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Uncommon biphasic behaviour induced by very high metal ion concentrations in HCl/H_2O/[P44414]Cl (tributyltetradecylphosphonium chloride) and HCl/H_2O/Polyethene glycol-600 systems

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In this work, the important role played by metal ions such as Fe(II/III), Cr(III) and Ni(II) in the formation and binodal behaviour of aqueous biphasic systems (ABS) composed of HCl and the ionic liquid, [P_{44414}]Cl, or the polymer, PEG-600, is investigated. The concentration of metal ions used in this work exceeds several g/L for an industrial foreseen application. Experiments have also been carried out by varying the concentration of metal ions at different temperatures. Fe exhibits a totally different behaviour compared to Ni and Cr. In particular, the binodal curves in presence of the ionic liquid are far from the classical curves found in the literature, displaying an onion-shape form, while for Ni and Cr, the curves follow the classical trend. When any of the three metal ions is mixed with the polymer and HCl medium, only Fe(III) induces a biphasic system. Insights into the chemical driving forces at work are discussed.Introduction

In recent years, neutral Aqueous Biphasic Systems (ABS), composed of different polymer-polymer, polymer-salt or salt-salt combinations, plus water as the main protagonist, have been taken into consideration to selectively extract metal ions. In particular, the use of the [P_{44414}]Cl (tri-butyl tetradecyl phosphonium chloride) ionic liquid (IL) or of the polyethene glycol (PEG) polymer for metal extraction has already been the subject of several papers.
[1–6] The use of these compounds, more appropriately called biphasic inducers in these classical ABS, helps to make the process eco-sustainable. The [P_{44414}]Cl hydrophilic ionic liquid (i) is less toxic than the respective hydrophobic IL[7], (ii) can be used in much lower quantities than organic volatile solvents and (iii) the extraction kinetics is favored by its low viscosity. In regards to the PEG, this is an inexpensive, nontoxic, non-flammable compound which is commercially available in very large quantities. These systems are intrinsically much eco-friendlier than the classical liquid-liquid systems where organic solvents are used as main components and could thus be favorably considered by the industry. However, in order to comply with any industrial demand, extraction should proceed from highly loaded wastes, which is currently very rarely the case in the literature. Furthermore, most industrial wastes are highly acidic, which is not compatible with the most classical ABSs.

Therefore, in the first step, we took advantage of the recently described Acidic Aqueous Biphasic Systems (AcABS)[8] loaded with very high concentrations of either Cr, Ni or Fe to perform fundamental studies in view of potential industrial applications.

In this work, aqueous biphasic systems (ABS) are formed from solutions containing a single metal element, HCl as the acid, and using either [P_{44414}]Cl or PEG as biphasic inducer. We focused on the influence of the metal, in particular on the contribution coming from the type of metal used and on its concentration. Furthermore, the influence of temperature has been taken into consideration for industrial needs. Finally, we reviewed past literature which proposed some possible explanations and we discussed these under the light of our experimental results.

Experimental Section

Chemicals

Polyethene glycol with an average molecular weight of 600 (abbreviated as PEG-600) was acquired from Acros Organics. The ionic liquid ~~tributyl tetradecyl phosphonium chloride~~, [P_{44414}]Cl, was acquired from Interchim (Montluçon, France). The declared purity was > 95%. Some basic physicochemical properties of PEG-600 are reported in the supplementary materials.

The hydrochloric acid, HCl, (37 wt% = 12 mol/L, in water) was acquired from Sigma-Aldrich. The following hydrated salts have been used: $NiCl_2.6H_2O$ pure at 98% acquired from Rectapur, $CrCl_3.6H_2O$ pure at 98% acquired from Fluka, $FeCl_2.4H_2O$ pure at 98% and $FeCl_3.6H_2O$ pure at 99% were acquired from Merck. All the chemicals were used without further purification.

The water used in all experiments was passed through a Milli-Q apparatus purification system commercialized by Merck (18MΩ).

AAS (Atomic Absorption Spectroscopy) single element standard solutions (1000 mg/L) were acquired from Perkin Elmer for Cr and from Chem-Lab for Fe and Ni.

Sample preparation

In order to investigate the effect of large amounts of metal ions onto the biphasic behaviours of the systems $[P_{44414}]Cl$ /HCl/H_2O and PEG-600/HCl/H_2O, aqueous acidic solutions of Ni(II), Cr(III), Fe(II) and Fe(III) have been prepared in HCl/H_2O 37 wt%, at metal concentrations below their maximum solubilities, as described in Table 1. Weights have been measured with a balance (Precisa gravimeters AG ± 0.0001 g), and volumetric flasks have been used to prepare the solutions.

Table 1 Concentrations of the metal ions in HCl 37wt% used for the binodal curves determinations and estimated maximum solubility limits.

	Ni(II)	Cr(III)	Fe(II)	Fe(III)
Metal concentration in 37%wt HCl (g/L)	2.5 - 15	2.5 - 15	1 - 20	2.5 - 40
Maximum solubility (g/L)[a] at 50°C	40	50	90	75

[a]: estimated value for the chloride salt in HCl 37 wt%.

Each solution was left under stirring at 700-800 rpm with a magnet overnight, until total dissolution.

Electrospray Ionization– mass spectrometry measurements

The different species present in the various stock solutions were detected by Electrospray Ionization– Mass Spectrometry (ESI-MS) using Bruker Amazon Speed apparatus. The working temperature chosen for the experiments was 40°C.

Phase diagrams: Turbidity and battle ship methods

The binodal curves were obtained with two different methods: the traditional turbidity method[9] and a new method proposed by our research team, which will be referred to as the 'battle ship method' in the following.

For the turbidity method, it is more convenient to work with liquid aliquots of low viscosity. The IL or the polymer can be either solid or liquid. Therefore, in a first step, a small amount of water was added to either the IL or the polymer in order to ease their handling. Then a known mass of the moistured IL or polymer was poured into a beaker, constituting the initial limpid monophasic solution. Then, the acidic solution was added dropwise to the system, under stirring, until the appearance of turbidity, which indicated the biphasic state creation. The turbid appearance of the sample is due to the fact that the two phases are not fully separated yet. A known amount of water was then added to the system until the mixture became transparent again. As there was systematically a rise in temperature during the addition of water and/or the acidic solution, consistent with the exothermic behaviour of such mixtures, stabilisation of the temperature was checked before the addition of the following reagent. All the weights were determined using an analytical balance Precisa gravimeters AG, with an accuracy of ± 0.0001 g and the procedure was repeated several times to build the curve. Experiments were performed at a controlled temperature of T = (25 or 50 ±1) °C by the use of a thermostatic bath.

For the battle ship method, several samples were prepared in glass vials by mixing different amounts of polymer or IL, water and stock solutions of acid and metal salts. Then the temperature of the vials was controlled in the range 25 °C – 50 °C by the use of a water bath. At the given temperature, a visual observation easily allowed sorting the samples as either monophasic or biphasic.

The battle ship method was chosen because it allows obtaining data faster than the turbidity method, in particular, when the temperature investigation is required. By transporting all the samples from the bath at 25°C to another bath at 50°C, it was possible to define the biphasic or monophasic state of the samples, after leaving them 30 minutes in each bath. In the turbidity method case, it is necessary to perform a new experimental session if different temperature conditions are taken into account, so the time required to perform the turbidity experiments increases. Furthermore, another time-consuming aspect in the turbidity method is due to the waiting time between one drop and the following one in order to re-stabilize the temperature within the solution.

The uncertainty of the turbidity method is related to the ability of the operator to well-distinguish between the biphasic or the monophasic behaviour of the sample in the vicinity of the binodal curve. In particular, the uncertainty is even linked to the number of drops (1 or 2) to pass from one region to the other. For the battle ship method, the uncertainty is due to the reasonable number of samples prepared by the operator to confirm with exactitude the position of the binodal curve. The two methods have been proved to give coherent experimental results (see Figure 8).

System notation and graphical display

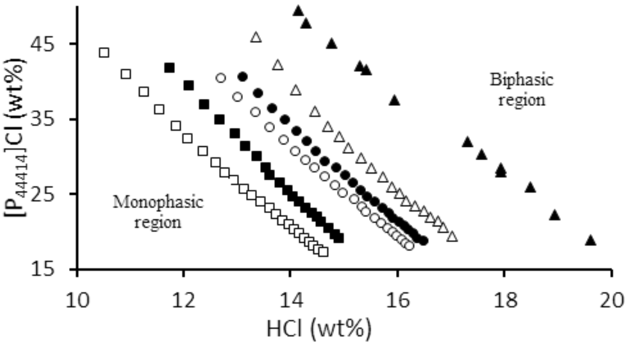

Figure 1 Binodal curves of the systems: $[P_{44414}]Cl/[HCl\ 37\ wt\%]/H_2O$ (IL= Cytec) (▲)[10]; $[P_{44414}]Cl/[HCl\ 37\ wt\%]/H_2O$ (IL= Interchim) – this work (Δ); $[P_{44414}]Cl/[Cr(III)+HCl\ 37\ wt\%]/H_2O$ – [Cr(III)] = 2.5 g/L (●); $[P_{44414}]Cl$ /$[Cr(III)+HCl\ 37\ wt\%]/H_2O$ – [Cr(III)] = 5 g/L (○); $[P_{44414}]Cl/[Cr(III)+HCl\ 37\ wt\%]/H_2O$ – [Cr(III)] = 10 g/L (■); $[P_{44414}]Cl/[Cr(III)+HCl\ 37\ wt\%]/H_2O$ – [Cr(III)] = 15 g/L (□) at 25°C.

In the following, the prepared systems are noted as $[P_{44414}]Cl$ /$[Me(x)+HCl\ 37wt\%]/H_2O$ or PEG-600/$[Me(x)+HCl\ 37wt\%]/H_2O$, where Me stands for the metal of interest and x is the corresponding oxidation state. This notation highlights the fact that $[P_{44414}]Cl$ or PEG-600 and, in some cases, ultra-pure water, were added to a stock solution containing a metal salt dissolved in 37 wt% HCl/H_2O (cf Table 1). The systems in the absence of metals are noted $[P_{44414}]Cl/[HCl\ 37\ wt\%]/H_2O$ and PEG-600/$[HCl\ 37\ wt\%]/H_2O$.

~~Following a previous publication[10], the reference systems noted $[P_{44414}]Cl/[HCl\ 37\ wt\%]/H_2O$ and PEG-600/$[HCl\ 37\ wt\%]/H_2O$ are called quaternary systems, as the number of different species is equal to four: (H^+, Cl^-, $[P_{44414}]^+$, H_2O) or (H^+, Cl^-, PEG-600, H_2O) respectively. Adding a chloride metal salt then only increases the number of species by one unit (either Ni(II), Cr(III), Fe(II), Fe(III)) and consequently, the systems $[P_{44414}]Cl/[Me(x)+HCl\ 37wt\%]/H_2O$ or PEG-600/$[Me(x)+HCl\ 37wt\%/]/H_2O$, will be called quinary systems.~~

In order to compare data obtained with different metals and/or oxidation states, the 2D graphical display has been chosen, with IL or PEG-600 (in wt%) on the y-axis and HCl wt% on the x-axis.[10] The amount of water is the sum of ultra-pure water added, the water present in the hydrochloric acid, in the hydrated metal salts and in the IL or in the polymer. Compared to other components the quantity of metal ions in the IL-system is negligible (≤ 1%wt), while in the polymer system it ranges from 0% to 2 wt % (see suppl. materials).

Sample characterisations

Some samples being under a biphasic state at 25 °C were agitated and left overnight at 25 °C. Then the coexisting phases were carefully separated and weighed. The determination of the metal concentrations was carried out by ~~Atomic Absorption Spectroscopy (AAS)~~ using a Perkin Elmer Pinaacle 900F apparatus with an accuracy of ± 0.5%. The measurements were accomplished by calibration curves using mixed standard solutions. All calibration curves were based on six standards, including a blank. The calibration ranges were selected within 1 mg/L to 50 mg/L range (1 – 4 – 10 – 25 – 50 mg/L). Standard solutions for AAS analyses were prepared by diluting the commercial 1000 mg/L mixed element solution for each element in 250 mL flasks.

The water content of the IL was determined by thermogravimetric analysis (TGA - Mettler Toledo, with an accuracy of 0.0025%) The initial water content in all IL samples was found to be less than 3% of the total mass. The water content of the polymer was determined by Karl-Fischer titration. It was found to be below 25 ppm.

Results

IL-based systems

Figure 1 displays the binodal curves obtained for several initial Cr(III) concentrations ranging from 0 to 15 g/L. The binodal curve of the system composed of $[P_{44414}]Cl/[HCl\ 37wt\%]/H_2O$ was compared with the previous one from Mogilireddy *et al*.[10]

As can be seen in Figure 1, the two binodal curves obtained without Cr and performed with the same IL supplied by two different producers do not superimpose. This difference between the curves without metal ions is ascribed to the different providers (i.e. Cyphos® IL 167-Cytec[10] versus Interchim, this work). According to the literature, phosphonium based ILs are prepared by nucleophilic addition of tertiary phosphines to haloalkanes.[11,12] The used phosphines can contain several isomers and other impurities (such as phosphine oxides) that can then be found in the resulting IL[12] and depending on their quantity influence their extraction properties. In Figure 1 two different providers have been compared as the supplied products had different purities. The different level of impurities is probably responsible of binodal curves shifts, although no information on this particular phenomenon has been found in the literature. Fortunately, this observation did not impact the results of this study as only Interchim's product has been used in this work.

In contrast, it has been checked that using different HCl providers (i.e. Fluka and Sigma Aldrich) does not induce discrepancies in the binodal determinations (see Figure S1, supplementary materials).

The addition of Cr(III) to the solution leads to an increase in the biphasic domain of the system, shifting the binodal curve to the left side (i.e. lesser amount of HCl is needed to promote biphasic regime), while the shape of the curves does not show any significant change. The more pronounced is the initial Cr(III) concentration, the more are the curves shifted to the left and thus less HCl is necessary to induce the phase separation.

Figure 2 displays the binodal curves obtained for several initial Ni(II) concentrations ranging from 0 to 15 g/L.

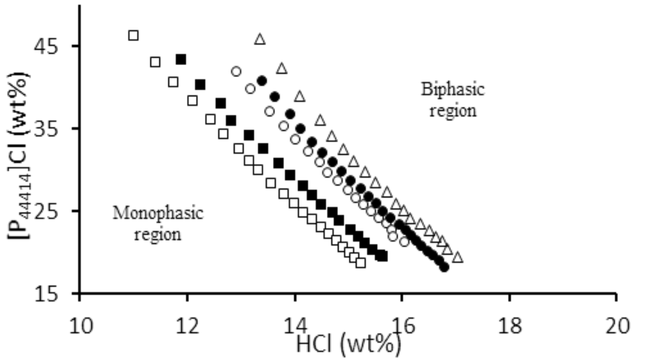

Figure 2 Binodal curves of the system: $[P_{44414}]Cl$/ [HCl 37wt%]/H_2O – [Me(x)] = 0 g/L (Δ); $[P_{44414}]Cl$/[Ni(II)+HCl 37 wt%]/H_2O – [Ni(II)] = 2.5 g/L (●); $[P_{44414}]Cl$/[Ni(II)+HCl 37 wt%]/H_2O – [Ni(II)] = 5 g/L (○); $[P_{44414}]Cl$ /[Ni(II)+HCl 37 wt%]/H_2O – [Ni(II)] = 10 g/L (■); $[P_{44414}]C$ /[Ni(II)+HCl 37 wt%]/H_2O – [Ni(II)] = 15 g/L (□) at 25°C.

The same behaviour is observed for both Cr(III) and Ni(II) containing systems, i.e. an increase in the concentration of metals in the solution leads to a growth of the biphasic domain of the system.

However, when comparing identical concentrations of Ni(II) and Cr(III) in the same graph, as shown in **Erreur ! Source du renvoi introuvable.** for 5 g/L and 15 g/L, it is relevant to notice significant differences in the increase of the binodal region when Ni(II) is changed to Cr(III).

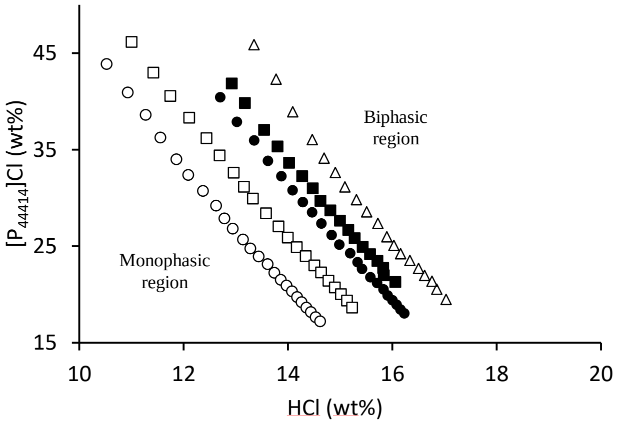

Figure 3 Binodal curves of the systems: $[P_{44414}]Cl$/[HCl 37 wt%]/H_2O, [Me]= 0 g/L (Δ); $[P_{44414}]Cl$/[Ni(II)+HCl 37 wt%]/H_2O at 5 g/L (■) or 15 g/L (□) of Ni(II); $[P_{44414}]Cl$/[Cr(III)+HCl 37 wt%]/H_2O at 5 g/L (●) or 15 g/L (○) of Cr(III) at 25°C.

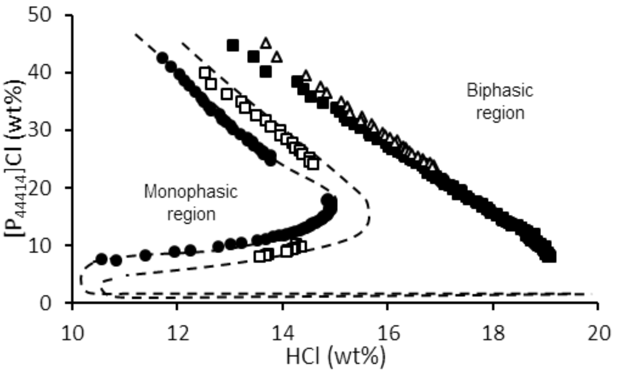

Figure 4 Binodal curves of the system $[P_{44414}]Cl$/[Fe(II)+HCl 37 wt%]/H_2O at: [Fe(II)] = 0 g/L (Δ), [Fe(II)] = 1 g/L (■), [Fe(II)] = 10 g/L (□) and [Fe(II)] = 15 g/L (●) at 25°C. Dashed lines (- - -) are only a guide for the eye.

The experimental points corresponding to Cr(III) are always on the left of the points corresponding to Ni(II) for the same concentration of metals. It seems, that chromium(III) has always a higher capacity than nickel(II) to induce the biphasic system.

The experimental curves also show that as the metal concentrations are increased, the difference between the curves of the two metals is more significant. Molecular weight of Ni (58.69 g/mol) is slightly higher than the molecular weight of Cr (51.99 g/mol), so the difference is of *ca.* 11% and may explain part of the observed differences. However, this should induce a constant effect over the studied range of metal concentrations, which is not experimentally observed. Therefore, the difference cannot be solely ascribed to the difference of molar weight of the two studied components and other phenomena should be considered.

Figure 4 and Figure 5 display, respectively, the binodal curves for the systems [P_{44414}]Cl/[Fe(II)+HCl 37 wt%]/H_2O and [P_{44414}]Cl/[Fe(III)+HCl 37 wt%]/H_2O obtained for several Fe concentrations. A rather particular behaviour is seen when Fe(II) or Fe(III) is used instead of Ni(II) or Cr(III). There is still an increase in the biphasic domain of the system when the Fe concentration is increased but there is also a substantial change in the shape of the curve as compared to curves obtained for Ni(II) or Cr(III).

In general, the binodal curves found in the literature are smooth decreasing curves, oriented from top left to bottom right. Curves presenting this kind of deformation have been scarcely reported in the literature. Two IL-based ABS binodal curves with this characteristic “onion shape” were reported by Neves et al.[13] and Mogilireddy et al.[10] However, in the former case the curves are deformed under the effect of the IL, namely by number of alkyl groups present at the cation, the cation side alkyl chain length and the presence of double bonds, aromatic rings and hydroxyl groups on this alkyl chain. In the latter case, the curves are deformed under the effect of the temperature of the system. By contrast, the deformation of the curves observed in Figure 4 and 5 is simply obtained by raising the Fe concentration in the solution at fixed temperature. Moreover, the elbow of these curves is oriented towards right in an opposite direction compared to Mogilireddy *et al.*[10], whose curves were oriented towards left.

Regarding the repartition of different elements of the system, the ~~Atomic Absorption Spectroscopy (AAS)~~ analyses performed for systems comprising 25 wt% of HCl and 30 wt% of [P_{44414}]Cl show that 80% of Fe(II) and 100% of Fe(III) are extracted in the IL-rich phase (upper phase) while Ni(II) and Cr(III) are not extracted. One can thus wonder whether the binodal curves deformation is related or not to the metals’ extraction.

Finally, Figure 6 (obtained *via* the battleship method explained in the Experimental section) highlights the influence of the temperature in the system [P_{44414}]Cl/[Fe(II)+HCl 37wt%]/H_2O at [Fe(II)] = 20 g/L. The biphasic area significantly increases as T is increased from 25 °C to 50 °C.

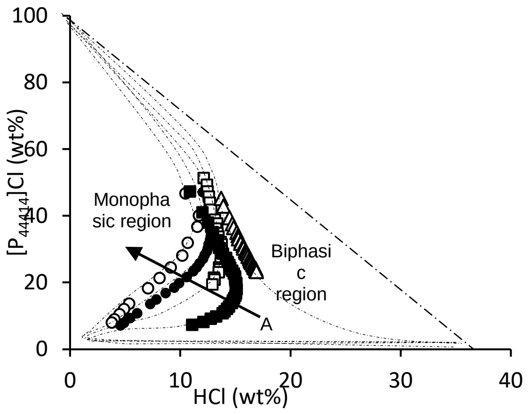

Figure 5 Binodal curves of the system [P_{44414}]Cl/[Fe(III)+HCl 37 wt%]/H_2O at [Fe(III)] = 0 g/L (Δ), [Fe(III)] = 2.5 g/L (■), [Fe(III)] = 5 g/L (□), [Fe(III)] = 10 g/L (●) and [Fe(III)] = 15 g/L (○) at 25°C (Point A position explained later in the discussion section).

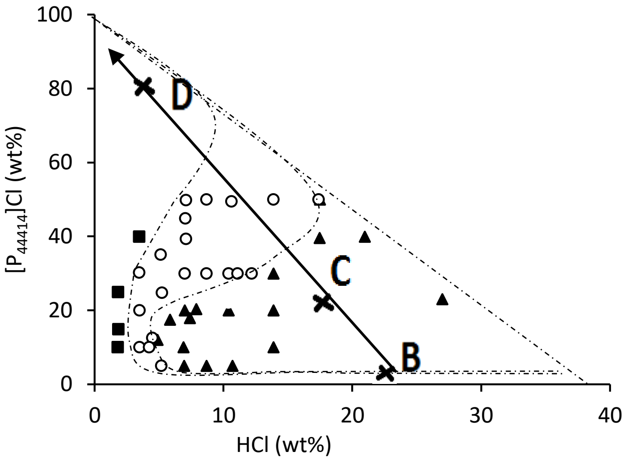

Figure 6 Phase diagram obtained with the battle ship method for the system [P_{44414}]Cl/[Fe(II)+HCl 37wt%]/H_2O – [Fe(II)] = 20 g/L. Monophasic samples at both T = 25 °C and 50 °C (■), biphasic samples at both T = 25 °C and T = 50 °C (▲)and samples that become biphasic passing from 25 °C to 50 °C (○). Experimental points B, C, D. The arrow (→) indicates the displacement direction of the point B, C, D increasing the wt% of IL (see text). Dashed lines (- - -) are only a guide for the eye.

Polymer-based systems

By using PEG-600 instead of the ionic liquid [P_{44414}]Cl, no biphasic behaviour is observed for the system PEG-600/HCl 37 wt%/H_2O whatever its composition, as ranges from 0 wt% to 99 wt% of PEG-600 and from 0 wt% to 37 wt% of HCl have been explored. Similarly, the systems PEG-600/[Me(x)+HCl 37wt%]/H_2O with Fe(II), Ni(II) and Cr(III) are monophasic at 25 °C and at 50 °C, whatever the composition (see Table S19 in the supplementary materials for all the compositions investigated).

By contrast, the systems PEG-600/[Fe(III)+HCl 37 wt%]/ H_2O with [Fe(III)] = 10 g/L and 40 g/L (Figure 7) display a large biphasic area, being this area increased with the increase of [Fe(III)] concentration.

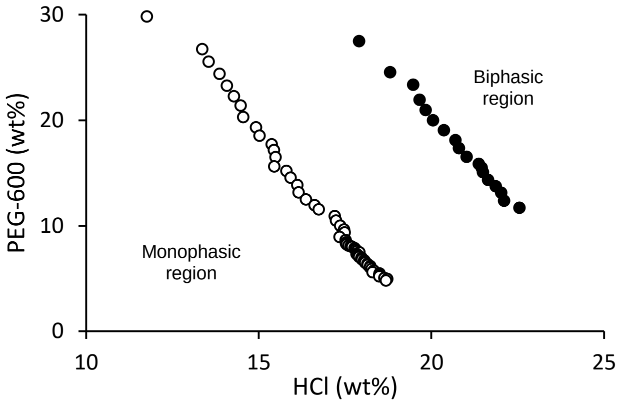

Figure 7 Phase diagram obtained by turbidity method for the systems PEG-600/[Fe(III)+HCl 37wt%]/H2O – [Fe(III)] = 10 g/L (●) and 40 g/L (○) at 25 °C.

As well as in the case of the IL-system, the binodal curves obtained for the polymer-system with Fe(III) at 50 °C (Figure 8) present a different shape compared to the classical binodal curves found in the literature.[14–16]

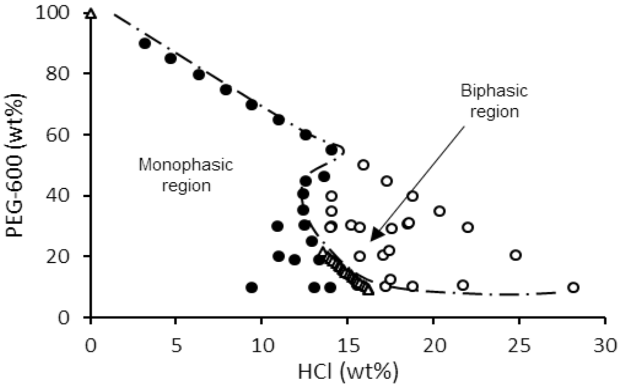

Figure 8 Phase diagram obtained by battle ship and turbidity method for the system PEG-600/[Fe(III)+HCl 37wt%]/H_2O – [Fe(III)] = 40 g/L at 50°C. Monophasic region (●), biphasic region (○), binodal curve obtained by the turbidity method (Δ). The dashed line (- - -) is only a guide for the eye.

Figure 9 compares binodal curves of the system PEG-600/[Fe(III)+ HCl 37wt%]/H_2O ([Fe(III)] = 10 g/L and 40 g/L) obtained at T = 25 °C and T = 50°C (Please note that only a small portion of the binodal curve from Figure 8 - triangles - is shown in Figure 9 – empty squares). These results evidence, independently of [Fe(III)] concentration, a widening of the biphasic area when the temperature increases.

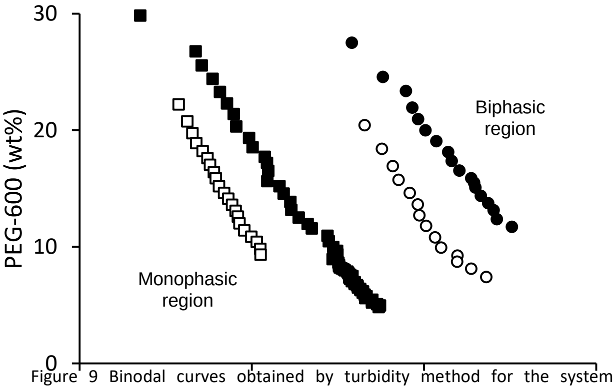

Figure 9 Binodal curves obtained by turbidity method for the system PEG-600/[Fe(III)+HCl 37wt%]/H_2O – [Fe(III)] = 40 g/L at 50°C (□) and at 25°C (■) and for the systems PEG-600/[Fe(III)+HCl 37wt%]/H_2O – [Fe(III)] = 10 g/L at 50°C (○) and at 25°C (●).

The AAS analyses performed for systems comprising 25 wt% of HCl and 30 wt% of PEG-600 show that 50% of Fe(III) remains in the aqueous phase. The calculation was performed considering an arbitrary volume repartition of 95 wt% of upper phase (aqueous phase) and 5 wt% of lower phase (polymer phase) due to the difficulty to quantify the low amount of bottom phase obtained, starting from a total volume of 10 mL of sample. This is thus the second time in this article when the deformation of the binodal curve is linked to an extraction phenomenon.

Discussion

The effects of metal salts observed by us are very uncommon in the literature. To the best of our knowledge, only two papers have evidenced changes in the cloud point temperature of a system by addition of rather large amounts of a metal salt or an oxide: Rim et al.[17] evidenced the effect of large Cr(III) nitrate additions (from 0 to 10 g/L) in the cloud point of an aqueous/surfactant system while Fagnant and co-workers[18] got a decrease of the cloud point temperature by *ca*. 20 °C by adding up to 4 wt% of Nd_2O_3 in the $HbetTf_2N/H_2O$ system. However, these two systems are somewhat different from the current work. Our data address several aspects of the impact of high metal ion concentrations onto the binodal curves for one phosphonium IL-based and one PEG-based ABS. Considering the different nature of $[P_{44414}]Cl$ and PEG-600, the latter being a neutral molecule while the former is formally a salt, we have divided the discussion into two parts, for these two rather different systems.

$[P_{44414}]$Cl-based ABS

The fact that metal salts could be part of IL-based ABS is not new. As reviewed by Freire and co-workers[19] some examples with Ca(II) and Mg(II) can be found in literature. Moreover, ABS containing Al(III) salts[20] have also been described. Yin et al. investigated ABS composed of ILs and either Rb(I) or Cs(I)[21]. The amounts of metal salts in such systems are in the range of *ca*. 5 to 45 wt% and the ILs used belong mainly to the imidazolium family, although ILs constituted by phosphonium and pyridinium cations can also be found. IL-based ABS induced by Sr(II), Eu(III) and Cs(I) have also been the topic of molecular dynamic simulations[22]. However, these systems can only bear metal ions that are not liable to hydrolysis because their working pH is close to neutrality, so the variety of metal elements composing them is somehow limited.

On the other hand, metal salts, introduced as traces in already formed ILs-based ABS, experience a partition between the upper and lower phases. This is in turn used to perform selective extraction, with numerous examples involving Sc(III)[3], Cr(VI)[23], Ru(III)[24], Co(II) versus Ni(II)[25], Ag(I) versus Cd(II)[26], and Cd(II) versus Co(II), Cu(II), Fe(III) and Zn(II)[27]. Again, imidazolium, phosphonium and ammonium ILs' families are the most studied. Similarly, these systems are not compatible with metal ions suffering hydrolysis. More recently, the extraction of metal ions, *i.e.* Pt(IV) and Fe(III), at the trace levels, has been performed in novel AcABS ~~acidic ABS~~[8] ~~(AcABS)~~.

Our study differs markedly from these previous works for two main reasons: *i*) the presence of HCl does prevent hydrolysis of the metal ions; *ii*) the metal ions, present in large amounts, can be regarded as modifiers of the original ABS composed of $[P_{44414}]Cl$, HCl (at 37 wt%) and H_2O, and not as trace level solutes.

First, the addition of Ni(II) and Cr(III) salt, at 25 °C, leads to an enlargement of the biphasic area, in comparison with the system in the absence of metal ions (Figure 1 and Figure 2). This effect is metal concentration-dependent, being more significant above ca. 1 g/L of metal ion, increases with concentration and is more pronounced for Cr in comparison to Ni (**Erreur ! Source du renvoi introuvable.**).

Second, one of the striking results of this work is the change in the shape of the binodal curves upon Fe(II) or Fe(III) addition (Figure 4 and Figure 5), which tends to disappear at a higher temperature (see Figure 6). At 25 °C, the effect of Fe(II) or Fe(III) addition onto the shape of the binodal curves is different from that observed for Ni(II) or Cr(III) (this work) or Na(I)[28]. It is evident that the physico-chemical mechanisms behind the effects of the salts in the phase demixing cannot be solely ascribed to the oxidation state of the metal and are far more complex.

Data displayed in Figure 4 and Figure 5 evidence a rather unusual phenomenon as soon as Fe ions are added to the system. In the absence of Fe ions, the sample (point A, Figure 5) is monophasic. Adding increasing amounts of pure IL to this sample will move the point towards a pure IL composition (reached upon infinite addition of pure IL only), along the arrow and the sample will remain in a monophasic state whatever the amount of added IL. By contrast, in case Fe(III) ions are added in HCl at 2.5 g/L, point A corresponds to a biphasic region and by addition of pure IL amounts, the sample will change from biphasic to monophasic along the arrow at *ca*. 15 wt% of HCl and 15 wt% of IL. Increasing the amount of Fe(III) ions will modify the values at which the sample will turn monophasic, stressing the complexity of the phenomena involved in such biphasic/monophasic behaviour. There is another aspect of the binodal curves in the presence of Fe(III) ions that can be deduced from the plots in Figure 5. Extrapolations of the three binodal curves converge towards an equivalent point on the x-axis, corresponding to the chemical composition of *ca.*2 wt% HCl and no IL (see dashed-dotted lines in Figure 5). However, such an intersection with the x-axis is chemically impossible, as it would mean that a sample composed of water and, for example, 5 wt% of HCl in water would be biphasic, which is not the case. Similar reasoning leads to the conclusion that the binodal curves cannot cross the y-axis either. As the binodal curves cannot present a critical point as for the gas-liquid equilibrium, the only possibility to extend any of the binodal curves in Figure 5 in a chemically meaningful way is to have an onion-shaped curve as experimentally observed in Figure 6 for [Fe(II)] = 20 g/L at T = 25°C. In this case, starting from a monophasic sample composition corresponding to point B, adding increasing amounts of pure IL will first turn the sample to a biphasic state (C) and in a second step, back to a monophasic state (D), along the arrow B, C, D. See another comment in supplementary materials (Figure S2).~~Furthermore, considering the contribution of metal ions as a function of the acid concentration (in wt%), the binodal curves for the systems containing Ni(II) and Cr(III) are parallel, while for Fe(II) and Fe(III), the curves do not present a parallel tendency. This can be confirmed by plotting HCl concentration at the binodal curve as a function of metal concentration at different IL wt% (20/30/40). The plots are straight lines with slopes almost identical for Ni and Cr, while slopes differ markedly for Fe(III) and Fe(II) (see Figure S2 of the supplementary materials).~~

Many works have been devoted to the empirical fitting of classical binodal curves.[29] These empirical expressions have already been shown to be irrelevant for the fitting of onion-shaped curves as those evidenced in this work[10].

On a more theoretical aspect, several papers have dealt with the formation mechanism of IL-based ABS. Some explanations focus on entropic reasons while others put the emphasis on Gibbs free energy. Recently, Schaeffer and co-workers[30] suggested an explanation for the ABS formation in the [P_{44414}]Cl/HCl/H_2O system and the effect of NaCl addition based on the comparison of entropy of hydration of NaCl and HCl. Using dynamic molecular simulations and experimental data, they supported the idea that the phenomenon is related to a competition for the water molecules between Na^+, [P_{44414}]$^+$ and H_3O^+, together with the relative interactions occurring between all these ions. For these authors, [P_{44414}]Cl forms micelles, the size of which is increased by the presence of Na^+. By contrast, the presence of H_3O^+ has no direct effect on the micelles size but impacts micelles interactions, bringing water molecules to the micelles and thus being unfavourable to ABS formation. Due to these different interactions arising from NaCl or HCl addition, the system [P_{44414}]Cl/HCl/H_2O is less prone to ABS formation than ABS containing other chloride salts, in particular, NaCl. Indeed, Schaeffer et al.[1] proposed to use a mixture of NaCl and HCl instead of a pure AcABS only with HCl. In this way, the metal extraction efficiency is preserved and a lower amount of HCl is used. To summarise, additions of NaCl induce a shift of the binodal curve of the system [P_{44414}]Cl/HCl/H_2O to the left, with no change in the shape of its binodal, while keeping a reasonable amount of HCl allows extraction of metal ions prone to hydrolysis.

In our work, chloride salts of Ni(II), Cr(III), Fe(II) and Fe(III) were used instead of Na(I). Based on literature data[31], the order of conventional standard molar entropies of hydration of the studied ions ($\Delta_{hydr}S_i°_{conv}$, at 25°C and expressed in $JK^{-1}mol^{-1}$) is as follows: Na(I) >> Ni(II) ≥ Fe(II) > Cr(III) ≥ Fe(III). As suggested by Schaeffer et al.[1], the purpose of our work was to extend the range of chloride salts and to evaluate their effect on the phase separation. However, as demonstrated in **Erreur ! Source du renvoi introuvable.**, at the same concentration the ABS formation is favoured in the case of Cr compared to Ni. Moreover, the unusual shape of Fe containing system is not well explained by this parameter either and hydration entropy parameter fails thus to explain our experimental results.

For example, the binodal curve of the system with 5 g/L of Fe(III) is an almost vertical linear curve (see Figure 5), which crosses the onion-shaped binodal curve of the Fe(II)-based ABS (Figure 4). It is important to note that the $\Delta_{hydr}S_i°_{conv}$ values for Ni(II) and Fe(II) are very similar (-307 $JK^{-1}mol^{-1}$ for Ni(II) and -318 $JK^{-1}mol^{-1}$ for Fe(II)), as well as both Cr(III) and Fe(III) ions (-448 $JK^{-1}mol^{-1}$ for Cr(III) and -490 $JK^{-1}mol^{-1}$ for Fe(III)), but the shapes of the corresponding binodal curves are fully distinct, either between Ni(II) and Fe(II) or between Cr(III) and Fe(III). These differences in the shape of respective binodal curves indicate that $\Delta_{hydr}S_i°_{conv}$ is not the only parameter to be considered.

The second type of explanation for the ABS formation is related to the Gibbs free energy of hydration of ions ($\Delta_{hydr}G°$). Marcus et al.[32] determined the $\Delta_{hydr}G°$ of a wide range of ions and the concept of the hydration of metal ions. In 2007, Bridges and co-workers[33] formed salt/salt ABS composed of K_3PO_4, K_2CO_3, $(NH_4)_2SO_4$, and hydrophilic imidazolium-, pyridinium-, phosphonium-based ILs. They demonstrated that, like in the polymer-salt ABS, the salting-out strength of the highly charged inorganic salts (*i.e.* water-ion interaction stronger than water-water interactions) follows the Hoffmeister series which can be related to the ions' Gibbs free energy of hydration ($\Delta_{hydr}G°$). The molar Gibbs energy of hydration of the studied ions ($\Delta G^*_{hydr.}$) differs (Ni^{2+}= -1980; Cr^{3+}= -4010; Fe^{2+}= -1840; Fe^{3+}= -4265, all expressed in $kJmol^{-1}$) and the values follow the order: Fe(II) > Ni(II) > Cr(III) > Fe(III). The order of this series is identical to the one of the series based on entropy considerations, except for Ni(II) and Fe(II), which are inverted. As a consequence, the points raised above (shape of the binodal curves and atypical behaviour of Fe(II) *versus* Fe(III)) remain unexplained, and thus the conclusion is that Gibbs free energy considerations are not sufficient to explain our whole data set.

Apart from the $\Delta_{hydr}S_i°_{conv}$ or Gibbs free energy possible involvement in the formation of ABS, the chloride ion is another important partner in the systems under study which role should not be minimized. Onghena et al.[25] worked with $[P_{44414}]Cl/NaCl/H_2O$ while Gras et al.[8] used $[P_{44414}]Cl/HCl/H_2O$, both of them to separate Co(II) and Ni(II). These two studies pinpoint the decisive effect of Co(II)-Cl^- complexation and anionic species formation for its extraction to the IL-rich upper phase via an anion exchange, while Ni remains in the aqueous phase as a cation due to its limited coordination with chloride anions. In these works, the concentrations of Co and Ni were in the traces range[8] or *ca*. 1 g/kg[25], to be compared to our maximum value equal to *ca*. 12.5 g/kg. We have also used chloride salt and can thus confirm, that the increased concentration of Ni used in our work does not affect the observed results, which are similar to the previous ones, *i.e.* Ni remains in the lower aqueous phase and is not extracted.

Therefore, one possible additional phenomenon at work in the formation of $[P_{44414}]Cl/[Me(x)+HCl\ 37\ wt\%]/H_2O$ ABS is the complexation of metals with chloride and evolution of their chemical speciation caused by concentration and temperature changes of the system. Values for the first complexation constant, K_1, for various metal ions and several temperatures can be found in the literature.[34] Unfortunately, there's a lack of reliable data related to the chloride systems, namely when the influence of increasing temperature is looked for. We have only been able to found these values for perchlorate based systems: For Fe(III) in 1 mol/L $HClO_4$, values range from $K_1 = 0.36$ (14.3-16.3 °C); 0.46 (25 °C); 0.49 (30.1 °C) until 0.68 (44.3 °C). The K_1 increases with the temperature, which can be correlated with the enlargement of the biphasic region, *i.e.* when the temperature was changed from 25 to 50 °C. ~~However, the involved physico-chemical phenomenon related to this correlation is not clear.~~ As a consequence of the formation of $FeCl_4^-$, the new compound $[P_{44414}][FeCl_4]$ is thus theoretically formed, although there is no proof yet that the two ions are associated. Other iron-containing ILs, based on dialkylimidazolium cations, have been shown to display a thermomorphic behaviour in pure water, with a Lower Critical Solution Temperature (LCST)[35]. To the best of our knowledge, a LCST behaviour for $[P_{44414}][FeCl_4]$ has not been reported but could be involved in the change of the binodals we observed. Similarly, considering Cr(III) in 4.4 mol/L $HClO_4$ medium, following values evidence an increase in K_1: $K_1 = -0.62$ (30 °C); -0.42 (46.3 °C); -0.19 (63.5 °C) until 0.16 (95.4 °C). Finally, comparing the chloride complexation constants of Cr(III) and Ni(II) in almost identical media (K_1 for Cr(III) = 0.18 measured in 1 mol/L $NaClO_4$ medium and K_1 of Ni(II) = -0.25 measured in 1.5 mol/L $NaClO_4$ medium), it is observed that it also correlates with the ability of Cr(III) to display a larger biphasic area than Ni(II) (Figure 2). However, ~~as highlighted previously,~~ the involved physico-chemical phenomenon remains unclear.

Moreover, the difference in complexation constants do not explain the particular shape of binodal curves for iron containing systems. The deformation may be related to the extraction phenomenon, but it should be further investigated._These comparisons are thus only limited ones and are not substantiated by a deeper theoretical approach.

Thus, whatever the explanation for ABS formation as discussed above, none of these can fully explain our data sets. Further computational studies would be very important in revealing the main mechanisms behind their phase separation, in particular, why Fe containing systems display binodal curves of a very different shape as compared to Ni and Cr containing systems characterized by more traditional curve shapes.

PEG-based ABS

Regarding PEG 600 based systems, our data showed that PEG-600/HCl 37 wt%/H_2O system is never biphasic, neither at 25 °C nor at 50 °C. Four metal salts were added as adjuvants to verify whether these elements can induce the phase separation. Although the addition of Fe(II), Ni(II) and Cr(III) salts did not induce the formation of a biphasic region, interestingly Fe(III) acted as a biphasic inducer (see Figure 7). Our data have already pinpointed Fe(III) as specific IL-based ABS modifier (owing to the shape of the binodal curves Figure 5) and this ion is also peculiar in the case of PEG-based ABS. However, one can notice differences between the PEG-based and IL-based systems involving Fe(III) ions as far as the temperature is concerned. Actually, as T increases from 25°C to 50°C, the onion shape behaviour becomes more obvious for the IL-based systems (Figure 5). As already discussed for the IL-based systems, these data cannot be described by using traditional empirical models, owing to the onion shape of the binodal curves. This remark is also valid for the Setschenow equation (Ni et al.[36]), another empirical function that is nevertheless related to some physicochemical parameters of the system and has been proposed for the mutual solubility of an electrolyte and a polymer.

By contrast to the IL-based ABS, one can find many works devoted to PEG-based ABS and the possible reasons behind the formation of the biphasic state or its absence, as in the case of PEG-600/[HCl 37 wt%]/H_2O. Among the proposed hypotheses can be cited those referring to the changes in the hydration of the polymer or to the existence of strong interactions between multivalent cations, particularly metal ones, and ether oxygens of PEG and will be discussed below under the light of our data.

First, the absence of biphasic state for mixtures of PEG-600, HCl and water should be explained. Huddleston et al[37] stated that the formation of a biphasic regime by dissolving water-soluble polymer and inorganic salts results from the competition for hydration between the polymer and the salts. This is dependent on the relative hydrophobicity of the polymer (based on polymer type or average molecular weight) and the salting-out strength of the inorganic salt ions, i.e. ions' Gibbs free energies of hydration[38]. Water is the main component in this system and PEG-600 is highly hydrophilic, interacting actively with 2 or 3 water molecules per each ethylene oxide (EO) unit. As most ionic species, Cl^- anions are also highly water-soluble. Therefore, to induce a phase demixing, the salt should exhibit a salting-out aptitude enough to dehydrate, at least partially, the PEG-600. Although hydrogen chloride (HCl) when dissolved in water behaves as a strong electrolyte, its preferential hydration is not strong enough to dehydrate and expel the hydrophilic PEG-600 to another incompatible phase. Thus, all compounds are remaining dissolved in a monophasic aqueous solution. Additionally, as demonstrated by Tomé et al.[39], it has also to be considered that Cl^- anions can establish an equivalent of hydrogen bonds with the -OH end group of the PEG polymers, favouring their mutual solubility in water. Therefore, in addition to the water solvation of the ether groups of the oxygen chain, the formation of ABS when mixing aqueous solutions of PEG and chloride-based salts is also a result of the ability of the PEG terminal groups to preferably interact with water or the chloride anion (Pereira *et al*.[40]).

Second, the biphasic inducing property of Fe(III) should be examined, together with the inefficiency to do so of the other metal ions tested in our work. As already discussed for the IL-based data, it is known that the complexation constant[33] of Fe-Cl is higher than the Ni-Cl or the Cr-Cl complexation constants. The charge density[41] of the metal ions is also quite different (Ni^{2+} = 82; Cr^{3+} = 261; Fe^{2+} = 181; Fe^{3+} = 349, all expressed in C mm^{-3}) and follows the order: Ni<Fe(II)<Cr(III)<Fe(III). If the behaviour is influenced by the charge density, then the ABS formation "ability" would follow this order (in both cases, *i.e.* IL and PEG), which is not the case. Moreover, it does not explain the iron case particularities. Finally, the molar Gibbs energy of hydration of ions ($\Delta G^*_{hydr.}$) values already given in the previous section differ markedly for the studied ions, whereas very close values are ascribed in the literature for Ni and Fe(II) and then again for Cr(III) and Fe(III). So if the biphasic behaviour and partition phenomenon were governed solely by this parameter, one could expect that Ni and Fe(II) will behave similarly and then again Cr(III) and trivalent iron, which is clearly not the case.

To go a step further, one has to recall that the formation of a biphasic state imposes electro-neutrality to both the upper (PEG and iron-rich) and lower phases. From the electrospray ionization – mass spectrometry (ESI-MS) analyses, the main species present in the acidic solution of Fe(III) and HCl (37 wt% = 12 mol/L) is $[Fe(III)Cl_4]^-$ (Figure S3 supp. materials). This implies that the $[Fe(III)Cl_4]^-$ species, which is responsible for the biphasic formation, is accompanied by a positively charged species during the phase separation. In our system, the only available cation is the H^+. Therefore, one has to consider at the same time the ability of H^+ and $[FeCl_4]^-$ to be trapped in the PEG-rich phase.

Regarding the cationic moiety, Sartori et al.[42] described PEG's ability to absorb ions from solutions containing an alkali-metal cation (Li^+, Na^+, Rb^+, K^+ and Cs^+) and a series of anions including Cl^-. Furthermore, they showed that the polymer strongly interacts with the cations they examined. This leads to the formation of a positively charged surroundings that "attracts the anions (…) to the vicinity of the PEG molecule"[42]. Although H^+ was not studied in the work of Sartori *et al*., it is reasonable to assume that the proton plays the role of an alkali metal cation in our system. However, this first hypothesis does not exclude the strong contribution of the anion to the system partition. Bulgariu et al.[43] suggested that chloride anionic species based on Zn(II), Hg(II) and Cd(II) are ''fixed'' by the O-groups present in the ether chain of the PEG by ionic forces. It could thus be envisioned that the same phenomenon occurs with $[Fe(III)Cl_4]^-$.

As shown in Figure 10, the chemical structure that can be proposed is the intramolecular bonding between two polymer chains of PEG that are connected *via* the water molecules.

The anionic iron species interacts then with the oxygens present within the polymer. It is important to underline that the interaction between Fe and O is not based on a covalent bond but is rather an ionic interaction due to the differences in the electronegativities of the two atoms. This is supported by the ESI-MS results that showed the absence of a stable covalent bond between the PEG and the metal ions (Figure S4 Supplementary materials). In this sense the schematic view, as displayed in Figure 10 is in line with the comment of Sartori and co-workers[42], who pinpointed that “the anions remain mainly outside the polymer coil”. Furthermore, it seems that in a high concentrated HCl medium, the structure of the Fe(III) is an equilibrium between an octahedral (Figure 10-C) and a tetrahedral structure (Figure 10-D)[44].

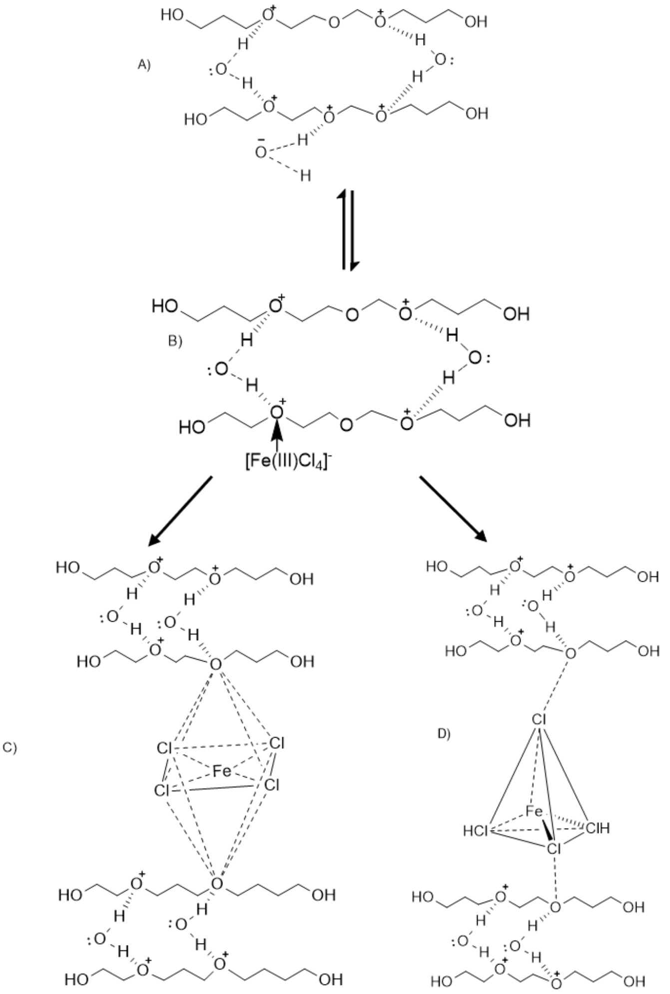

Figure 10 Mechanism of PEG extraction of Fe(III). 10-A: inter-chain connection proposed by Bulgariu *et al.*[42]; 10-B: Fe(III) connection with the ether group of the polymer; 10-C: octahedral structure of the species (Fe(III)Cl4)-; 10-D: tetrahedral structure of the species (Fe(III)Cl4)-; Adapted from ref. Bulgariu *et al.*[42].

Conclusions

In the absence of metal ions, the mixture [P_{44414}]Cl/[HCl 37 wt%]/H_2O is an ABS, while the corresponding system with PEG-600 instead of IL is not. In this work, we investigate the impact of 4 different types of metal ions: Fe(II)/(III), Ni(II) and Cr(III) onto the behaviour of these mixtures.

In the case of IL, it was possible to obtain a biphasic system with all four different metal ions. The peculiarity of these systems lies in the particular onion shape form that presents the binodal curve of the system with Fe(II)/(III).

Regarding PEG-600-based systems, only Fe(III) can induce a biphasic system in the presence of HCl, and also in this case the binodal curve has an atypical shape. As far as the efficiency of the extraction of these systems is concerned, 80 wt% of Fe(II) and 100 wt% of Fe(III) are extracted in the IL phase, while 50 wt% of Fe(III) is extracted in the polymer phase, considering the difficulty to determine the distribution of metal ions for the PEG-600 systems, due to the small remaining volume of the polymer phase.

The investigation of the influence of factors such as the presence of metals and the temperature on the binodal curves of ABS is important at the fundamental level for the understanding of these systems. In particular, close to the elbow of the onion-shaped binodal curve, addition of PEG will turn the system from monophasic to biphasic and finally back to monophasic for rather small amounts of polymer. This means that the sample is susceptible to small concentration changes and this could be an interesting experimental and theoretical point to study in the near future.

On another hand, these investigations have also a very pronounced practical aspect, given the high potential for industrial use of this knowledge. There are many industrial aqueous liquid wastes that contain a very high concentration of iron. Our work demonstrates that there is a very cheap and efficient way to significantly reduce the amount of iron ions in these wastes by adding PEG polymer. A clear advantage is that the more concentrated the iron is, the lower amount of PEG is required to remove this element from its solution. Once iron is extracted, it should be easier to recover the other minor but valuable elements possibly present, either by traditional means (electrodeposition, precipitation etc.) or by inducing the formation of another ABS system. Furthermore, it is already known[45] that increasing the molecular weight of the polyethene glycol, the hydrophobicity of the polymer increases, so this is another parameter to play with. Work on these lines is currently under progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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