

Are Aqueous Biphasic Systems Composed of Deep Eutectic Solvents Ternary or Quaternary Systems?

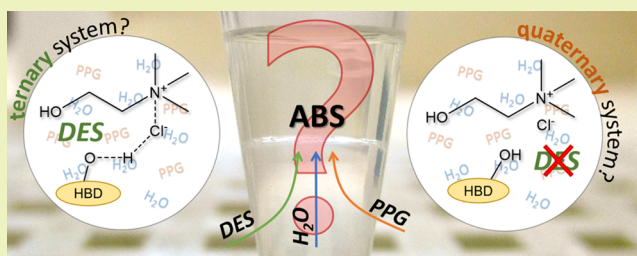
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S Supporting Information

ABSTRACT: Deep eutectic solvents (DES) have emerged in the past few years as a new class of solvents with promising applications in several fields. In the present work, the application of DES (formed by binary mixtures of cholinium chloride and carboxylic acids or urea) as phase-forming components of aqueous biphasic systems (ABS) is investigated. The mechanisms associated with the phases demixing of ABS composed of DES, as well as the DES stability in aqueous solutions, are investigated to address the critical question whether DES-based ABS are in fact ternary or quaternary mixtures. It is shown that the DES integrity is destroyed in ABS by the disruption of the hydrogen-bonding interactions of the complex (a result of the isolated components preferential solvation by water), and as confirmed by a nonstoichiometric partition of the DES components between the coexisting phases. As a result, there are no “real” DES-based ABS; instead, there is the formation of ABS composed of four components, where the carboxylic acid used as the hydrogen-bond donor species seems to act as an additive. Finally, it is shown that these ABS have an outstanding potential to be used in extraction processes, as it is here demonstrated with the complete separation of two dyes. However, the volatile nature of short chain carboxylic acids and the nonstoichiometric partition of the DES components in ABS make the development of recovery and recycling steps more difficult to accomplish.

KEYWORDS: Deep eutectic solvents, Hydrogen-bonding, Aqueous biphasic systems, Ternary/quaternary systems, Liquid–liquid extraction, Selective separation



INTRODUCTION

Deep eutectic solvents (DES) were introduced in 2003, when Abbott and co-workers¹ demonstrated the possibility of producing a liquid solvent at room temperature by mixing two solid starting materials with considerably higher melting points (e.g., urea and cholinium chloride ($[N_{111}(2OH)]Cl$), with melting temperatures of 133 and 302 °C, respectively). After this proof of concept, the number of works concerning the understanding of the underlying molecular-level scenario, their physical and chemical properties, as well as their applications as alternative solvents, increased significantly.^{2–4}

The formation of DES results from the formation of strong hydrogen bonds between the two starting materials, namely, a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA). The formation of ion–HBD complexes leads to a lower entropic difference of the phase transition and to the further depression of the freezing temperature.^{5–7} The first reported DES (composed of $[N_{111}(2OH)]Cl$ and urea)¹ remains the most widely investigated. However, DES can be formed by mixing other substituted tetralkylammonium or phosphonium salts with a HBD, such as amines, carboxylic acids, and carbohydrates, among others.^{8–10}

Many DES share some of the unique characteristics of ionic liquids (ILs), namely, a low volatility, high conductivity, wide liquid temperature range, and high solvation ability for a large

number of compounds.^{3,4} DES are also able to overcome some of the disadvantages related to ILs. They are easier to prepare, by a simple mixture of the starting materials at moderate temperatures, without requiring a reaction step. Furthermore, the addition of an agent able to disrupt hydrogen-bonding interactions can lead to the recovery of at least one of the initial compounds.^{3,4,11,12} The starting materials are usually cheaper, toxicologically well-characterized, and often derived from renewable resources, which results in low-cost and more environmentally friendly products.^{3,4,11,12} As in ILs, innumerable combinations of the starting materials can be attempted, and therefore, DES may also be classified as “designer solvents”. Since DES have fewer restrictions in terms of stoichiometry, their properties and phase behavior can be tuned by changing the ratio of their components, thus adding one more degree of freedom to their design.^{3,4,11,12} Although reports regarding the applications of DES are still limited, a reasonable number of studies have shown the potential of DES as alternative solvents in electrochemistry, catalysis, synthesis, and separation processes.^{3,4,13–15}

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In the past decade, aqueous biphasic systems (ABS) composed of ILs and a wide number of salts, carbohydrates, polymers, or amino acids have been extensively studied for the extraction and purification of bioactive compounds.¹⁶ IL-based ABS lead to remarkable extraction efficiencies and selectivities by a proper tailoring of their phases' polarities and affinities.¹⁶ Albeit scarcely investigated, the potential of DES as phase-forming components of ABS was recently reported by Xu and co-workers.^{17,18} Yet, those pioneering phenomenological results did not comprise the mechanisms associated with the coexisting phases demixing and the stability of the HBD:HBA complex in aqueous media. Only "ternary" phase diagrams for each ABS were reported, and their applications to the extraction of proteins were presented.^{17,18} Whether DES in the form of a HBD:HBA complex will form a ternary system, as in common ABS, or the alleged DES-based ABS is a quaternary system that phase separates with a nonstoichiometric partition of the HBD and HBA species between the two phases remains an open question. In this context, the present work aims at shedding light on this subject. For this purpose, novel ABS composed of water, poly(propylene) glycol with an average molecular weight of 400 g mol⁻¹ (PPG 400), and several DES formed by [N₁₁₁(2OH)]Cl and carboxylic acids or urea were investigated. PPG 400 was selected for its good ability to form ABS^{19,20} and because the use of polymers instead of ILs or salts to form DES-based ABS prevents the introduction of other ionic species into solution and possible ion exchange between the two phases. The studied DES allow the analysis of the effect of the urea or carboxylic acid:[N₁₁₁(2OH)]Cl ratio and the impact of the HBD species on their ability for the creation of ABS, as well as to infer on their nonstoichiometric partition between the coexisting phases. The phase-formation capability of these systems is also herein compared with ABS formed by [N₁₁₁(2OH)]-based ILs, with anions corresponding to the investigated acids, and PPG 400. Finally, the application of these systems for the selective separation of dyes is investigated to ascertain on their potential applicability.

EXPERIMENTAL SECTION

Materials. The determination of the liquid–liquid phase diagrams was performed using aqueous solutions of PPG with an average molecular weight of 400 g mol⁻¹ (from Sigma-Aldrich, Germany) and individual aqueous solutions of DES, prepared by us, using the following components: [N₁₁₁(2OH)]Cl (98 wt % pure from Sigma-Aldrich, Germany), glycolic acid (>99 wt % pure from Sigma-Aldrich, Germany), acetic acid (>99 wt % pure from Sigma-Aldrich, Germany), lactic acid (88–92 wt % pure from Riedel-de Haën, Germany), citric acid tetrahydrated (100% pure from Fisher Scientific, USA), and urea (99.0–100.5% pure from Panreac, Spain). All components used on the DES preparation were dried under vacuum (10 Pa) at room temperature for a minimum of 24 h. The cholinium-based ILs used on the dyes' selective extraction were [N₁₁₁(2OH)]Cl, cholinium dihydrogen citrate, [N₁₁₁(2OH)][DHC] (98 wt % pure from Sigma-Aldrich, Germany), cholinium acetate, [N₁₁₁(2OH)][Ac] (98 wt % pure from Iolitec, Germany), cholinium glycolate, [N₁₁₁(2OH)][Gly] (97 wt % pure and synthesized by us), and cholinium lactate, [N₁₁₁(2OH)][Lac] (99 wt % pure and synthesized by us). The ILs synthesized by us were prepared according to well-established protocols.^{21,22} The required precursors were commercially acquired, namely, cholinium hydroxide [N₁₁₁(2OH)][OH] (40 wt % in methanol) from Sigma-Aldrich (Germany) and glycolic acid and lactic acid as described before. After the synthesis and before use, all ILs were purified and dried for a minimum of 24 h at constant agitation, at a moderate temperature (~70 °C) under vacuum (10 Pa). The extracted dyes were Sudan III (>99 wt % pure) from Merck (Germany) and pigment

blue-29 (PB29) obtained from Holliday Pigments (France). The chemical structures of studied DES, ILs, PPG, and dyes are presented in the Supporting Information, Figure S1. The water used was double distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 apparatus.

DES Preparation. For the preparation of DES, both the hydrogen-bond donor (carboxylic acids or urea) and acceptor ([N₁₁₁(2OH)]Cl) species were added gravimetrically within ±10⁻⁴ g to closed vials, at three different mole ratios, 1:2, 1:1, and 2:1 of carboxylic acid:[N₁₁₁(2OH)]Cl and urea:[N₁₁₁(2OH)]Cl, and heated in an oil bath with constant agitation. The maximum temperature reached was 60 °C for the DES composed of acetic acid and 100 °C for DES composed of glycolic acid, lactic acid, and urea. For the preparation of the citric-acid-based DES, higher temperatures, close to 120 °C, were required until the formation of a transparent liquid. After the formation of a liquid, the mixture was maintained for 1 h at the final temperature and was then cooled down to room temperature. All the procedure was executed under an inert atmosphere. The water content of the DES constituents was measured using a Metrohm 831 Karl Fischer coulometer that was taken into consideration during the preparation of each mixture. The final physical state (liquid or wet solid) and composition of the synthesized DES at room temperature are described in the Supporting Information, Tables S1 and S2, respectively.

Phase Diagrams and Tie-Lines. The solubility curves were determined through the cloud point titration method^{23,24} at 25 °C (±1 °C) and atmospheric pressure. Aqueous solutions of PPG at approximately 80 wt % and aqueous solutions of the different DES at 75 wt % were prepared and used for the determination of the binodal curves. Repetitive dropwise addition, under constant stirring, of the aqueous DES solution to the aqueous solutions of PPG was carried out until the detection of a cloudy (biphasic) solution, followed by the dropwise addition of ultrapure water until the finding of a monophasic region (clear and limpid solution). The ternary system compositions were determined by weight quantification within ±10⁻⁴ g.

The experimental binodal curves were fitted by eq 1.²⁵

$$[\text{PPG}] = A e^{(B[\text{DES}]^{0.5}) - (C[\text{DES}]^3)} \quad (1)$$

Here [PPG] and [DES] are the PPG and DES weight fraction percentages, respectively, and A, B, and C are constants obtained by the regression of the experimental binodal data. Further details on the determination of the tie-lines (TLs) and tie-line length (TLL) are given in the Supporting Information.

The pH values (±0.02) of the PPG- and "DES"-rich aqueous phases were measured at (25 ± 1) °C using a Mettler Toledo SevenMulti dual pH meter.

DES Stability in Aqueous Media. To evaluate if the HBD-[N₁₁₁(2OH)]Cl hydrogen-bonding interactions are maintained when DES are dissolved in water or in the ABS formation, the mole ratio between each carboxylic acid or urea and the cholinium cation in each phase of the corresponding ABS was determined by ¹H nuclear magnetic resonance (NMR), in solution and neat, respectively, using a Bruker Avance 300 at 300.13 MHz, with deuterium oxide (D₂O) as solvent and trimethylsilyl propanoic acid (TSP) as the internal reference. For this, individual ABS composed of PPG + DES + water at the biphasic region were gravimetrically prepared within ±10⁻⁴ g, vigorously agitated, and centrifuged at 3500 rpm for 30 min at (25 ± 1) °C, in order to reach the equilibrium and a complete separation of the coexisting phases. Samples of each phase were then taken for the quantification of each carboxylic acid or urea and the cholinium cation by ¹H NMR.

Selective Extraction of Textile Dyes. Two textile dyes, Sudan III and PB29, were studied as model molecules to demonstrate the potential application of DES-based ABS. A ternary mixture with a common composition, and within the biphasic region, was prepared with 21 wt % of DES, 40 wt % of PPG, and 39 wt % of water with the exception of the ABS constituted by the following DES: 1:1 and 2:1 of citric acid:[N₁₁₁(2OH)]Cl. With these two systems, the following mixture point was used: 25 wt % of DES + 50 wt % of PPG + 25 wt %

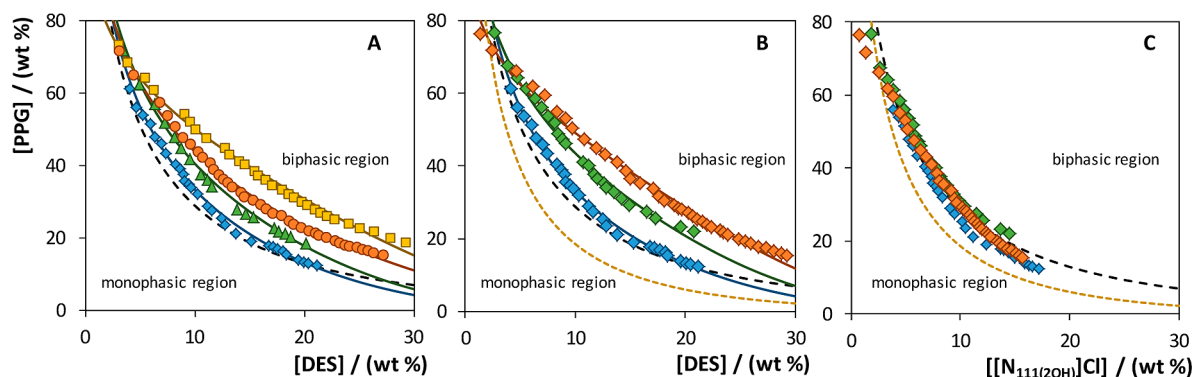


Figure 1. Phase diagrams of DES-based ABS at 25 °C. (A) Carboxylic acid nature effect on ABS formation: DES constituted by 1:2 mol proportion of acetic acid:[N_{111(2OH)}]Cl (blue ◆), glycolic acid:[N_{111(2OH)}]Cl (green ▲), lactic acid:[N_{111(2OH)}]Cl (orange ●), and citric acid:[N_{111(2OH)}]Cl (yellow ■); fitting of the binodal data by eq 1 (—); [N_{111(2OH)}]Cl-based ABS binodal curve (---). (B) Carboxylic acid concentration effect on ABS formation: DES composed of acetic acid:[N_{111(2OH)}]Cl mole proportion of 1:2 (blue ◆), 1:1 (green ▲), and 2:1 (orange ●); fitting of the binodal data by eq 1 (—); [N_{111(2OH)}]Cl-based ABS binodal curve (---); [N_{111(2OH)}][Ac]-based ABS binodal curve (yellow ---). (C) Representation of the binodal curves of acetic acid:[N_{111(2OH)}]Cl-based ABS as a function of the [N_{111(2OH)}]Cl concentration: DES composed of acetic acid:[N_{111(2OH)}]Cl mole proportion of 1:2 (blue ◆), 1:1 (green ▲), and 2:1 (orange ●); [N_{111(2OH)}]Cl-based ABS binodal curve (---); [N_{111(2OH)}][Ac]-based ABS binodal curve (yellow ---).

of H₂O. In each system, with a total weight of 3 g, a small amount of each dye (≈ 0.30 mg) was added. After the total dissolution of both dyes, each mixture was centrifuged at 1500 rpm for 10 min at (25 \pm 1) °C to achieve the complete partitioning of each dye between the two phases.

After a careful separation of both phases, the quantification of each dye in the two phases was carried by UV–vis spectroscopy, using a synergy/HT microplate reader, at a wavelength of 348 nm for Sudan III and 725 nm for PB-29. At least three individual experiments were performed in order to determine the average in the extraction efficiency, as well as the respective standard deviations. The interference of the polymer and DES with the quantification method was also taken into account, and blank control samples were always employed. The percentage extraction efficiency of Sudan III is defined as the percentage ratio between the amount of dye in the PPG-aqueous-rich phase and that in the total mixture. Similarly, the percentage extraction efficiency of PB29 is defined as the percentage ratio between the amount of dye in the “DES”-aqueous-rich phase and that in the total mixture.

RESULTS AND DISCUSSION

A total of 15 DES formed by [N_{111(2OH)}]Cl, as the HBA, and four carboxylic acids as the HBD, namely, lactic, glycolic, citric and acetic acids, or urea, at three mole composition ratios (2:1, 1:1, and 1:2), were prepared. The liquid–liquid phase diagrams of some ABS composed of DES + PPG 400 + H₂O are depicted in Figure 1. For all phase diagrams, the biphasic region is located above the binodal curve, and the monophasic region is localized below. The detailed experimental weight fraction data and the representation of the phase diagrams for the remaining DES-based ABS are presented in the Supporting Information, along with the compositions of the coexisting phases (tie-lines). In the studied ABS, the top phase corresponds to the PPG-rich phase, while the bottom phase is mainly composed of an aqueous solution enriched in DES.

Figure 1A allows the evaluation of the effect of the carboxylic acid nature on the ABS formation ability. It is well-established that the higher the ion’s ability to create hydration complexes is the easier the formation of salt–polymer or IL–salt ABS is.^{16,25} The DES ability to form ABS is in the following order: acetic acid:[N_{111(2OH)}]Cl > glycolic acid:[N_{111(2OH)}]Cl > lactic acid:[N_{111(2OH)}]Cl > citric acid:[N_{111(2OH)}]Cl. In a comparison of the DES capability to form ABS with the corresponding

[N_{111(2OH)}]-based ILs ([N_{111(2OH)}][Gly] \sim [N_{111(2OH)}][Ac] > [N_{111(2OH)}][Lac] \sim [N_{111(2OH)}]Cl > [N_{111(2OH)}][DHC]),²⁶ it is possible to identify a similar trend. According to the [N_{111(2OH)}]Cl position in this trend, it is however evident that there is a stronger aptitude of the [N_{111(2OH)}]-based ILs to form ABS (cf. the Supporting Information). In general, and as represented in Figure 1A, it seems that carboxylic acids with shorter alkyl side chains have a higher liquid–liquid demixing ability. Nevertheless, when the weight fraction of the several acids is not considered, a different scenario emerges, with a nonsignificant impact of the acid nature as discussed below.

Figure 1B depicts the carboxylic acid concentration effect, where an increase of the acid content leads to a decrease on the area of the biphasic regime. This behavior is always observed and appears to be independent of the acid nature. Furthermore, with consideration of the eutectic point of the DES studied ($\sim 2:1$ for acetic and lactic-acid-based DES, 1:1 for glycolic acid:[N_{111(2OH)}]Cl DES, and 1:2 for citric acid:[N_{111(2OH)}]Cl DES),¹¹ it is clear that the application of an eutectic mixture does not change this trend. It was previously reported that [N_{111(2OH)}]Cl is the salting-out agent in PPG-based ABS.²⁶ As shown in Figure 1A, the presence of a non-salting-out species, such as a carboxylic acid, seems to decrease the ability of ABS formation by [N_{111(2OH)}]Cl. However, when the binodal curves are presented as a function of the isolated [N_{111(2OH)}]Cl concentration, Figure 1C, there is an almost complete superposition of the solubility curves. This pattern supports the vision of a mechanism of salting-out of [N_{111(2OH)}]Cl over PPG in aqueous media, with the carboxylic acid contributing with a minor effect on the ability of ABS formation.

Although the formation of ABS using DES is unquestionable, there remains the major question of whether the carboxylic acid:[N_{111(2OH)}]Cl DES complexes are maintained when dissolved in aqueous media (for ABS formation). To gather novel insights on this matter, ¹H NMR spectra of both phases were acquired to evaluate the content and ratio between each acid and [N_{111(2OH)}]Cl. Examples of these spectra are provided in the Supporting Information.

Figure 2 depicts the HBD:[N_{111(2OH)}]Cl mole ratio obtained for both “DES”- and PPG-rich phases. The number of moles of each DES component in each phase, as well as mole ratio

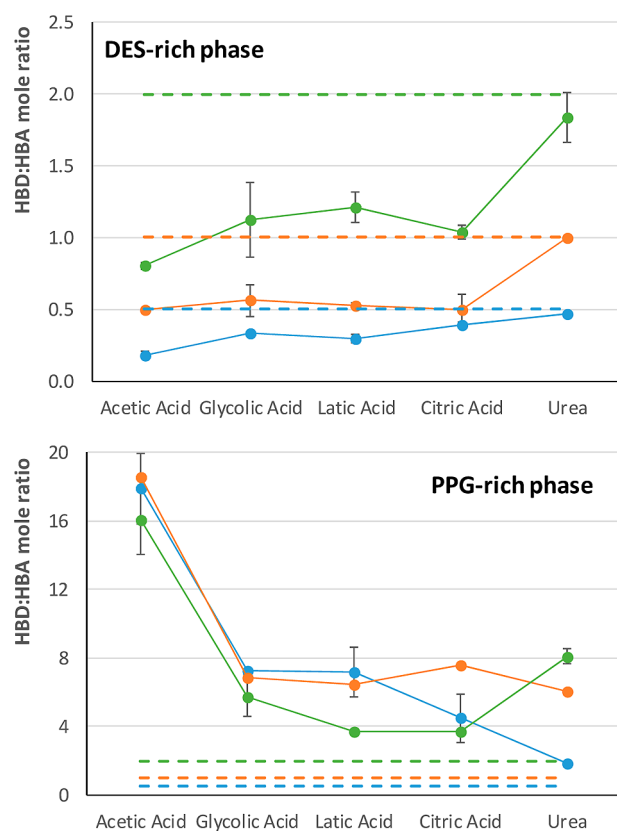


Figure 2. Mole ratio between the HBD and $[N_{111(2OH)}]Cl$ (HBA) in the coexisting phases of ABS composed of DES + PPG + H_2O (solid lines) and in DES initial composition (dashed lines): 1:2 (blue), 1:1 (orange), 2:1 (green).

between the HBD and HBA species, are presented in the [Supporting Information](#). These results reveal that the carboxylic acid: $[N_{111(2OH)}]Cl$ complexes are destroyed, since the ratio used on DES preparation is not maintained in the coexisting phases of DES-based ABS. This nonstoichiometric partitioning of the DES components also reinforces the hypothesis that these ABS are formed by the salting-out effect exerted by $[N_{111(2OH)}]Cl$ over the polymer in aqueous media, since the formation of two-phase systems was always observed. As previously highlighted, carboxylic acids slightly affect the solubility curves; however, they partition in different amounts between the coexisting phases. The extent of their partition is presented in the [Supporting Information](#). Although more than 40% of carboxylic acids remain in the “DES”-rich phase, in the PPG-rich phase the amount of carboxylic acids is considerably higher than that of $[N_{111(2OH)}]Cl$. In summary, there are no “real” DES-based ABS. There are, on the other hand, ABS formed by $[N_{111(2OH)}]Cl$ and PPG, where carboxylic acids seem to act as additives and tend to partition to different extents (according to the acid nature) between the coexisting phases.

The water effect on the DES integrity is one of the major gaps in the DES research field. The observed nonstoichiometric partitioning of the DES components between the coexisting phases reveals that the DES integrity is destroyed in an ABS by the disruption of the hydrogen-bonding interactions within the HBD:HBA complex. These results are further corroborated by some recent works^{27–31} which demonstrated that the dilution of DES in water results in a progressive rupture of the hydrogen bonds between the starting materials. For each DES, there

seems to exist a maximum amount of water that can be added before the complete disruption of the DES complex followed by the formation of an aqueous solution containing the solvated individual components.

On the basis of the results reported here, it can be concluded that ABS composed of carboxylic-acid-based DES are indeed quaternary systems and not ternary systems as other types of ABS. The formation of the ABS seems to be controlled by PPG 400 and $[N_{111(2OH)}]Cl$, with a minor effect of the carboxylic acids. There are no “real” DES-based ABS; instead, these systems are ABS formed by $[N_{111(2OH)}]Cl$ and PPG 400, as previously reported,²⁶ where the carboxylic acid acts as a fourth compound or additive in the ABS.

The interactions between carboxylic acids and $[N_{111(2OH)}]Cl$ are weaker than those observed in DES constituted by urea and $[N_{111(2OH)}]Cl$.¹ As a further confirmation test, ABS composed of the DES formed by urea: $[N_{111(2OH)}]Cl$ (at the mole composition ratios of 1:2, 1:1, and 2:1) and PPG 400 were also studied. The detailed experimental weight fraction data, respective phase diagrams, and compositions of the phases are presented in the [Supporting Information](#). As observed with the ABS formed by carboxylic acids: $[N_{111(2OH)}]Cl$ DES, PPG is salted-out by $[N_{111(2OH)}]Cl$, while urea has a negligible effect on the phase diagram behavior. However, unlike for the other systems discussed above, the urea: $[N_{111(2OH)}]Cl$ mole ratio in the “DES”-rich phase depicted in [Figure 2](#) is the same as the initial mole ratio used in the DES preparation. The question of the stability of this particular DES complex is thus not settled by the results reported here. A finer analysis of these results is thus in order. From all HBD species studied in this work, urea presents the lowest octanol–water partition coefficient (K_{OW}), thus presenting a higher affinity for salt-aqueous-rich phases when compared with the carboxylic acids. Contrary to that observed for carboxylic acids, the extraction efficiency of urea is higher than 90% meaning that most urea on the system remains in the cholinium-rich phase; the number of moles of each species in each phase is provided in the [Supporting Information](#). Since PPG-aqueous-rich phases are composed of a large amount of polymer (>70 wt % from tie-lines data, cf. [Supporting Information](#)), with only a small amount of water and other components, the distribution data obtained by ¹H NMR spectroscopy for the coexisting phases of the urea: $[N_{111(2OH)}]Cl$ -based ABS could be a result of the almost total partition of both the $[N_{111(2OH)}]Cl$ and urea to the most hydrophilic phase, which would explain the results obtained (cf. [Supporting Information](#)). In fact, literature results^{27–31} support the idea that this complex is not stable at water concentrations higher than 50 wt % (cf. [Supporting Information](#)), as those observed in the “DES”-rich phase of our systems. Overall, the obtained results suggest that DES-based ABS are quaternary systems composed of $[N_{111(2OH)}]Cl$, PPG 400, and water, with carboxylic acids or urea acting as additives.

Although ABS composed of DES are quaternary instead of ternary systems, their applicability may not be conditioned by the DES nonstoichiometric partitioning. To demonstrate their potential in separation processes, the selective extraction of two textile dyes, namely, pigment blue (PB29) and Sudan III, was evaluated, [Figure 3](#). Mixture compositions and extraction efficiencies ($EE_{dye}\%$) are described in detail in the [Supporting Information](#). In all DES-based ABS, Sudan III preferentially partitions to the PPG-rich phase, while PB 29 completely migrates to the opposite phase. Sudan III has a less polar character ($\log(K_{OW}) = 7.74$)³⁵ than PB29 and therefore

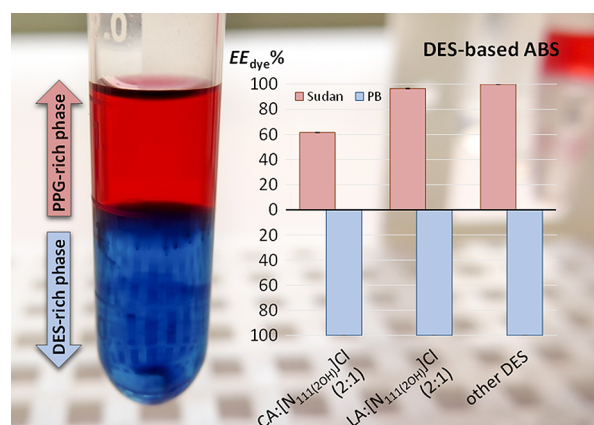


Figure 3. Selective extraction of the textile dyes Sudan III and PB 29 with ABS composed of DES.

preferentially partitions to the more hydrophobic PPG-rich phase, while the inorganic pigment partitions to the more polar salt-rich phase.

Remarkably, for 10 of the 12 studied systems, the complete separation of the two dyes was achieved; i.e., they are completely enriched in one of the phases. Only the systems composed of citric acid:[N₁₁₁(2OH)]Cl (2:1) and lactic acid:[N₁₁₁(2OH)]Cl (2:1) display lower extraction efficiencies for Sudan III, 61.6% and 96.6%, respectively (Figure 3). The worst performance of these two systems seems to be related to their lower ability to create ABS. Furthermore, the extraction performance of DES-based ABS is identical to that of IL-based ABS formed by [N₁₁₁(2OH)]-based ILs, [N₁₁₁(2OH)]Cl, [N₁₁₁(2OH)][Ace], [N₁₁₁(2OH)][Gly], [N₁₁₁(2OH)][Lac], and [N₁₁₁(2OH)][DHC], and PPG 400 (cf. the Supporting Information), which means that DES-based ABS are able to compete in terms of extraction performance with IL-based systems. Nevertheless, contrary to IL-based ABS, the presence of volatile acids and the nonstoichiometric partition of the DES isolated components between the coexisting phases makes the design of a sustainable process more difficult, particularly when the recovery and recycling of the phase-forming components is envisaged. For instance, two approaches were previously proposed by Ferreira et al.³⁶ for the recovery of textile dyes (by induced precipitation) from the coexisting phases of ABS composed of ILs and salts by a reduction in temperature or by water evaporation, which further permits the recycling of the phase-forming components. In DES-based ABS, the presence of volatile acids and the nonstoichiometric partition of the DES isolated components between the coexisting phases require the design of more complex recovery processes.

In summary, the results reported here demonstrate that the DES integrity is destroyed in ABS by the disruption of the DES hydrogen-bond complex and preferential solvation of the isolated components by water. This is confirmed by the nonstoichiometric partition of the HBD and HBA species between the coexisting phases supporting the idea that DES-based ABS are in fact quaternary instead of ternary systems. These ABS are formed by [N₁₁₁(2OH)]Cl and PPG 400 in water, where the carboxylic acids or urea act as the fourth component or an additive in the overall system. It was also shown that DES-based ABS have potential to be used in extraction and purification processes, as it is here demonstrated with the complete separation of two dyes for opposite phases in a single step. However, it should be kept in mind that the non-

stoichiometric partition of the DES components and the volatile nature of short chain carboxylic acids make the design of an integrated and sustainable separation process more complex than that required, for instance, with IL-based ABS.³⁶

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00485.

Detailed experimental data of binodal curves, DES stability, and textile dyes extraction efficiencies (PDF)

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Notes

The authors declare no competing financial interest.

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