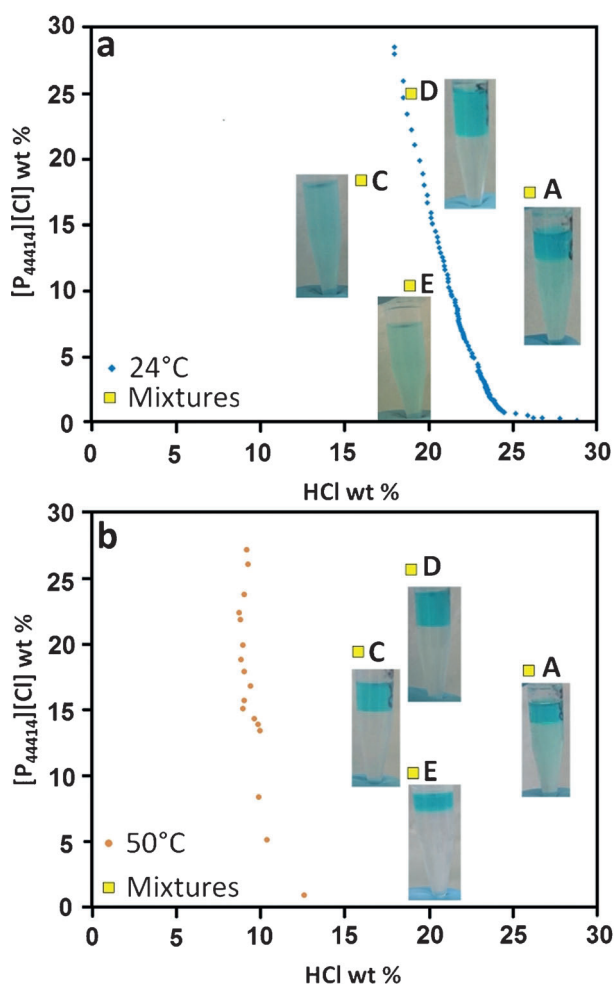
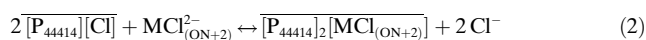


Figure 4. Phase diagrams at 24 and 50°C and related snapshots taken after extraction of Co^{II} using [P₄₄₄₁₄][Cl]-HCl-H₂O. Upper diagram a) binodal curve obtained at 24°C. Snapshots were obtained when preparing mixtures A, C, D and E. Lower diagram b) binodal curve measured at 50°C.

phobic 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C₁C₈IM][Tf₂N] or trihexyltetradecyl phosphonium chloride [P₆₆₆₁₄][Cl] was found to be due to the formation of a hydrophobic pair [C₁C₈IM]₂[PtCl₆]^[25] or [P₆₆₆₁₄]₂[PdBr₄]^[25] accordingly. On this basis, we suggest the following mechanism as described through Equations (1) and (2),



where the bar denotes species present in the IL-rich phase and ON stands for the oxidation number.

In agreement with Equations (1) and (2), Fe^{III} and Pt^{IV} display a high affinity for [P₄₄₄₁₄][Cl] at all tested conditions due to the predominant formation of FeCl₄⁻ and PtCl₆²⁻ in solutions containing high concentrations of HCl. In the case of Co^{II}, its speciation is known to change significantly depending on the ratio of the concentration of metal to the concentration of chloride ions in solution. For instance, at 24°C, for a fixed amount of cobalt(II), Co(H₂O)₆²⁺ is formed

in pure water, while CoCl₃⁻ and CoCl₄²⁻ are found at high concentrations of HCl.^[26]

In all cases, extraction of Co^{II} using this AcABS led to IL-rich phases exhibiting a blue color, as shown in Figure 4. This color is characteristic of negatively charged complexes such as CoCl₃⁻ or CoCl₄²⁻ and was confirmed by UV/Vis absorption spectroscopy (Figure S5). Such complexes are obtained because of the presence of a large amount of Cl⁻ in the IL-rich phase, originating from the HCl and the ionic liquid itself. The transition from anionic chloro-cobalt species to hexa-aquocobalt in the HCl-rich phase can be observed as decreasing the concentration of acid in the lower phase from mixture point A to E or C leads to a the corresponding shift from a blue to pink solution color. This in turns has an impact of on the partition of Co^{II} in the system. In contrast, Ni^{II} hardly exists as a negatively charged chlorocomplex in water.^[26] Since it cannot form a hydrophobic ion pair with the ionic liquid cation, this results in a low extraction of the metal ion.

As a proof of concept of the application of these new acidic ABS to the separation of metal ions, the competitive extraction of Co^{II} and Ni^{II}, relevant to the recycling of NiMH batteries, was studied at 24 and 50°C. As shown in Figures 2 and 5, efficient separation of both metals can be achieved in

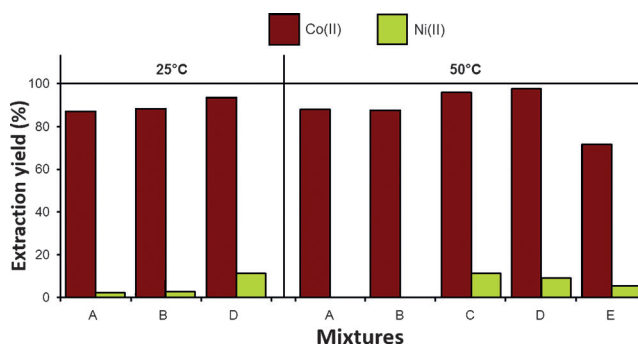


Figure 5. Extraction yields for the separation of Co^{II} from Ni^{II} using [P₄₄₄₁₄][Cl]-HCl-H₂O at 24 and 50°C. Initial concentrations for metals were 10 mmol L⁻¹.

a single step using this AcABS. Furthermore, the extraction of both metals can be tuned depending on the mixture and the temperature used. Specifically, mixtures A and B at 50°C yield a nearly pure Co^{II} in the IL-rich phase, with a separation factor of 400 and 376, respectively. These promising results demonstrate that AcABS can be used simply and efficiently for the critical separation of Co^{II} and Ni^{II} directly from HCl leachates of NiMH batteries.

The results obtained here are a proof of concept for the application of these new AcABS to metal ion extraction processes. These systems display important advantages over other extracting solvents. Most importantly, the use of the leachate solution itself as a salting out agent allows a “one pot” leaching and separation of critical metals. Furthermore, as the system is aqueous, no stripping steps are required. This drastically reduces the complexity of extraction processes. In addition, unlike classical systems based on an organic solvent and an extracting agent, [P₄₄₄₁₄][Cl]-HCl-H₂O exhibits a thermotropic behavior. The ability to manipulate the formation of

a biphasic system starting from a monophasic one and vice-versa simply by changing the temperature avoids the kinetic limitations related to the mass transfer between two-immiscible systems. Moreover, given the poor miscibility of the IL in the lower phase, after extraction, this HCl-rich phase can be recycled into a further leaching step. This process based on acidic aqueous biphasic systems can thus be applied to the separation of various strategic metals with reduced amounts of cheap, and more environmentally friendly ILs than those often studied based on fluorinated ions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hydrometallurgy · ionic liquids · metal recycling · noble metals · sustainable chemistry

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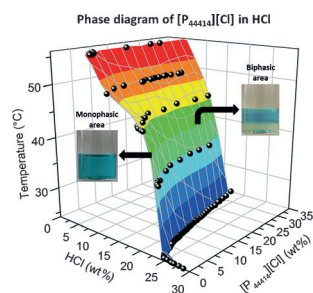
Communications



Sustainable Chemistry

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Ionic-Liquid-Based Acidic Aqueous
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Leaching and Extraction of Metallic Ions



Metal recovery from acidic solutions: A novel type of acidic aqueous biphasic systems (AcABS) based on an inorganic acid and an ionic liquid is presented. This system has been successfully applied to the extraction of metal ions. The thermotropic behavior and the use of large acid concentrations in the AcABS provide a promising alternative to conventional extracting systems.