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1 Factors driving metal partition in ionic liquid-based acidic aqueous biphasic
2 systems

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14 Abstract

15 The factors influencing metal partition in acidic aqueous biphasic systems (AcABS) containing
16 phosphonium-based ILs are still poorly explored. To assess their influence the effect of the IL
17 counter anion, acid and its concentration, and temperature, were systematically evaluated on
18 the extraction of four transition metals (Cu(II), Co(II), Ni(II), and Mn(II)) and the lanthanide Ce(IV).
19 The AcABS based on HCl showed good ability to extract Co(II) and Cu(II) to the IL-rich phase. In
20 contrast, AcABS based on H₂SO₄ showed overall poor metal extraction, except for the [P₄₄₄₁₄]Cl +
21 H₂SO₄ + H₂O system. The latter showed good Cu(II) affinity at higher H₂SO₄ concentrations. The
22 biphasic systems based on HNO₃ were unable to extract transition metals to the IL-rich phase,
23 with chloride from [P₄₄₄₁₄]Cl hampering Ce(IV) extraction. The [P₄₄₄₁₄]Cl + H₂SO₄ + H₂O system
24 was further optimized by adding small amounts of HCl to the system. The extraction efficiency of
25 the metals is linked to the charge density of the metal-complex and its inherent free energy of
26 hydration, the anion/water molar ratio changes induced by temperature and ionic strength, and
27 the dissociation degree of the acid. By using these parameters it was possible to tune the
28 selectivity and efficiency of the AcABS. Moreover, metal extraction was found to preferentially
29 occur via an ion-pair mechanism, with split anion extraction taking place in AcABS containing
30 different anions.

31 Keywords:

32 Liquid-liquid extraction, hydrometallurgy, alternative solvents, metal separation, ion-pair
33 mechanism.

34 1. Introduction

35 Solvent extraction is a widely used separation technique based on the distribution of a target
36 molecule between two immiscible phases.[1] Conventional metal liquid-liquid extraction systems
37 often rely on non-ecofriendly volatile organic diluents to overcome the viscosity of extractants.
38 Ionic liquids (ILs) were identified as a possible solution to this issue.[2] ILs are an alternative class
39 of solvents composed of a large organic cation and an organic or inorganic anion. When carefully
40 designed they have negligible vapor pressure, high solvation capacity, good chemical stability and
41 low-flammability. [2][3] Hydrophobic ionic liquids (ILs) were proposed as a good option for metal
42 extraction since they can simultaneously act as metal extractants and diluents.[4] Although
43 liquid-liquid extraction systems based on hydrophobic ILs are a potential upgrade from the
44 conventional solvent extractions systems, they still pose some issues. The structural
45 requirements to achieve hydrophobic ILs constrain their chemical diversity. Moreover, the
46 viscosity and toxicity of such ILs raise concerns[5,6] It is important to highlight that due to their
47 ionic nature even “hydrophobic” ILs are hygroscopic and can incorporate significant amounts of
48 water, especially when converted to mole fraction.[7] In the context of this work, we assign the
49 term hydrophobic to designate ILs that present limited aqueous solubility whilst hydrophilic ILs
50 are fully miscible with water across all binary compositions.

51 The disadvantages of hydrophobic ILs are fueling the transition from liquid-liquid extraction
52 systems based on hydrophobic ILs to hydrophilic ones when applicable. The use of hydrophilic
53 ILs for the formation of aqueous biphasic systems (ABS) is versatile, allowing the use of a larger
54 variety of more benign ILs, and applicable to metal extraction.[8–10] Overall ABS are seen as
55 more biocompatible liquid-liquid extraction systems due to water being the main component of
56 their two-phases.[11] In the formation of a ternary ABS, a hydrophilic IL is combined with water
57 and a salting-out agent that, in the correct proportions, results in the formation of two immiscible
58 aqueous phases. The incorporation of ILs in ABS for metal extraction has the potential to increase
59 tunability, decrease the viscosity associated with ILs and reduce the necessary quantity of IL.[12]
60 However, most ABS are not stable at low pH values,[13] which is a key requirement to prevent
61 metal hydrolysis and precipitation. To address this issue acidic aqueous biphasic systems (AcABS)
62 have recently been proposed.[14] In AcABS, the salts conventionally used as salting-out agents

63 are replaced by an acid which acts as a salting-out agent and simultaneously enables the leaching
64 and stability of metals. Typically, the phase with the highest acid weight percentage (wt %) is
65 named as acid-rich phase and the one with the highest IL wt % is referred to as IL-rich phase.
66 Similarly to ABS, AcABS can feature a thermoresponsive behavior, namely lower critical solution
67 temperature (LCST).[15,16] The potential thermoresponsive character of AcABS provides another
68 degree of freedom to adjust the metal extraction performance.

69 The novelty of AcABS and the ionic nature of ILs can be a challenge for the identification of
70 possible metal extraction mechanisms in these systems.[17,18] Typically, metal cations are highly
71 hydrated causing them to have an affinity to the acid-rich phase and low extraction to the IL-rich
72 phase. For metal extraction to be successful it is important to promote the formation of more
73 hydrophobic metal complexes.[19] Although this is often accomplished by adding extractants, in
74 AcABS the IL simultaneously acts as a phase-forming agent and extractant.[14] Similarly to other
75 liquid-liquid extraction systems, several metal extraction mechanisms can occur in AcABS with
76 unfunctionalized ILs, such as anion-exchange or ion-pair extraction.[5,19] The anion-exchange
77 mechanism is a metathesis reaction in which the transfer of the negatively charged metal-
78 complex to the IL-rich phase is dependent on the migration of the IL anion to the acid-rich
79 phase.[5] The ion-pair extraction mechanism occurs when the metal speciation in the aqueous
80 and IL-rich phase differ such that the IL forms a hydrophobic ion pair with the aqueous metal
81 complex to promote its partition. The hydrophobic ion-pair can be formed using cations present
82 in the acid phase or in the IL-rich phase. It is important to note that the final extracted metal ions
83 by unfunctionalized ILs are often present as anionic complexes in the IL-rich phase regardless of
84 the extraction mechanism.

85 Several AcABS were shown to extract and separate transition metals and rare earth elements.
86 [14,20,21] Despite their promising efficiency, the influence of the IL anion and acid on the
87 mechanisms of extraction of metals in AcABS remain poorly studied particularly for systems in
88 which the IL and acid anions are not identical (split-anion extraction).[22] To address the gaps in
89 this field, herein we develop AcABS based on hydrophilic ILs (tributyltetradecylphosphonium
90 chloride, [P₄₄₄₁₄]⁺Cl⁻, and tributyltetradecylphosphonium sulfate, [P₄₄₄₁₄]⁺[HSO₄]⁻) and biphasic
91 systems based on the hydrophobic IL tributyltetradecylphosphonium nitrate, [P₄₄₄₁₄]⁺[NO₃]⁻ for the

92 extraction of four transition metals – Cu(II), Co(II), Ni(II) and Mn(II) – and a rare-earth metal,
93 Ce(IV). To evaluate the influence of the acid in the extraction of different metals, hydrochloric,
94 sulfuric and nitric acid were used to form the different biphasic systems. The thermoresponsive
95 character of the systems was also explored and metal partition was evaluated at 298 K and 323
96 K.

97 2. Experimental section

98 2.1. Materials

99 The ILs [P₄₄₄₁₄]Cl (> 95 wt %), [P₄₄₄₁₄][HSO₄] (> 95 wt %) and [P₄₄₄₁₄][NO₃] (> 95 wt %) were
100 purchased from Iolitec and used as received. The inorganic acids HCl (37 wt %) and H₂SO₄ (95 wt
101 %) were obtained from Fisher Scientific and HNO₃ (65 wt %) was obtained from Chem-Lab.
102 CoCl₂·6H₂O (> 99 wt %), CoSO₄·7H₂O (> 99 wt %), Co(NO₃)₂·6H₂O (> 99 wt %), CuSO₄·5H₂O (> 99
103 wt %), Cu(NO₃)₂·3H₂O (>99.5 wt %), MnCl₂·4H₂O (> 99 wt %) and Ni(NO₃)₂·6H₂O (> 99 wt %) were
104 obtained from Merck. CuCl₂·2H₂O (> 98 wt %) and NiCl₂·6H₂O (> 98 wt %) were purchased from
105 Analar. NiSO₄·6H₂O (> 99 wt %) and Mn(NO₃)₂·4H₂O (> 96 wt %) were purchased from Riedel de
106 Haen. Ce(SO₄)₂·4H₂O (> 98 wt %) and MnSO₄·4H₂O (> 99 wt %) were obtained from Alfa Aesar
107 and Panreac, respectively. The deionized water was obtained through a Millipore filter system
108 MilliQ[®]. Yttrium standard (1000 mg·L⁻¹ of Y(III) in 2 % nitric acid) was purchased from Sigma
109 Aldrich.

110 2.2. Acidic aqueous biphasic systems

111 The use of [P₄₄₄₁₄]Cl to form an AcABS with HCl (298 K and 323 K), H₂SO₄ (298 K) and HNO₃
112 (298 K) as salting-out agents was previously reported.[23] The remaining ternary phase diagrams
113 presented in this work – [P₄₄₄₁₄]Cl-H₂SO₄-H₂O (323 K), [P₄₄₄₁₄][HSO₄]-HCl-H₂O (298 K and 323 K),
114 [P₄₄₄₁₄][HSO₄]-H₂SO₄-H₂O (298 K and 323 K) – were determined using the cloud point titration
115 method.[24,25] Temperature was controlled using a thermostatic bath ME-18 V Visco-
116 Thermostat Julabo and a temperature-controlled cell at 298.0 K or 323.0 K (± 0.1 K), atmospheric
117 pressure and continuous stirring. The binodal curves were determined by adding an acid aqueous
118 solution dropwise to a known amount of IL until the mixture becomes cloudy. At this point, water
119 is added dropwise until the mixture becomes clear. This procedure was alternately repeated as

120 many times as necessary. The composition of the ternary systems was determined via weight
 121 quantification ($\pm 10^{-4}$ g) upon the addition of all components. Details related to the
 122 determination of the phase diagrams, namely the experimental weight fraction data, can be
 123 consulted in Table S1 and S2.

124 The mixture points used for metal extraction were selected considering the phase diagrams
 125 in mol of solute (IL or acid) per kg of solvent (water + acid or water + IL, respectively). **More details**
 126 **are given in the Supporting Information.** The IL concentration was set constant for all systems
 127 and equal to $0.85 \text{ mol}\cdot\text{kg}^{-1}$. Depending on the binodal curve, different acid concentrations were
 128 used, as shown in Table 1. Mass fraction was calculated considering the total mass of the system
 129 (water + acid + IL). The water content of the system was considered as the sum of the added
 130 water plus the inherent water present in the acid solution (63 wt % for HCl, 35 wt % for HNO_3
 131 and 5 wt % for H_2SO_4).

132 **Table 1.** Extraction mixture points in $\text{mol}\cdot\text{kg}^{-1}$ and wt %, with mixture point 1 ([Acid]₁) having a
 133 lower acid content than mixture point 2 ([Acid]₂).

Biphasic system	Extraction points ($\text{mol}\cdot\text{kg}^{-1}$)			Extraction points (wt %)		
	[IL]	[Acid] ₁	[Acid] ₂	[IL]	[Acid] ₁	[Acid] ₂
[P ₄₄₄₁₄]Cl + HCl	0.85	6.5	8.0	27	19	23
[P ₄₄₄₁₄][HSO ₄] + HCl	0.85	6.5	8.0	30	19	23
[P ₄₄₄₁₄][HSO ₄] + H ₂ SO ₄	0.85	2.5	4.0	30	20	28
[P ₄₄₄₁₄]Cl + H ₂ SO ₄	0.85	3.0	4.0	27	22	28
[P ₄₄₄₁₄]Cl + HNO ₃	0.85	2.5	4.0	27	14	20
[P ₄₄₄₁₄][NO ₃] + HNO ₃	0.85	2.5	4.0	28	14	20

134
 135 To evaluate the effect of temperature on metal extraction, assays were carried out at $(298 \pm$
 136 $1) \text{ K}$ and $(323 \pm 1) \text{ K}$. All solutions and mixture points were prepared gravimetrically by weighting
 137 the correct amount of each component ($\pm 10^{-4}$ g). The mixture points were stirred and left to
 138 equilibrate at $(298 \pm 1) \text{ K}$ for at least 3 h, followed by centrifugation at 10 000 rpm for 2 min. The
 139 extractions carried out at $(323 \pm 1) \text{ K}$ were performed following a slightly different procedure.
 140 Mixture points were prepared gravimetrically, stirred, and left to equilibrate at $(323 \pm 1) \text{ K}$. After

141 1 h, each mixture point was stirred again and the phases were left to separate overnight. In all
142 cases, the mass ($\pm 10^{-4}$ g) and volume ($\pm 5 \times 10^{-3}$ mL) of each phase after separation were
143 registered.

144 **2.3. Metal solution preparation**

145 A multi-elemental stock solution (Co(II), Cu(II), Mn(II) and Ni(II)) was prepared with a
146 concentration of $0.2 \text{ mol}\cdot\text{L}^{-1}$ of each metal ion and diluted in the biphasic systems to yield a final
147 concentration of $0.01 \text{ mol}\cdot\text{L}^{-1}$. To minimize the number of species present in each system, the
148 anion of the metal salt was selected to match the anion of the acid. Yet, $\text{Ce}(\text{SO}_4)_2$ was used as
149 Ce(IV) source in all ternary systems independently of the used acid. Due to the limited solubility
150 of Ce(IV) in certain systems, its partition was studied individually by preparing an aqueous
151 solution at $2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ of Ce(IV) in 37 wt % HCl, 50 wt % H_2SO_4 or 65 wt % HNO_3 , the final
152 concentration of Ce(IV) being $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ in each system.

153 **2.4. Instrumentation and measurements**

154 **2.4.1. Metal quantification**

155 The quantification of metal in each phase of the system was done using the total reflection
156 X-ray fluorescence spectrometer using a Picofox S2 (Bruker Nano (Billerica, MA, USA)) equipped
157 with a molybdenum X-ray source. The analysis was conducted at a 50 kV voltage and 600 μA
158 current. The quartz glass carriers were previously coated with 10 μL of silicon in isopropanol
159 solution and dried at $(323 \pm 1) \text{ K}$. Samples from each phase were diluted in polyvinyl alcohol (1
160 wt %) and spiked with a known concentration of yttrium. Of this solution, 10 μL were transferred
161 to a pre-treated quartz carrier and dried under high vacuum for at least 30 min. This procedure
162 was not applied for the top phase of the HNO_3 -based systems since they are hydrophobic. For
163 this reason, the metal quantification in the top phase of these systems was accomplished by mass
164 balance from measurements of the acid-rich phase.

165 The distribution coefficient (D) was calculated as shown in Equation 1:

$$166 \quad D = \frac{[\text{M}]_T}{[\text{M}]_B} \quad (1)$$

167 where $[M]_T$ is the metal concentration in the IL-rich top phase and $[M]_B$ is the metal concentration
168 in the bottom phase of the system. The extraction efficiency percentage ($EE\%$) of each mixture
169 point was calculated according to Equation 2:

$$170 \quad EE\% = \frac{m_T}{m_{Total}} \times 100 \quad (2)$$

171 where m_T is the mass of metal in the top phase and m_{Total} is the total mass of metal in the system.

172 The separation factor (Sf) of the system was calculated according to Equation 3:

$$173 \quad Sf = \frac{D_{M1}}{D_{M2}} \quad (3)$$

174 where D_{M1} is the distribution coefficient of the most extracted metal and D_{M2} is the distribution
175 coefficient of the second most extracted metal to the top phase.

176 **2.4.2. In-phase water quantification**

177 To better understand the $H_2O:HCl$ ratio in the top phase of the system composed of 27 wt % of
178 $[P_{44414}]Cl$ and 23 wt % of HCl at various temperatures ($(298, 313 \text{ and } 323) K \pm 1 K$), the water
179 content of the top phase of this system was measured by coulometric Karl Fischer titration
180 (Metrohm, model 831). All measurements were performed in triplicates.

181 **2.4.3. Dynamic light scattering**

182 Dynamic Light Scattering (DLS) measurements (Malvern Zetasizer Nano-ZS) were performed on
183 the $[P_{44414}]Cl-H_2SO_4-H_2O$ system spiked with 5 wt % of HCl to study the correlation between the
184 IL aggregate size and temperature. Briefly, samples were exposed to red light (HeNe laser, 565
185 nm) and the intensity variations of the scattered light were detected at a backscattering angle of
186 173° . The autocorrelation function was cumulatively analyzed by DTS v 7.03, which yielded the
187 aggregate size and the distribution. To complement this study, the type of $Co(II)$ complexes
188 present in one of the systems was evaluated using a UV-Vis Synergy HT microplate reader from
189 BioTek at different temperatures.

190 **2.4.4. Ion-exchange evaluation**

191 The possibility of ion-exchange on the $[P_{44414}]Cl-H_2SO_4-H_2O$ at $3.0 \text{ mol}\cdot\text{kg}^{-1}$ or $4.0 \text{ mol}\cdot\text{kg}^{-1}$ of
192 H_2SO_4 and on the $[P_{44414}][HSO_4]-HCl-H_2O$ systems at $6.0 \text{ mol}\cdot\text{kg}^{-1}$ or $8.0 \text{ mol}\cdot\text{kg}^{-1}$ of HCl was

193 evaluated in the biphasic region by selecting a mixture point with $0.85 \text{ mol}\cdot\text{kg}^{-1}$ of IL. The mixtures
194 were agitated and left to equilibrate at $(298 \pm 1) \text{ K}$ overnight. The two phases were separated
195 and weighed. The $[\text{P}_{44414}]^+$ was quantified by ^1H NMR. Chloride and hydrogen were quantified via
196 chloride ion-selective electrode (Metrohm) and titration, respectively.

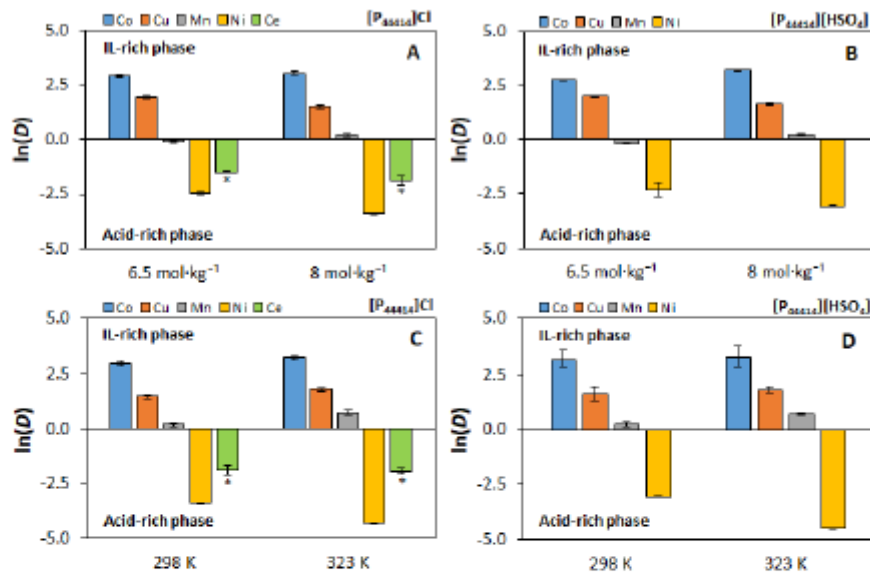
197 3. Results and discussion

198 Aiming to better understand the effect of the IL anion and the acid on the partition of Cu(II) ,
199 Co(II) , Ce(IV) , Ni(II) and Mn(II) , the following ternary systems were prepared:
200 $[\text{P}_{44414}]\text{Cl}/[\text{P}_{44414}][\text{HSO}_4]\text{-HCl-H}_2\text{O}$, $[\text{P}_{44414}]\text{Cl}/[\text{P}_{44414}][\text{HSO}_4]\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $[\text{P}_{44414}]\text{Cl}/[\text{P}_{44414}][\text{NO}_3]\text{-}$
201 $\text{HNO}_3\text{-H}_2\text{O}$ (cf. Table 1). Unlike $[\text{P}_{44414}]\text{Cl}$ for instance, $[\text{P}_{44414}][\text{NO}_3]$ is hardly miscible in water, and
202 can therefore be considered hydrophobic. For this reason, the $[\text{P}_{44414}][\text{NO}_3]\text{-HNO}_3\text{-H}_2\text{O}$ system is
203 not an AcABS, but was studied for comparative purposes. Since the evaluated AcABS are
204 reversible temperature-induced systems with an LCST behavior, the effect of temperature on
205 metal partition was also evaluated at 298 K and 323 K ($\pm 1 \text{ K}$). Transition metals Cu(II) , Co(II) , Ni(II)
206 and Mn(II) were studied in multi-elemental assays. The effect of the initial transition metal
207 concentration within the ternary systems was evaluated in the $[\text{P}_{44414}]\text{Cl-HCl-H}_2\text{O}$ system and
208 details can be consulted in the Supporting Information Table S3 with no change in behavior
209 observed. Ce(IV) was studied in mono-elemental assays and only in the nitrate and chloride
210 systems due to its solubility limitations in systems containing $[\text{HSO}_4]^-$. All distribution coefficients
211 and extraction efficiencies presented are listed in the Supporting Information.

212 3.1. Metal distribution on $[\text{P}_{44414}]\text{Cl}/[\text{P}_{44414}][\text{HSO}_4]\text{-HCl-H}_2\text{O}$ systems

213 Ion-exchange in the $[\text{P}_{44414}][\text{HSO}_4]\text{-HCl-H}_2\text{O}$ system at 6.5 and $8.0 \text{ mol}\cdot\text{kg}^{-1}$ of acid was
214 evaluated by ^1H NMR, chloride ion-selective electrode and titration. The $[\text{P}_{44414}]^+$ cation is
215 quantitatively in the top phase. Chloride and hydrogen were similarly quantified in the bottom
216 phase at $6.5 \text{ mol}\cdot\text{kg}^{-1}$ ($55 \% \text{ Cl}^-$ vs $58 \% \text{ H}^+$ of ions total amount in the system) and $8.0 \text{ mol}\cdot\text{kg}^{-1}$ of
217 HCl ($69 \% \text{ Cl}^-$ vs $73 \% \text{ H}^+$) (see Table S4). Therefore, no significant ion-exchange was detected in
218 the $[\text{P}_{44414}][\text{HSO}_4]\text{-HCl-H}_2\text{O}$ system. The binodal curves of all systems evaluated and mixture
219 points for metal extraction are represented in Figure S1 in the Supporting Information. The
220 influence of the IL anion (Cl^- vs $[\text{HSO}_4]^-$) and acid content (HCl) on the extraction of the transition

221 metals Co(II), Cu(II), Ni(II), and Mn(II) and the lanthanide Ce(IV) were evaluated at 298 K with the
 222 results presented in Figure 1.



223
 224 **Figure 1.** Effect of HCl concentration at (298 ± 1) K (A and B) and of temperature on metal
 225 distribution coefficient (D) in AcABS with 8.0 mol·kg⁻¹ of HCl (C and D). The asterisk above Ce(IV)
 226 bars indicates that this element was studied in a mono-elemental assay.

227 Regardless of the HCl concentration, the distribution coefficient of metals increases in both
 228 AcABS in the following way: Ni(II) < Ce(IV) < Mn(II) < Cu(II) < Co (II). The divergent distribution of
 229 Co(II) and Ni(II) was also demonstrated when the [P₄₄₄₁₄]Cl-HCl-H₂O system was first reported
 230 [14] whilst Deferm *et al.* [26] reported a similar metal distribution ratio tendency (Ni(II) < Mn(II)
 231 < Cu(II)) in the equivalent hydrophobic systems with the ILs [P₆₆₆₁₄]Cl and [N₁₈₈₈]Cl. The IL anion
 232 (Cl⁻ vs [HSO₄]⁻) had a small influence on the distribution of metals considering the large excess of
 233 Cl⁻ provided by the acid (consult Table S5). Nevertheless, increasing the HCl concentration from
 234 6.5 to 8.0 mol·kg⁻¹ improved the distribution partition of Co(II) and Mn(II) and decreased the
 235 distribution partition of Cu(II) and Ce(IV). This led to the enhancement of the $Sf_{Co(II)/Cu(II)}$ in the

236 AcABS based on $[P_{44414}Cl]$ and $[P_{44414}][HSO_4]$ from 2.6 to 4.6 and 2.1 to 4.8, respectively, at 6.5 to
237 $8.0 \text{ mol}\cdot\text{kg}^{-1}$. Despite the improvement of the distribution coefficients – excluding Cu(II) and
238 Ce(IV) – increasing the acid concentration did not impact the extraction efficiency values (see
239 Table S6). This is probably linked to the volume reduction of the IL-rich phase from 0.94 to 0.85
240 mL and 0.95 to 0.82 mL for $[P_{44414}Cl]$ and $[P_{44414}][HSO_4]$, respectively, when the HCl content
241 increases from 6.5 to $8.0 \text{ mol}\cdot\text{kg}^{-1}$.

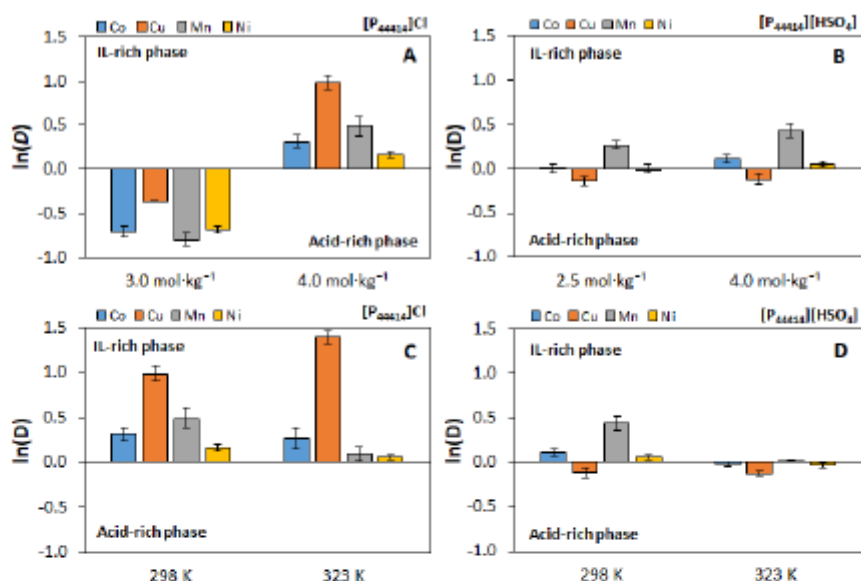
242 Extracted metal ions by unfunctionalized quaternary phosphonium or ammonium ILs
243 primarily exist as anionic complexes with the stability of the extracted metallic complex in the IL-
244 rich phase being typically independent of the acid-rich phase composition. However, this must
245 not be confused with the extraction efficiency which is strongly dependent on the overall system
246 composition. As such, the relative difference in the distribution ratio between the two species is
247 assigned to the dominant complex in the acid-rich phase, which is manipulated by the ionic
248 strength and complexing anion concentration in the solution. In Cl-rich systems, the distribution
249 ratio of each metal is related to their ability to form chloro-complexes and their respective
250 stability and affinity to the IL-rich phase.[14,17] This occurs through the displacements of water
251 molecules from the inner-sphere of the metal cation by chloride anions and the associated
252 change in the complex geometry in the case of Cu(II) and Co(II), and to a lesser extent Mn(II),
253 from octahedral to tetrahedral with the change in speciation.[17,27,28] A second less intuitive
254 contribution is the charge density of the resulting chloro-complexes and its influence on the
255 differing $D_{Co(II)}$ and $D_{Cu(II)}$ values given that the Co(II) and Cu(II) complexes identified in $6.5 \text{ mol}\cdot\text{kg}^{-1}$
256 HCl by UV-vis are the positive $[CoCl(H_2O)_5]^+$ and anionic $[CuCl_4]^{2-}$ complexes respectively (Figure
257 S2). The Gibbs free energy of hydration (ΔG_{Hyd}°) for a given ionic complex is related to its charge
258 (z) and volume (V_m) by $\Delta G_{Hyd}^\circ \propto z^2/V_m^{1/3}$, [29] with smaller absolute ΔG_{Hyd}° values associated
259 with increased extraction.[30] As such, the $[CoCl(H_2O)_5]^+$ specie is expected to present a greater
260 distribution to the IL phase through an ion-pair mechanism compared to the $[CuCl_4]^{2-}$ anion
261 which occurs via anion-exchange. The low extraction of Ni(II) can be explained by its inability to
262 form fully dehydrated chloro-complexes under the studied conditions, preventing the formation
263 of hydrophobic interactions with the IL cation and, consequently, disabling its extraction towards
264 the IL-rich phase.[14,27] **Poor Ni(II) extraction in chloride rich media was also reported by Zante**

265 *et al.*[31] In the mentioned study, supported ionic liquid ([P₆₆₆₁₄][Cl]) membranes afforded great
266 extraction of Co(II) over Ni(II), being this more evident at higher HCl concentrations. In the
267 [P₄₄₄₁₄][Cl]-HCl-H₂O system, higher temperatures result in higher distribution coefficients of the
268 studied metals (except Ni(II) and Ce(IV)) towards the IL-rich phase. The same trend was observed
269 in the [P₄₄₄₁₄][HSO₄]-HCl-H₂O system, although to a lower extent. Increasing temperature caused
270 changes in the phase ratio and composition. At higher temperatures, the top phase shrinks,
271 leading to generally higher partition coefficient values. To better understand this phenomenon,
272 the H⁺ content on each phase of the [P₄₄₄₁₄][Cl]-HCl-H₂O system with 8.0 mol·kg⁻¹ of HCl was
273 evaluated by titration at 298 K, 313 K and 323 K (see Table S7). By considering all IL is in the top
274 phase it was possible to determine the water and acid content in each phase. The Cl/H₂O molar
275 ratio at 298 K, 313 K and 323 K is as follows: 0.26, 0.33 and 0.38. Therefore, as temperature
276 increases water is expelled from the IL-rich phase to the acid-rich phase, translating into a
277 decreased distribution of complexes with inner-sphere water molecules such as Ni(II) and Ce(IV).

278 3.2. Metal distribution on [P₄₄₄₁₄][Cl]/[P₄₄₄₁₄][HSO₄]-H₂SO₄-H₂O systems

279 Ion-exchange in the [P₄₄₄₁₄][Cl]-H₂SO₄-H₂O system at 3.0 and 4.0 mol·kg⁻¹ of acid was evaluated
280 by ¹H NMR and a chloride ion-selective electrode (see Table S8). The [P₄₄₄₁₄]⁺ cation is partitioned
281 quantitatively to the top phase without traces of its presence in the bottom phase. Concerning the
282 Cl⁻, 53 % and 57 % of this anion were found at the bottom phase at 3.0 and 4.0 mol·kg⁻¹ of H₂SO₄,
283 respectively, being a clear indicator that considerable ion-exchange occurs in the [P₄₄₄₁₄][Cl]-
284 H₂SO₄-H₂O system. This is in agreement with results reported by Mogilireddy *et al.*[23]

285 Similar to the study performed for the HCl-based systems, the effect of the IL anion, acid
286 concentration and temperature were evaluated for the AcABS based on H₂SO₄. Due to the low
287 solubility of Ce(IV) in sulfate-rich systems, this metal was not evaluated in these AcABS. The
288 obtained results for the transition metals (Co(II), Cu(II), Mn(II) and Ni(II)) are represented in Figure
289 2. The differing biphasic region area of the [P₄₄₄₁₄][Cl]-H₂SO₄-H₂O and [P₄₄₄₁₄][HSO₄]-H₂SO₄-H₂O
290 systems (see Figure S1) prevented the use of the same acid concentration for the mixture point
291 with lower acid content. At 2.5 mol·kg⁻¹ of acid the [P₄₄₄₁₄][Cl]-H₂SO₄-H₂O system is in the
292 monophasic region. Thus, 3.0 mol·kg⁻¹ of H₂SO₄ was considered as the lower acid content for this
293 system.



295

296 Figure 2. Effect of H₂SO₄ concentration at (298 ± 1) K (A and B) and of temperature on metal
 297 distribution (D) in AcABS containing 4.0 mol·kg⁻¹ of H₂SO₄ (C and D).

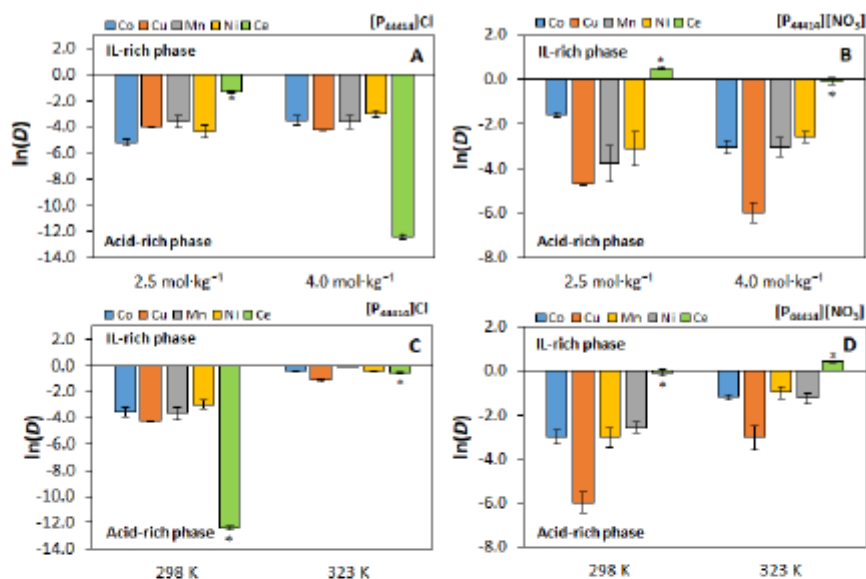
298 Concerning the [P₄₄₄₁₄]Cl system, at 3.0 mol·kg⁻¹ of H₂SO₄ all metals partition preferentially to
 299 the acid-rich phase. Increasing the H₂SO₄ content to 4.0 mol·kg⁻¹ increased the distribution of all
 300 metals to the IL-rich phase and changed the previously mentioned distribution coefficient trend
 301 to Ni(II) < Co(II) ≈ Mn(II) << Cu(II), with all metals showing a preference for the IL-rich phase. In
 302 the [P₄₄₄₁₄][HSO₄] ternary system the metal distribution coefficient maintains the same tendency
 303 regardless of the acid concentration: Cu(II) < Ni(II) ≈ Co(II) < Mn(II). Similarly, Onghena *et al.* [32]
 304 reported that Co(II) extraction using a quaternary phosphonium IL increased with increasing
 305 H₂SO₄ concentration, attaining a maximum extraction at 11 mol·L⁻¹ of H₂SO₄. The IL anion has a
 306 significant impact on the metal distribution behavior. The presence of Cl⁻ from [P₄₄₄₁₄]Cl
 307 promotes the extraction of Cu(II) to the IL-rich phase, especially at higher H₂SO₄ concentrations.
 308 The presence of different anions in the [P₄₄₄₁₄]Cl-H₂SO₄-H₂O system enables the occurrence of a
 309 split anion extraction.[33] In this case, the metal ions are extracted from the acid-rich phase

310 containing $[\text{HSO}_4]^-/\text{SO}_4^{2-}$ anions to the IL-rich phase with Cl^- from the IL anion. Although the
311 formation of tetrahedral Cu(II)-chloride complexes is expected (as further confirmed and
312 discussed in sub-section 3.4.), the formation of mixed chloride-sulfate complexes may also be
313 possible. The formation of a metal-chloride complex with low charge density and thus lower
314 hydration enthalpy promotes the selective extraction of metals to the IL-rich phase. Charge
315 neutrality is maintained by restricted anion-exchange of the different anions between the two
316 phases. Higher H_2SO_4 concentrations translate into higher ionic strength within the AcABS which
317 improved the distribution ratio of Cu(II).

318 Increasing temperature was only relevant in the $[\text{P}_{44414}]\text{Cl}$ ternary system with Cu(II) having a
319 higher distribution coefficient and the remaining metals having a slightly lower distribution
320 coefficient to the top phase (Table S9). Despite the improvement in $D_{\text{Cu(II)}}$ with temperature (from
321 2.7 to 4.0), the extraction efficiency to the top phase remained very similar (73.4 to 74.7 %, cf.
322 Table S10). Once again, this is attributed to the phase ratio changes induced by temperature.
323 Increasing the temperature to 323 K resulted in the shrinkage of the top phase from 0.80 to 0.73
324 mL due to water expulsion as shown for the $[\text{P}_{44414}]\text{Cl-HCl-H}_2\text{O}$ system (see Table S11).
325 Nevertheless, increasing temperature provided better selectivity values in the $[\text{P}_{44414}]\text{Cl}$ ternary
326 system (from $S_{\text{Cu(II)/Mn(II)}} = 1.6$ to $S_{\text{Cu(II)/Mn(II)}} = 3.6$). This feature enables the enhancement of the
327 separation factor of the AcABS without the need for additional acid or IL, making AcABS a
328 versatile and efficient alternative to other conventional solvent extraction techniques.

329 3.3. Metal distribution on $[\text{P}_{44414}]\text{Cl}/[\text{P}_{44414}][\text{NO}_3]\text{-HNO}_3\text{-H}_2\text{O}$ systems

330 The IL anion and acid concentration influence was evaluated for the systems composed of
331 HNO_3 at 3.0 and 4.0 $\text{mol}\cdot\text{kg}^{-1}$ with the distribution coefficients presented in Figure 3. In the
332 system composed of $[\text{P}_{44414}]\text{Cl}$ there is quantitative ion-exchange between the IL anion and
333 nitrate, leading to the formation of the hydrophobic IL $[\text{P}_{44414}][\text{NO}_3]$. [23] The hydrophobic
334 character of $[\text{P}_{44414}][\text{NO}_3]$ leads to the formation of a conventional liquid-liquid system, thus, the
335 designation AcABS is not applicable here.



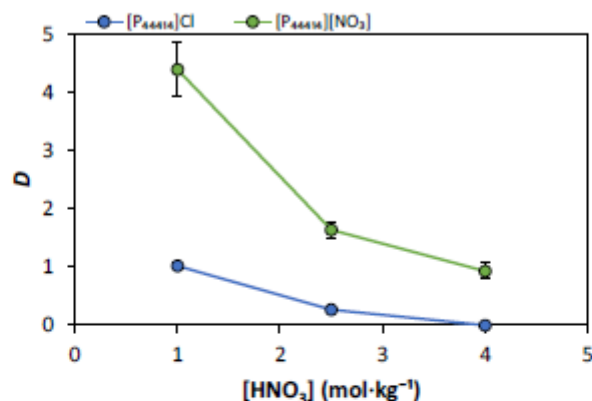
337

338 Figure 3. Effect of HNO_3 concentration at (298 ± 1) K (A and B) and of temperature on metal
 339 distribution (D) in the biphasic systems containing $4.0 \text{ mol}\cdot\text{kg}^{-1}$ of HNO_3 (C and D).

340

341 Regardless of the IL anion, Co(II) , Cu(II) , Mn(II) and Ni(II) display very low affinity for the IL-
 342 rich phase ($D \ll 1$). In contrast, Ce(IV) affinity for the IL-rich phase improved by changing the IL
 343 anion from Cl^- to NO_3^- (Table S12 and S13). The favored distribution of Ce(IV) over transition
 344 metals to the IL-rich phase in AcABS composed of HNO_3 was also reported by Schaeffer *et al.*[20]
 345 The ternary system $[\text{N}_{4444}][\text{NO}_3] + \text{HNO}_3 + \text{H}_2\text{O}$ was shown to be selective for Ce(IV) against other
 346 trivalent lanthanides and transition metals. In this system, extraction was suggested to occur via
 347 ion-pair formation as the identified $[\text{Ce}(\text{NO}_3)_6]^{2-}$ complex in the IL-rich phase was absent in the
 348 acid-rich phase before extraction. A similar ion-pair mechanism is proposed herein. However, the
 349 distribution coefficient of Ce(IV) decreases as the HNO_3 concentration increases, which may be
 350 related to the HNO_3 accumulation in the IL-rich phase.[20]

351 Since lower acid concentrations seem to enhance the affinity of Ce(IV) to the IL-rich phase,
352 an additional assay was performed at 1.0 mol·kg⁻¹ of HNO₃. The results obtained are presented
353 in Figure 4.



354
355 **Figure 4.** Metal distribution coefficient of the rare earth Ce(IV) on the [P₄₄₄₁₄]Cl-HNO₃-H₂O (blue)
356 and [P₄₄₄₁₄][NO₃]-HNO₃-H₂O (green) systems at 1.0, 2.5 and 4.0 mol·kg⁻¹ of HNO₃ at (298 ± 1) K.

357
358 Reducing the acid concentration to 1.0 mol·kg⁻¹ improved the extraction of Ce(IV) in both
359 systems. These results further support the hypothesis that nitric acid competes with metal ions
360 for the extractant (IL). Still, this does not seem to occur in other liquid-liquid extraction systems,
361 where increasing HNO₃ concentration affords better extraction efficiency values.[34]

362 Finally, increasing temperature results in higher values for metal distribution coefficients.
363 Still, the distribution coefficients values for all transition metals remain below 1, indicating a
364 better affinity for the acid-rich phase.

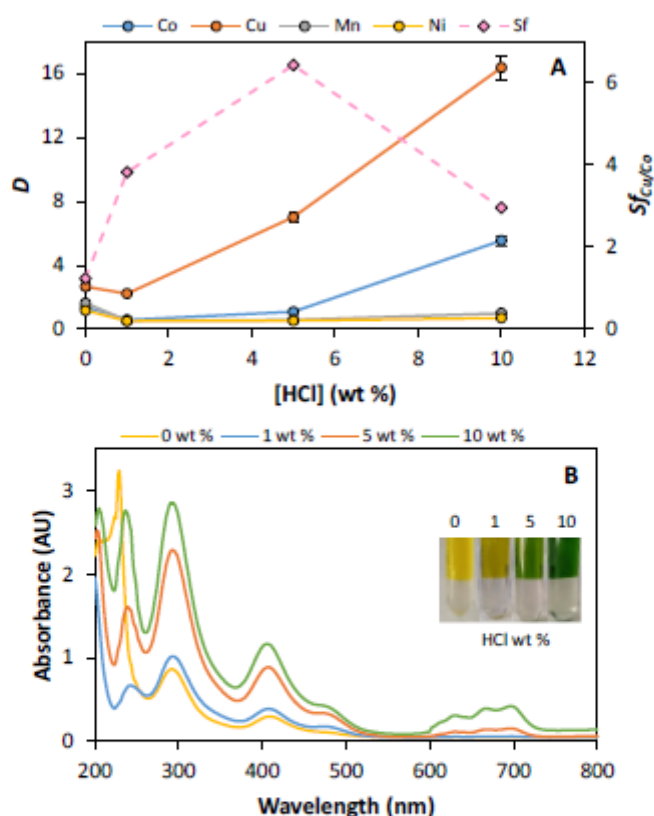
365 3.4. Tuning AcABS extraction

366 Results in the previous sections indicate that the primary factors influencing metal distribution
367 in AcABS can be summarized as listed below. These are meant to be used as general guidelines
368 based on systems studied here. However, it cannot be excluded that for certain AcABS-metal
369 pairings exceptions might occur.

- 370 (i) Charge density of the metal complex. Metal complexes with lower charge density are
371 more likely to partition to the IL-rich phase. This is affected by the presence of anions
372 (A^-), coming either from the IL or the acid, liable to form the anionic complexes
373 stabilized in the IL-rich phase. For example, Cu(II) extraction results in the $[P_{44414}]Cl$ -
374 HCl systems indicate that $D_{Cu(II)}$ decreases with increasing HCl concentration as the
375 copper complex transitions from $CuCl_3^-$ to $CuCl_4^{2-}$ (Figure 1).
- 376 (ii) Absence of coordinated water molecules in the inner solvation sphere of the metal
377 cation in the IL-rich phase. For example, Ni(II) presents a stable octahedral geometry
378 across a wide range of chloride concentration, ensuring that even complexes of low
379 charge density such as $[NiCl_5 \cdot 5H_2O]^+$ and $[NiCl_2 \cdot 4H_2O]$ present a hydrophilic character
380 and are therefore poorly extracted. Furthermore, whilst tetrahedral complexes of
381 nickel are reported at elevated chloride concentrations and temperature
382 ($[NiCl_2(H_2O)_2]$ and $[NiCl_3(H_2O)]^-$), the fully chlorinated $[NiCl_4]^{2-}$ complex was not
383 observed.[35]
- 384 (iii) $n(A^-)/n(H_2O)$ ratio, keeping in mind that this ratio is significantly higher in the IL-rich
385 phase after phase separation. The local $n(A^-)/n(H_2O)$ ratio in the IL-rich phase can be
386 modified through changes in the AcABS composition and temperature of the system.
- 387 (iv) Acid co-extraction, which can impair the extraction of the metal complexes to the IL-
388 rich phase. In the systems studied, HNO_3 is a weaker acid than HCl and its protonated
389 and dissociated form exist in equilibrium above $3.0 \text{ mol} \cdot L^{-1}$, with the equilibrium likely
390 shifted towards the protonated species in the IL-rich phase.[36] A similar reasoning
391 applies in the case of sulfuric acid to the $[HSO_4]^- \leftrightarrow SO_4^{2-}$ pair.

392 Based on these findings, it is possible to tune the selectivity of the systems as exemplified
393 below. In the $[P_{44414}]Cl-H_2SO_4-H_2O$ system increasing H_2SO_4 concentration from 3.0 to $4.0 \text{ mol} \cdot kg^{-1}$
394 was found to cause significant changes in the distribution coefficient and the extraction efficiency
395 of Cu(II), which improved from 0.70 to 2.67 and from 39 to 73% , respectively (*cf.* Table S9 and
396 S10 in the Supporting Information). Since H_2SO_4 is the acid most extensively used in the industry,
397 the selectivity of the $[P_{44414}]Cl-H_2SO_4-H_2O$ system is of interest. Aiming to take advantage of
398 different acid selectivity, 1, 5 or 10 wt % of HCl was added to this system to improve Cu(II)

399 distribution. Values obtained for metal distribution coefficients and UV spectra of the top phases
 400 of these systems are depicted in Figure 5 and further details can be found in Table S14.

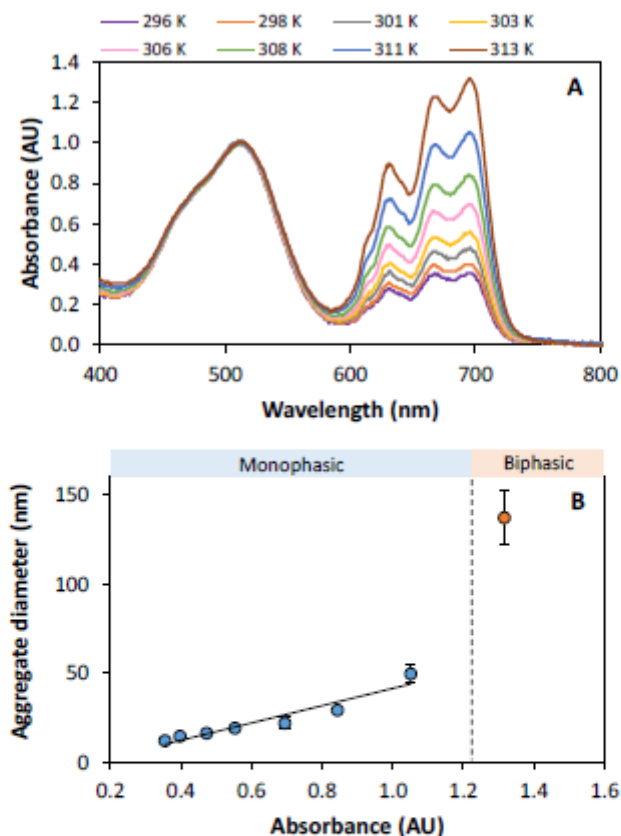


401
 402 **Figure 5.** (A) Metal distribution coefficient (D) of different metals and separation factor (Sf) of
 403 Cu(II) over Co(II) on the $[P_{44414}]Cl-H_2SO_4-H_2O$ system at $4.0 \text{ mol}\cdot\text{kg}^{-1}$ of H_2SO_4 , and 0, 1, 5 or 10 wt
 404 % of HCl at $(298 \pm 1) \text{ K}$. (B) UV spectra of the top phases of each $[P_{44414}]Cl-H_2SO_4-H_2O$ system
 405 spiked with 0, 1, 5 or 10 wt % of HCl.

406 Addition of 1 wt % of HCl caused a small decrease in the extraction of Cu(II) to the top phase
 407 and a significant decrease in the extraction of the remaining metals, causing the $Sf_{Cu(II)/Co(II)}$ to
 408 improve from 1.2 to 3.8. Addition of higher amounts of HCl caused the formation of chloro-

409 complexes and a better distribution of Co(II) to the top phase. This is further confirmed by the
410 UV spectra of the top phases of these systems (Figure 5B). At 0 and 1 wt % HCl, no traces of
411 $[\text{CoCl}_4]^{2-}$ complexes are visible (≈ 600 to 730 nm). However, increasing the HCl to 5 and 10 wt %
412 leads to the formation of cobalt-chloride complexes (≈ 600 to 730 nm), followed by their
413 migration to the top phase resulting in higher distribution coefficients for Co(II). According to the
414 obtained UV spectra, copper-chloride complexes are present in the system regardless of the
415 addition of HCl (≈ 250 to 500 nm). This shows that in this system, Cl^- from the IL anion is sufficient
416 to form copper-chloride complexes, leading to their partition to the top phase. Regarding the
417 selectivity of the system, addition of 5 wt % HCl leads to a $S_{f_{\text{Cu(II)/Co(II)}}} = 6.4$. However, increasing
418 the amount of added HCl to 10 wt % caused Co(II) to partition to a higher extent towards the top
419 phase, decreasing the $S_{f_{\text{Cu(II)/Co(II)}}}$ to 2.9. Adding 5 wt % of HCl provided the best selectivity, but
420 depending on the application, it may be profitable to simultaneously extract Co(II) and Cu(II) to
421 a higher extent by adding 10 wt % of HCl ($EE_{\text{Cu}} \% > 93$ % and $EE_{\text{Co}} \% > 83$ %, see Table S15). The
422 addition of small amounts of HCl to the $[\text{P}_{44414}]\text{Cl}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ system and the subsequent
423 formation of Cu(II)/Co(II)-chloro-complexes is a good way to promote system selectivity.
424 Although it is beyond the scope of this work, a similar behavior is anticipated if HCl is substituted
425 by chloride salts.

426 To gain a better understanding of the metal extraction mechanism of AcABS at ligand
427 concentrations below that for which anionic metal complexes are reported, the chloride deficient
428 $[\text{P}_{44414}]\text{Cl}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ system spiked with 5 wt % of HCl was further studied for the extraction of
429 Co(II). The system was prepared in the monophasic region by using $0.85 \text{ mol}\cdot\text{kg}^{-1}$ of $[\text{P}_{44414}]\text{Cl}$, 1.0
430 $\text{mol}\cdot\text{kg}^{-1}$ of H_2SO_4 and $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ as a metal source. The type of cobalt-complexes and the IL
431 aggregate size were studied with temperatures ranging from 296 K to the appearance of the
432 biphasic regime at 313 K by UV-Vis and DLS, respectively. The obtained results are represented
433 in Figure 6. The same mixture was prepared with the same Cl^- amount but without IL and
434 analyzed by UV-Vis for comparison purposes (see Figure S3).



435

436 Figure 6. (A) UV-Vis spectrum of the $[P_{44414}]Cl-H_2SO_4-H_2O$ mixture at $1.0 \text{ mol}\cdot\text{kg}^{-1}$ of H_2SO_4 , 5 wt
 437 % of HCl and Co(II) as a metal source at different temperature values. The spectrum was taken at
 438 the monophasic region and standardized according to the peak at 514 nm. (B) Correlation
 439 between the average aggregate diameter present in the $[P_{44414}]Cl-H_2SO_4-H_2O$ mixture and Co(II)
 440 relative absorbance at 695 nm ($Abs = Abs_{695}/Abs_{514}$) throughout the different evaluated
 441 temperature values.

442 At the lowest temperature values there is a high-intensity peak corresponding to Co^{2+} (514 nm)
 443 and a less intense peak corresponding to $CoCl_4^{2-}$ (695 nm). As the temperature increases and the
 444 system gets closer to the biphasic region, the peak intensity of $CoCl_4^{2-}$ increases. Recent SAXS

445 analysis on the $[P_{44414}]Cl-HCl-H_2O$ system showed that the increase of both acid concentration
446 and/or temperature leads to micelle flocculation and is consistent with the presented DLS
447 analysis (Figure 6B).[16] Furthermore, increased $[P_{44414}]Cl$ micelle counter-ion binding was
448 observed as the system approaches phase separation, resulting in the local accumulation of
449 chloride anion at the aggregate interface relative to the bulk concentration, thereby favoring the
450 interfacial formation of $CoCl_4^{2-}$. Moreover, in the absence of $[P_{44414}]Cl$, no $CoCl_4^{2-}$ is present in
451 the mixture regardless of the temperature (see Figure S3), reinforcing this interpretation.
452 Altogether, the obtained data suggest that the local increase in chloride anions through IL
453 aggregation induces the formation of $CoCl_4^{2-}$ even at low chloride concentration, suggesting an
454 ion-pair mechanism of extraction.

455 Overall, AcABS can be a promising alternative to conventional metal extraction techniques,
456 showing a good diversity of selectivities depending on the acid-IL conjugation, acid
457 concentration, temperature and target metal. The unlike distribution coefficient of the
458 transition metals and the rare earth studied herein also shows that AcABS could be a valuable
459 tool to separate lanthanides from transition metals. Besides the selectivity and versatility of
460 AcABS, these systems unlock the possibility to use the acid to simultaneously leach metals and
461 form the AcABS. This dual function of the acid is one of the main advantages of AcABS, enabling
462 to reduce the used amount of acid, the cost of the process and reducing the generated wastes.
463 In the case of split-anion extraction where significant anion-exchange occurs, care must be taken
464 during the stripping stage to regenerate the IL anion as this will otherwise affect the behavior of
465 the system over multiple extraction cycles.

466 4. Conclusion

467 Four AcABS and two hydrophobic liquid-liquid extraction systems were evaluated for the
468 separation of the transition metals $Cu(II)$, $Co(II)$, $Ni(II)$ and $Mn(II)$ and the rare earth $Ce(IV)$. The
469 influence of the IL anion, acid and its concentration and temperature on metal distribution was
470 studied. The acid has a preponderant impact on metal distribution, the latter generally improving
471 as follows: $HNO_3 < H_2SO_4 < HCl$ for transition metals and $HCl < HNO_3$ for $Ce(IV)$. The temperature
472 affected the distribution of metals and the phase ratio within the biphasic systems. This was
473 attributed to the migration of water from the top to the bottom phase. The $[P_{44414}]Cl-H_2SO_4-H_2O$

474 afforded good Cu(II) selectivity which was further improved by the addition of 1 to 10 wt % of
475 HCl. The best selectivity was achieved at 5 wt % of HCl ($Sf_{Cu(II)/Co(II)} = 6.4$) and the metal extraction
476 mechanism of this system was studied. The extraction of cobalt even at low chloride
477 concentration was induced by the IL aggregation, highlighting the favorable nature of the ion-
478 pair extraction mechanism and the versatile nature of AcABS. The versatility of AcABS makes
479 them a promising alternative to conventional liquid-liquid extraction systems, with ILs having a
480 dual role as phase forming agents and extractants. Altogether, this unlocks the possibility of
481 simultaneous leaching and extraction of metals in a one-pot way.

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493 **Conflicts of interest:** The authors declare no conflict of interest.

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