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Switchable (pH-driven) aqueous biphasic systems formed by ionic liquids as integrated production–separation platforms†

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The ability to induce reversible transitions between homogeneous solutions and biphasic systems is of paramount relevance in separation processes. In this context, pH-triggered aqueous biphasic systems composed of ionic liquids and salts are here disclosed as switchable mono/biphasic systems, and their potential application is further demonstrated through an integrated approach comprising both the production and separation of hydroxymethylfurfural from fructose.

Liquid–liquid extraction processes are of technological simplicity and of low cost, and are frequently a preferred strategy in separation processes engineering.¹ Nevertheless, the use of molecular and volatile organic solvents in separation routes presents major drawbacks due to their high volatility and recurrent toxicity.² In this context, and in addition to their tailoring ability, ionic liquids (ILs) represent a viable alternative as a result of their non-volatile nature under ambient conditions.^{3,4} The research on liquid–liquid extractions from aqueous media using ILs has focused on two main approaches: (i) the direct use of non-water miscible hydrophobic ILs; and (ii) the use of aqueous biphasic systems (ABS) composed of ILs and organic/inorganic salts. Within the two types of systems, ABS constitute a “greener” and more benign option since they are mainly composed of water (up to 70 wt% in the overall system).^{5–8} Moreover, a more delicate tuning of the phase polarities can be achieved with IL-based ABS, resulting in systems that usually allow the complete extraction and purification of a wide variety of compounds.^{5–8}

More recently, there has been a great deal of interest in the use/applications of dynamic and reversible mono/biphasic systems formed by ILs.^{9–11} It was demonstrated that phase transitions in IL-containing mixtures can be induced by a temperature-driven phenomenon or by CO₂/N₂ flushing.^{12–16} Both upper critical solution temperature (UCST)^{17–19} and lower critical solution temperature (LCST)^{20–22} phase behaviours have been reported for IL-solvent mixtures, whereas these temperature-dependent phase transitions have been shown to be advantageous in the selective separation of proteins²³ and metals.²⁴ Reversible liquid–liquid systems have also been prepared with molecular solvents that react with CO₂ forming salts and/or ILs, and applied in the separation of aliphatic and aromatic amines^{12–14} and in the synthesis/separation of gold (Au) porous films.¹⁵ However, common UCST and LCST behaviours in systems involving ILs typically occur at temperatures well above room temperature and a high energy input is required to trigger their phase switch, while the CO₂/N₂-dependent reversibility pattern requires the use of specific equipment. Furthermore, these systems are usually composed of an IL-rich phase (typically with hydrophobic characteristics) and a more hydrophilic molecular-solvent-rich phase.^{18,20–24} These systems are thus restricted in polarity differences amongst the coexisting phases, hindering improved extraction and selectivity performances to be obtained when dealing with the separation/fractionation of complex matrices. In this way, IL-based ABS can be seen as promising options, although the investigation on their use as reversible systems has lagged behind. To the best of our knowledge, only temperature-dependent reversible behaviours of IL-based ABS have been reported.²⁵ Contrary to most IL-based ABS, which display a weak dependence on temperature, it was recently found²⁵ that ABS formed by protic ILs and polymers are highly temperature dependent, thus allowing the triggering of reversible phase separations by small changes in temperature.

Given the application potential of the switchable (aqueous-rich) biphasic systems discussed above, in this work we demonstrate the reversibility of IL-based ABS attained by a

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pH-driven phenomenon and their use as integrated platforms comprising both the production and separation of 5-hydroxymethylfurfural (HMF) from fructose.

Aiming at evaluating the possibility of moving from monophasic to biphasic regimes (and *vice versa*) by a proper tailoring of the pH of the aqueous medium, ABS formed by a wide range of chloride-based ILs and potassium citrate were investigated. ILs with no speciation capability were chosen, and as such, the pH-triggered reversible phenomenon is a result of the salt (potassium citrate) speciation as a function of the pH. Citric acid presents 4 pK_a values, namely 3.05, 4.67, 5.39 and 13.92.²⁶ The speciation curves of citric acid are depicted in the ESI.† At pH values lower than 3.05, the non-charged citric acid is the dominant species present, whereas at pH values above 3.07, 4.67 and 5.39, there is the prevalence of the monovalent, divalent and trivalent charged dihydrogencitrate, hydrogencitrate and citrate anions, respectively. All these citrate-based species can be ranked within the Hofmeister series,⁶ in which higher charge density and higher charge valence anions are the better hydrated and stronger salting-out species, being thus more favourable for the creation of IL-based ABS. In fact, previous works have been published on the pH effect towards the formation of IL-based ABS,^{27–29} although no investigations on their reversible behaviour have been carried out hitherto. To be able to change the pH in the investigated ABS and to trigger the phase transition while avoiding the introduction of new species into the overall system, citric acid ($C_6H_8O_7$) and potassium hydroxide (KOH) were used. The potassium citrate/citric acid pair was also selected due to its biodegradable and non-toxic characteristics.³⁰ Fig. 1 sketches the principle of the reversible process under investigation, where the transitions between the monophasic and the biphasic regimes could be attained by the alternate addition of an acidic or an

alkaline species to the overall aqueous system. For mixture compositions above each solubility curve there is the formation of a two-phase system under the given conditions, while mixture compositions below the same curve result in the formation of a homogeneous solution (no phase-separation).

We first determined the liquid–liquid ternary phase diagrams at different pH values of ABS composed of ILs + $K_3C_6H_5O_7/C_6H_8O_7$ + water. These were determined at pH values ranging between 5 and 9 for the following hydrophilic ILs: $[C_4C_1im]Cl$, $[C_4C_1C_1im]Cl$, $[C_4C_1pip]Cl$, $[C_4C_1py]Cl$, $[C_4C_1im]Br$ and $[P_{4444}]Cl$. The definition of the IL acronyms is provided in a footnote;‡ details of their purity are given in the ESI.† Further details of the experimental procedure adopted are provided in the ESI.†

The ternary phase diagrams at 25 °C for the ABS composed of $[P_{4444}]Cl$ at different pH values are illustrated in Fig. 2. The depicted ABS phase diagrams at the most acidic pH values also denote the limit in compositions and pH values for which ABS no longer form. The experimental weight fraction data, as well as the representation of the phase diagrams for the remaining ILs, are given in the ESI.† All the phase diagrams were further characterized by the determination of several tie-lines to infer the phase compositions for given mixture compositions (*cf.* the ESI.†). In general, and for all ILs, there is a decrease in the ability for ABS formation with the pH decrease – the higher the pH of the aqueous medium, the larger is the biphasic region, and the lower the IL/salt amounts required to induce phase separation. Given that ILs with no speciation capability have been chosen, the observed dependency of the ABS formation on pH is related to the speciation performance of potassium citrate. As discussed before, at pH values lower than 3.05 and 4.07, the non-charged citric acid and the monovalent dihydrogencitrate anion are, respectively, the prevalent species, and none of these species is able to form ABS with the ILs investigated. At pH values above 4.67

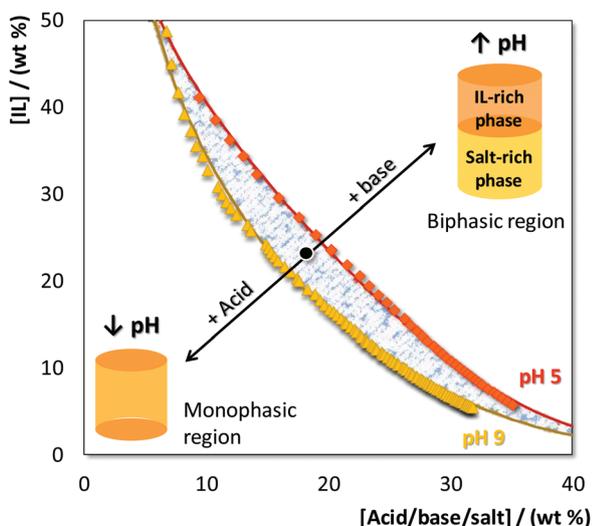


Fig. 1 Ternary phase diagrams of an IL-based ABS at 25 °C, at pH \approx 9 (\blacktriangle) and pH \approx 5 (\blacklozenge). In all the investigated ABS, the top phase corresponds to the IL-rich phase, while the bottom phase is mainly composed of salt and water.

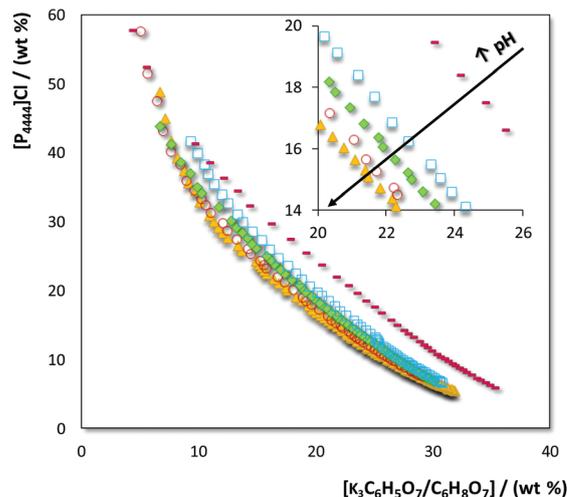


Fig. 2 Phase diagrams of ABS composed of $[P_{4444}]Cl$ + water + $K_3C_6H_5O_7/C_6H_8O_7$ at pH \approx 9 (\blacktriangle), pH \approx 8 (\circ), pH \approx 7 (\blacklozenge), pH \approx 6 (\square) and pH \approx 5 (\blacktriangledown).

and 5.39 there is the main presence of the divalent and trivalent charged hydrogen citrate and citrate anions, respectively. IL-based ABS are only formed at pH values higher than 5, meaning that only the divalent and trivalent citrate-based anions induce phase separation. This behaviour is in agreement with the Hofmeister series⁶ since higher charge density and higher charge valence anions are stronger salting-out species able to induce the salting-out of the IL, further resulting in the creation of IL-based ABS.

At a fixed pH, the IL ability to form ABS follows the order: $[P_{4444}]Cl > [C_4C_1im]Br > [C_4C_1py]Cl \approx [C_4C_1pip]Cl > [C_4C_1C_1im]Cl \approx [C_4C_1im]Cl$ (*cf.* the ESI† with all the phase diagrams). More hydrophobic ILs, resulting either from cations with longer and more aliphatic moieties or from anions of lower hydrogen-bond basicity,^{31,32} are more capable of forming ABS, *i.e.* are able to form two-phase systems at lower pH values or require lower amounts of the phase-forming components for phase separation. Examples of this are seen for $[P_{4444}]Cl$ and $[C_4mim]Br$, the only two ILs that form ABS at pH 5. On the other hand, ILs such as $[C_4C_1im]Cl$ and $[C_4C_1C_1im]Cl$, which are amongst the most hydrophilic ILs investigated, do not form ABS even at a pH of 6, being 7 the minimum pH value required for ABS formation with these ILs. This pattern also mirrors the salting-out effect of the citrate-based salt over the IL.^{5–8} A summary of the overall results according to the ability of each IL to form ABS at all the studied pH values is given in the ESI.†

After establishing the ternary phase diagrams, which describe the mixture compositions and pH values for which the liquid–liquid demixing occurs, the reversible IL-based ABS behaviour was further appraised by the alternate addition of citric acid and potassium hydroxide. For this purpose, an initial ternary mixture at the biphasic region (IL at 25 wt% + $K_3C_6H_5O_7$ at 35 wt% + water at 40 wt%) was prepared and allowed for phase separation at 25 °C. At this initial mixture composition the pH values of the aqueous medium of all IL-containing systems are *ca.* 9. An aqueous solution of citric acid at 50 wt% was added dropwise, under constant agitation, until the mixture became homogeneous (monophasic). Then, an aqueous solution of potassium hydroxide at 50 wt% was added, under agitation, to recover the initial pH value of 9 and the biphasic system. During these manipulations the pH of the aqueous solutions was experimentally controlled. Fig. 1 depicts the procedure carried out to attain the reversible process under investigation. It should be remarked that the differences in the phases' compositions are indeed negligible since a small amount of each aqueous solution (± 0.6 wt%) is enough to trigger the phase transition. The pH-driven reversibility was experimentally confirmed with all the ILs investigated, at least 3 times, with no significant changes in the phases' composition.

In summary, it is possible to prepare reversible IL-based ABS by varying the speciation behaviour of the organic salt. This phase reversibility takes place at room temperature (25 °C) and is achieved with cheap compounds already present in the original mixture and with no need for sophisticated

equipment. Hence, IL-based ABS can be envisaged as potential alternatives to the more complex reversible systems that require additional energy inputs or the addition of gases and more specific equipment. Their reversibility is a major advantage in liquid–liquid extractions to attain selective separations, as demonstrated hereinafter.

We investigated the possibility of using the proposed systems for the production of hydroxymethylfurfural (HMF) through fructose dehydration at acidic pH, and then to proceed with an integrated separation step of HMF from the unreacted precursor by an increase in the pH and the consequent formation of two-phase systems. The dehydration of carbohydrates (*e.g.* cellulose, glucose, fructose, sucrose, inulin, and cellobiose) to produce HMF has attracted a great deal of attention in the past few years.^{33,34} In fact, HMF is nowadays considered a key biomass-derived building block relevant in bio-based industries.^{33,35} The current applications of HMF are widespread and comprise the production of solvents,³⁶ bio-fuels (dimethylfuran),³⁷ polymeric materials (mainly based on its 2,5-furandicarboxylic acid derivative),³⁸ and fine chemicals,³⁹ among others. Recently, a straightforward synthesis of the active pharmaceutical ingredient ranitidine (Zantac) was also reported making use of HMF.⁴⁰ Typically, HMF is produced from fructose *via* a dehydration reaction, generally catalysed by acids (pH values ranging between 1.5 and 3).⁴¹ However, high temperatures (>200 °C), reduced pressure and long reaction times are usually required.⁴¹ More recently, IL–acid mixtures or acidic ILs have been used for sugar dehydration and production of HMF in high yields, obtained at lower temperatures (<120 °C) and within short reaction times.⁴² Although good results using ILs for the fructose dehydration have been described, the development of a cost-effective, integrated and more sustainable production–separation process is still in crucial demand. In this line, we propose herein the discussed switchable ABS as an integrated and more benign platform for the production and separation of HMF.

The production of HMF was carried out through fructose dehydration in acidic medium (pH *ca.* 1.5), at 80 °C for 80 min, in the IL-based ABS monophasic regions. After reaction, an aqueous solution of KOH was added to stop the reaction and to move the system into the biphasic region by a pH increase – Fig. 1. The creation of two-phase systems is intended for the selective separation (migration for opposite phases) of HMF and unreacted fructose. Further experimental details are given in the ESI.†

Fig. 3 depicts the results on the production of HMF in citric acid aqueous solutions at the monophasic region (corresponding to a mixture composition of 40 wt% IL + 30 wt% citric acid). The respective reactions were also carried out in the absence of ILs, as well as in the absence of citric acid, for comparison purposes. As shown, the use of an acidic medium is required for the production of HMF through the dehydration of fructose – when no acid was used a maximum yield of 0.00281 g L^{−1} of HMF was obtained. On the other hand, without IL, a maximum yield of HMF of 2.28 g L^{−1} was found. However, when ILs are used in acidic medium, HMF yields

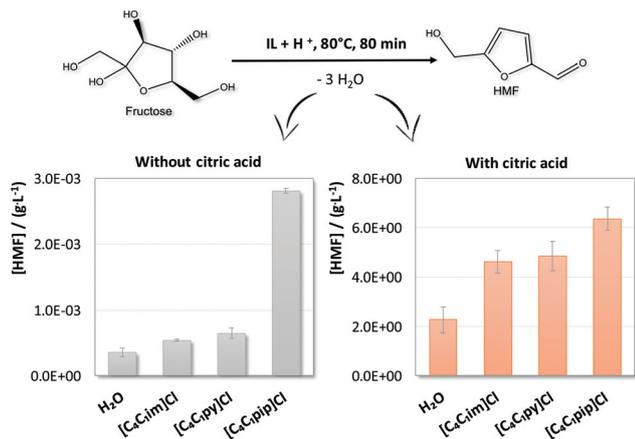


Fig. 3 Production of HMF through fructose dehydration in the presence (or not) of citric acid and ILs, at 80 °C for 80 min.

ranging between 4.61 and 6.37 g L⁻¹ have been observed, supporting the need for the presence of both the IL and the acidic medium to maximise the HMF production yield. These results are consistent with previous studies describing the requirement for the addition of ILs and acid catalysts to obtain high HMF yields.^{42,43}

After the HMF production, the reaction was stopped and the two-phase systems simultaneously formed by the addition of aqueous KOH (up to pH 7). Fig. 4 depicts the results regarding the selective separation of HMF from fructose using IL-based ABS. The results are given in extraction efficiencies of both HMF and fructose ($EE_{\text{HMF}}\%$ and $EE_{\text{Fructose}}\%$) for opposite phases. The extraction efficiencies are defined as the percentage ratio of the total weight of HMF or fructose in one of the phases to that in the total mixture (detailed results are given in the ESI[†]). The results on partition coefficient values, defined as the concentration of HMF between the IL-rich phase and the salt-rich phase, as well as the selectivity of the systems to HMF, are also provided in the ESI[†].

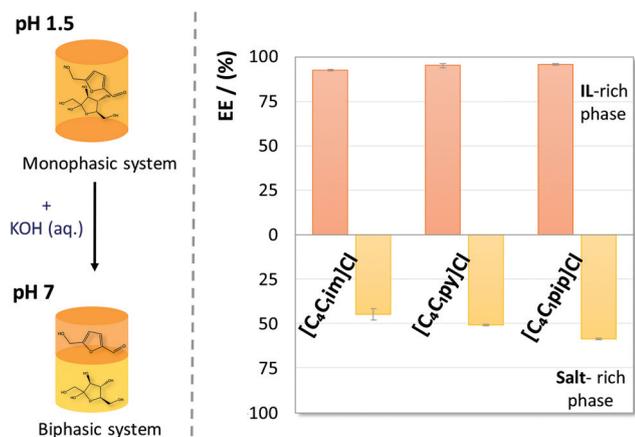


Fig. 4 Selective separation of HMF from fructose that did not react through the addition of KOH and formation of ABS.

In all the investigated systems, HMF preferentially migrates to the IL-rich phase while fructose is enriched in the opposite layer, allowing thus the separation of the two compounds. Remarkable extraction efficiencies of HMF to the IL-rich phase ranging between 92 and 96%, and of fructose to the salt-rich phase ranging between 45 and 59%, were obtained in a single step. This migration for opposite phases and selective separation results from the higher affinity of HMF to more hydrophobic (IL-rich) phases in contrast to the higher affinity of fructose to more hydrophilic (salt-rich) phases, as reflected by their octanol–water partition coefficients (K_{ow}) ($\log(K_{ow})$ of HMF = -0.10 ; $\log(K_{ow})$ of fructose = -2.76).²⁶ Although almost complete extraction of HMF to the IL-rich phase was achieved in a single step in all the studied systems, the extraction of fructose to the opposite phase seems to be more dependent on the nature of the IL employed; the selective separation of HMF and fructose increases in the following order: [C₄mim]Cl < [C₄mpy]Cl < [C₄mpip]Cl. This trend follows the IL hydrophobic nature as described by their ternary phase diagrams at a fixed pH shown in the ESI[†].

In what concerns the extraction performance and selectivity of the systems to HMF (ranging between 14 and 48; detailed data shown in the ESI[†]), our results are quite promising when compared to those reported in the literature.^{44,45} Partition coefficients of HMF ranging between 0.5 and 2.0 have been reported, with biphasic systems composed of water and butanol, methyl-iso-butylketone (MIBK), toluene, dichloromethane or other mixtures of organic volatile solvents.⁴⁴ More recently, Blumenthal *et al.*⁴⁵ suggested biphasic systems formed by water and *o*-propylphenol or *o*-isopropylphenol for the separation of HMF from the aqueous reaction medium, in which an increase, by up to five times, in the partition coefficients was reported when compared to the previously applied solvents.⁴⁴ The partition coefficients obtained in the current work range between 9 and 17 (*cf.* the ESI[†] with detailed data). Our results on the separation of HMF are thus better than the most promising ones reported hitherto in the literature. Moreover, with IL-based ABS, the use of volatile and often toxic organic solvents is avoided; instead, aqueous-rich media are used. Additionally, an integrated methodology is here proposed for the separation of HMF by the creation of two-phase systems only through a pH increase, representing thus a step forward towards the development of more sustainable production–separation processes.

In summary, the results herein reported demonstrate that pH-driven reversible ABS composed of ILs can be easily prepared by varying the speciation of at least one of the phase-forming components. Furthermore, these systems show potential to become remarkable integrated platforms, in which reaction and separation steps can be carried out sequentially by taking advantage of their switchable behaviour, as demonstrated here with the HMF production and separation from fructose as the reaction precursor. In addition to the example shown herein, reversible IL-based ABS can be certainly tailored to fit the requirements of other separation processes. Additional reactions or separation processes that occur at

other pH values can indeed be carried out with the proposed systems. They are only constrained by the minimum pH value at which they are able to form two phases to proceed with the separation step (the pH range in which all systems are able to form ABS is shown in the ESI†). To this end, it is only necessary to choose an appropriate mixture point in each phase diagram to move between the monophasic and biphasic regimes.

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Notes and references

† ILS used: 1-Butyl-3-methylimidazolium chloride, [C₄C₁im]Cl; 1-butyl-2,3-dimethylimidazolium chloride, [C₄C₁C₂im]Cl; 1-butyl-1-methylpiperidinium chloride, [C₄C₁pip]Cl; 1-butyl-1-methylpyridinium chloride, [C₄C₁py]Cl; 1-butyl-3-methylimidazolium bromide, [C₄C₁im]Br; tetrabutylphosphonium chloride, [P₄₄₄₄]Cl.

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