Universidade de Aveiro Departamento de Química
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Ana Maria da Conceição Ferreira

Separação de corantes com sistemas aquosos bifásicos reversíveis

Separation of dyes with reversible aqueous biphasic systems

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Separation of dyes with reversible aqueous biphasic systems

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química, realizada sob a orientação científica da Professora Doutora Ana Maria Clemente Fernandes, Professora Auxiliar do Departamento de Química da Universidade de Aveiro e coorientação da Doutora Mara Guadalupe Freire Martins, Investigadora Auxiliar do Departamento de Química, CICECO, da Universidade de Aveiro.

À mãe e ao pai …

o júri

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Palavras-chave

Extração líquido-líquido, separação seletiva, sistemas aquosos bifásicos reversíveis, líquidos iónicos, efluentes aquosos, indústria têxtil, corantes, ácido cloroanílico, azul indigo, sudão III, pigmento azul 27, pigmento azul 29.

Resumo

O principal objetivo do presente trabalho recai no estudo de sistemas aquosos bifásicos (SAB) reversíveis, constituídos por líquidos iónicos (LIs), bem como na sua potencial aplicação para a separação seletiva de corantes utilizados maioritariamente pela indústria têxtil. Esta é uma das principais indústrias que liberta uma grande quantidade de produtos químicos, destacando-se a descarga de elevadas quantidades de corantes através dos respetivos efluentes aquosos, o que é motivo de elevada preocupação tanto a nível ambiental como económico. Este trabalho centra-se no estudo da aplicabilidade de SAB reversíveis, através de variações de pH do meio aquoso, assim como na procura de SAB constituídos por LIs mais benignos que os estudados até ao momento, como uma técnica alternativa para a remoção de corantes de efluentes aquosos. Adicionalmente, também se deu um especial destaque à interpretação dos mecanismos que regem a partição de corantes entre as duas fases neste tipo de sistemas.

Os SAB constituídos por LIs apresentam uma grande aplicabilidade na extração e purificação de uma vasta gama de compostos, incluindo corantes. Assim, iniciou-se o presente trabalho com a extração de um conjunto de corantes (ácido cloroanílico, azul indigo, sudão III) utilizando SAB mais convencionais e constituídos por LIs e um sal orgânico/inorgânico. Nesta etapa avaliou-se o efeito da estrutura química do LI sobre a capacidade de extração, assim como o efeito do sal e consequente pH do meio. Os resultados obtidos revelaram que uma seleção adequada do LI e do sal pode conduzir à extração completa dos três corantes estudados e num único passo operacional.

Após demonstrar a elevada capacidade de SAB constituídos por LIs para extrair corantes de fases aquosas, estudou-se a aplicabilidade de SAB reversíveis, por variações de pH, na separação seletiva de corantes orgânicos e inorgânicos (sudão III e pigmento azul 27). A reversibilidade deste tipo de SAB foi conseguida com a manipulação da especiação do sal orgânico utilizado. Os resultados obtidos confirmaram a reversibilidade dos SAB, pelo menos até três vezes, por variação do pH, assim como uma capacidade de extração seletiva de cada um dos corantes para fases opostas.

Por fim, e após confirmada a existência de SAB reversíveis, estudaram-se misturas de um polímero e LIs da família das colinas com aniões derivados de ácidos carboxílicos com o intuito de encontrar sistemas mais benignos e biocompatíveis. A variação do pH e reversibilidade neste tipo de sistemas foi conseguida com a especiação do anião do LI. Estes sistemas foram finalmente avaliados no que respeita à sua capacidade de extração e separação seletiva de corantes (sudão III, pigmento azul 27 e pigmento 29), e o estudo revelou que os sistemas LI-polímero conduzem a uma extração seletiva entre os corantes orgânicos e os pigmentos inorgânicos.

Keywords

Liquid-liquid extraction, selective separation, reversible aqueous two-phase systems, ionic liquids, wastewaters, textile industry, dyes, chloranilic acid, indigo blue, sudan III, pigment blue 27, pigment blue 29.

Abstract

The main objective of this work conveys on the study of reversible aqueous two-phase systems (ATPS), constituted by ionic liquids (ILs), and their potential application for the selective separation of dyes mainly used in the textile industry. The textile manufacturing is one of the main industries which discharges a heavy load of chemicals, especially large contents of dyes during the dying process through wastewaters, which results in severe environmental and economic concerns. In this context, this work focuses on the applicability of reversible ATPS, as well as on the development of more benign systems than those studied hitherto, as an alternative technique for the removal of dyes from wastewaters. Additionally, special attention was also given to the understanding of the molecular mechanisms which rule the partitioning of dyes between the coexisting phases of ATPS.

IL-based ATPS display a widespread applicability in the extraction, concentration and purification of a large range of compounds, including dyes. Thus, this work started with investigations on the extraction of a set of dyes (chloranilic acid, indigo blue and sudan III) using more conventional ATPS composed of ILs and an organic/inorganic salt. At this stage, the influences of the IL chemical structure, the salting-out ability of the salt employed and the consequent pH of the aqueous medium were evaluated by the dyes extraction efficiencies. The results obtained reveal that a proper selection of the IL and salt can lead to the complete extraction of the three dyes studied for the IL-rich phase in a single-step procedure.

After demonstrating the high capacity of ATPS formed by ILs to extract dyes from aqueous phases, it was studied the applicability of pH-triggered reversible ATPS in the selective separation of organic and inorganic dyes (sudan III and pigment blue 27). The reversibility of this type of ATPS was achieved by the manipulation of the speciation of the organic salt used. The results obtained confirm the reversibility behaviour of ATPS by a pH-driven phenomenon, at least for three times, as well as their selective separation capability with both dyes being extracted for opposite phases.

Finally, and after demonstrating the existence of reversible pH-triggered ATPS, mixtures of a polymer and cholinium-based ILs combined with anions derived from carboxylic acids were investigated, foreseeing the search of more benign and biocompatible systems. The reversibility of these systems was achieved with the speciation of the IL anion as a function of the pH. These systems were finally evaluated in what concerns their performance for the extraction and selective separation of dyes (sudan III, pigment blue 27 and pigment 29), and the study revealed that IL-polymer systems are capable of selectively extract organic and inorganic dyes for opposite phases.

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List of symbols

wt % – weight fraction percentage (%);

λ – wavelength (nm);

σ – standard deviation;

Abs – absorbance (dimensionless);

M_w – molecular weight (g·mol^{-1});

K_{OW} – octanol-water partition coefficient (dimensionless);

R^2 – correlation coefficient (dimensionless);

α – ratio between the top weight and the total weight of the mixture (dimensionless);

$[IL]$ – concentration of ionic liquid (wt % or mol·kg^{-1});

$[IL]_{\mathrm{IL}}$ – concentration of ionic liquid in the ionic-liquid-rich phase (wt %);

$[IL]_{\mathrm{Salt}}$ – concentration of ionic liquid in the salt-rich phase (wt %);

$[IL]_{\mathrm{M}}$ – concentration of ionic liquid in the initial mixture (wt %);

$[Salt]$ – concentration of salt (wt % or mol·kg^{-1});

$[Salt]_{\mathrm{IL}}$ – concentration of salt in the ionic-liquid-rich phase (wt %);

$[Salt]_{\mathrm{Salt}}$ – concentration of salt in the salt-rich phase (wt %);

$[Salt]_{\mathrm{M}}$ – concentration of salt in the initial mixture (wt %);

$\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}}$ – absorbance of the dye, at the maximum wavelength, in the ionic-liquid-rich phase;

$\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}}$ – absorbance of the dye, at the maximum wavelength, in the salt-liquid-rich phase;

$EE_{\mathrm{dye}}\%$ – percentage extraction efficiency of each dye (%);

$EE_{\mathrm{CA}}\%$ – percentage extraction efficiency of chloranilic acid (%);

$EE_{\mathrm{IB}}\%$ – percentage extraction efficiency of indigo blue (%);

$EE_{\mathrm{Sud}}\%$ – percentage extraction efficiency of sudan III (%);

$EE_{\mathrm{PB}}\%$ – percentage extraction efficiency of pigment (%);

$EE_{\mathrm{PB27}}\%$ – percentage extraction efficiency of pigment blue 27 (%);

$EE_{\mathrm{PB29}}\%$ – percentage extraction efficiency of pigment blue 29 (%);

K_{dye} – partition coefficient of each dye (dimensionless);

K_{CA} – partition coefficient of chloranilic acid (dimensionless);

K_{IB} – partition coefficient of indigo blue (dimensionless);

K_{Sud} – partition coefficient of sudan III (dimensionless);

List of abbreviations

ATPS – aqueous two-phase system;

IL – ionic liquid;

PG27 – pigment blue 27;

PG29 – pigment blue 29;

PPG – polypropylene glycol;

PPG 400 – polypropylene glycol with a molecular weight of 400 $g \cdot mol^{-1}$;

TL – tie-line;

TLL – tie-line length;

UV – ultraviolet;

VOC – volatile organic compound;

[Ch][Ac] – (2-hydroxyethyl)trimethylammonium (cholinium) acetate;

[Ch][But] – (2-hydroxyethyl)trimethylammonium (cholinium) butanoate;

[Ch]Cl – (2-hydroxyethyl)trimethylammonium (cholinium) chloride;

[Ch][Gly] – (2-hydroxyethyl)trimethylammonium (cholinium) glycolate;

[Ch][Hex] – (2-hydroxyethyl)trimethylammonium (cholinium) hexanoate;

[Ch][Lac] – (2-hydroxyethyl)trimethylammonium (cholinium) lactate;

[Ch][Pro] – (2-hydroxyethyl)trimethylammonium (cholinium) propionate;

$[C_2mim][CF_3SO_3]$ – 1-ethyl-3-methylimidazolium trifluoromethanesulfonate;

$[C_4C_1mim]Cl$ – 1-butyl-2,3-dimethylimidazolium chloride;

$[C_4mpip]Cl$ – 1-butyl-1-methylpiperidinium chloride;

$[C_4mim]Br$ – 1-butyl-3-methylimidazolium bromide;

$[C_4mim]Cl$ – 1-butyl-3-methylimidazolium chloride;

$[C_4mim][N(CN)_2]$ – 1-butyl-3-methylimidazolium dicyanamide;

$[C_4mim][Tos]$ – 1-butyl-3-methylimidazolium tosylate;

$[C_4mim][CF_3SO_3]$ – 1-butyl-3-methylimidazolium trifluoromethanesulfonate;

$[C_4mpy]Cl$ – 1-butyl-3-methylpyridinium chloride;

$[P_{4444}]Br$ – tetrabutylphosphonium bromide;

$[P_{4444}]Cl$ – tetrabutylphosphonium chloride;

$[P_{4441}][CH_3SO_4]$ – tributylmethylphosphonium methylsulfate;

$[P_{i(444)1}][Tos]$ – tri(isobutyl)methylphosphonium tosylate.

1. General introduction

1.1. Scope and objectives

The textile manufacturing is one of the main industries which discharge a heavy load of chemicals during the dying process. As a result, the release of large contents of dyes for the aqueous effluents leads to both environmental and economic drawbacks. Moreover, most of the dyes are carcinogenic, mutagenic, allergenic and toxic, leading therefore to human health concerns [1].

The traditional approaches developed for the removal of synthetic dyes from wastewaters involve their adsorption on inorganic or organic matrices and their decolourization by photocatalysis or by oxidation processes [2]. However, traditional treatment technologies have found to be of high cost and of low efficiency [3]. Foreseeing more benign and cost-efficient techniques for the removal/extraction of dyes from aqueous effluents, aqueous two-phase systems (ATPS) composed of ionic liquids (ILs) were investigated, in this work

As a first approach, more conventional ATPS composed of ILs and salts were evaluated regarding their ability to extract several dyes from aqueous media. For that purpose, the ternary phase diagrams (and respective tie-lines) formed by ILs, water and salt were determined. The extraction capacity of the ATPS formed either with aluminium sulphate or potassium citrate was further addressed through their application to the extraction/removal of three textile dyes, namely sudan III, indigo blue and chloranilic acid. The influence of the IL structural features, the nature and salting-out ability of the salt employed, and the pH of the aqueous medium were also evaluated. The aluminium sulphate salt was chosen because it is already used in water treatment processes [4]. Nevertheless, there are some environmental concerns associated with the use of inorganic salts which tend to be non-biodegradable. Hence, a biodegradable organic salt - potassium citrate - was also studied.

The dynamic change between a homogeneous solution and a two-phase system is a crucial advantage in the separation field. In this context, the next stage of this work involved the investigation of pH-triggered reversible ATPS composed of ILs and organic salts, and their application in the selective separation of textile dyes. A large array of systems by the combination of potassium citrate with different ILs, and at different pH values, was investigated by the determination of their ternary phase diagrams. The reversible IL-based ATPS behaviour was ascertained by the addition of citric acid or potassium hydroxide to an initial ternary mixture at the biphasic region. The reversibility of this type of systems was proven for at least three times. Finally, the reversible capability of this type of ATPS was used for the selective separation of organic and inorganic dyes (sudan III and pigment blue 27) by their migration for opposite phases.

The last stage of this work addressed the study of reversible pH-triggered ATPS composed of cholinium-based ILs and a polymer aiming at finding more benign and biocompatible systems through the addition of the corresponding acid of the anion base composing the IL. After demonstrating their reversibility behaviour, these systems were finally applied in the selective separation of organic and inorganic textile dyes (sudan III, pigment blue 27 and pigment blue 29).

1.2. Textile industry and removal of dyes

Large quantities of dyes are recurrently used in different industries, including the textile, leather tanning, pulp and paper, plastics, food, cosmetic, among others, for the coloration of their related products [1, 5-7]. Unfortunately, and despite all their interest, dyes generally have a synthetic origin and are based on complex aromatic structures which make them stable and resistant to biodegradation [8, 9]. Annually, 1 million tons of dyes are produced worldwide [6], and 10–15 % of them are discharged by the textile industry [10]. The wastewaters of this manufacturing are a considerable source of pollution and it was already demonstrated that they largely affect the photosynthetic activity in aqueous effluents [1, 11]. Furthermore, most of these dyes and their metabolites are toxic and potentially carcinogenic in nature, affecting thus the aquatic biota and the human health [1]. In this context, environmental regulations are becoming stricter in what concerns the removal of dyes from aqueous effluents [11, 12].

Different methods for the removal of dyes from water and wastewaters have been investigated, and these include biological, physical (membrane filtration, adsorption, coagulation, flocculation, precipitation, reverse osmosis, ion exchange, etc) and chemical (oxidation, ozonation, among others) processes [11]. Nevertheless, most of these time consuming techniques display major drawbacks, such as a high-running cost and low-removal efficiency. Consequently, the development of alternative cost-effective removal strategies is a top priority in the treatment of dye-contaminated wastewaters [7, 11].

Liquid–liquid extraction processes usually lead to high effectiveness, technological simplicity and economic nature, and have often been a preferential choice in process engineering [13]. Usually, volatile organic compounds (VOCs) are used in liquid-liquid extractions. However, these compounds have major disadvantages, such as their high volatility and toxicity, as well as their denaturing effects on enzymes and proteins [14]. In this context, ionic liquids (ILs) represent a viable option in liquid-liquid extraction due to their unique properties, and mainly due to their negligible vapour pressure, and high thermal and chemical stabilities [15-17]. In fact, several research groups have studied the liquid-liquid extraction or separation of textile dyes from aqueous solutions using hydrophobic (non-water miscible) ILs [18-20]. Nevertheless, the use of ATPS composed of ILs for this application, as it will be demonstrated here, was not found in literature.

1.3. Ionic liquids (ILs)

ILs are ionic compounds (with a melting temperature below 373 K) that belong to the molten salts group; often, they are denominated by room temperature ILs when they are liquid at temperatures close to room temperature [21]. They are usually constituted by a large and organic cation and an organic or inorganic anion [21]. The low melting temperatures of ILs are typically associated with the lack of an ordered crystalline structure [21] - a main result of weak intermolecular interactions derived from the large size ions and their charge distribution [22, 23] .

The first IL synthesized was ethylammonium nitrate, in 1914 by Paul Walden [24]. Later, in 1934, Charles Graenacher filled the first patent regarding an industrial application of ILs in the preparation of cellulose solutions [25]. During the 2nd World War, new patents involving the use of ILs have appeared, while contemplating mixtures of aluminium chloride (III) and 1-ethylpyridinium bromide for the electrodeposition of aluminium [26, 27]. Despite these findings, only more recently, in 1992, air and water stable ILs were synthetized [28]. Due to their more advantageous features, the study of their possible applications and properties increased significantly in the past 30 years, and as can been seen in Figure 1.1.

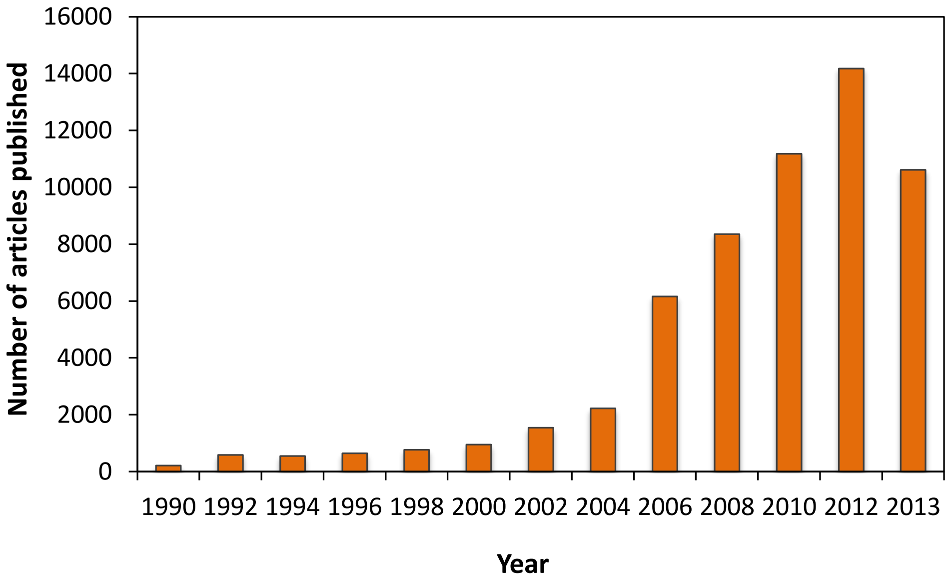

Figure 1.1. Number of papers published *per* year involving ILs. Values from ISI Web of Knowledge in October 17th, 2013.

The ionic nature of ILs is responsible for some of their unique properties, namely a negligible vapour pressure under atmospheric conditions, low flammability, high thermal and chemical stabilities, a large liquid temperature range, improved selectivity, high ionic conductivity, excellent microwave-absorbing ability, and a high solvating aptitude for organic and inorganic compounds [15-17]. All these properties made them improved alternatives to more typical solvents used nowadays in academia or industry, more specifically to VOCs. Currently, ILs are used in a wide range of applications, as in organic chemistry (Suzuki reaction [29]), as well as in new materials chemistry (electrolytes for the electrochemical industry [30]) and chemical reactions [31]. ILs are also applied in inorganic synthesis [32], polymerization [33], as solvents for multiphase biotransformation reactions [34], chromatographic separations [35], mass spectrometry analysis [36], and in batteries and fuel cells investigations [37]. Beyond these applications, ILs have also been used in liquid-liquid extractions of diverse biomolecules [38], metal ions [39], and organic compounds from aqueous solutions [40, 41].

Amongst the large range of ILs that can be synthesized, the most commonly studied are nitrogen-based ILs with their general cation structures presented in Figure 1.2. The cation can be highly complex with alkyl side chains of different length, diverse substitution positions and also additional functional groups [42]. Furthermore, the anion can be of a very different chemical nature, such as halogens, sulphates, cyano-based, fluorinated, etc. Thus, based on the theoretical vast number of cation/anion combinations it is possible to tune their physicochemical properties aiming at designing a specific IL for a target application [42-45], and so, ILs are commonly described as "designer solvents".

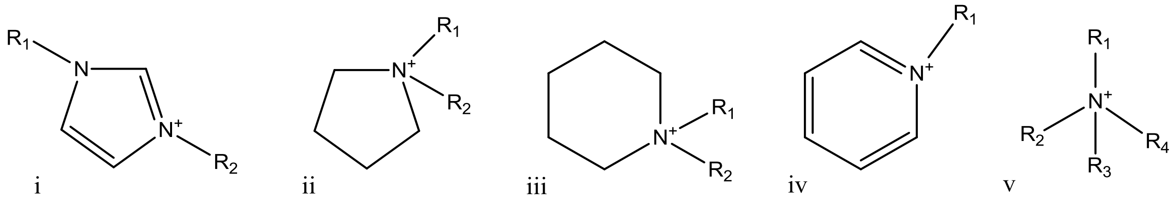

Figure 1.2. Cation structures of nitrogen-based ILs: (i) dialkylimidazolium, (ii) dialkylpyrrolidinium, (iii) dialkylpiperidinium, (iv) alkylpyridinium and (v) tetralkylammonium.

Besides the existence of over six hundreds of common solvents used in industry, most aprotic ILs are an innovative ambient-friendly alternative due to their unique combination of non-volatility and non-flammability [15, 16, 45]. In the environmental field, and with the intent of diminishing the air pollution, ILs are improved alternatives to VOCs due to their negligible vapour pressure. This is the main reason behind the categorization of ILs as "green solvents". However, the fact of displaying a negligible vapour pressure is not enough to assure that these compounds are in fact "green". Properties such as toxicity and biodegradability must be accessed before such assumptions. For instance, even the most hydrophobic ILs have a non-negligible miscibility with water, which can result in the contamination of aqueous streams [46, 47]. In recent years, several studies were conducted to evaluate the toxicity and biodegradability of ILs [46, 48-52], either by the combination of different anions and cations or by changing the alkyl side chain length and number of alkyl groups at the cation ring. One of these studies showed that the ILs toxicity is primordially determined by the cation nature and increases with the increase of the length of the alkyl side chain (increase in hydrophobicity) [47]. Commonly, the anion has a smaller influence on toxicity than the cation, and generally, short cation alkyl chains or more hydrophilic ILs display lower toxicity [49]. The solubility of ILs in water decreases with their hydrophobicity, *i.e.*, the more toxic ILs are those that usually exhibit lower mutual solubilities with water, and hence, their environmental impact in aquatic streams is somewhat minimized [46]. On the other hand, the ILs typically used to form ATPS, as stated below, tend to be completely miscible with water or hydrophilic, and thus, of lower toxicity.

1.4. Extraction of molecules using aqueous two-phase systems (ATPS)

Conventional techniques used for product recovery usually lead to low yields and require high energetic and chemical consumptions. To overcome these major drawbacks, there have been considerable efforts forecasting the development of sustainable and cost-effective separation techniques. In addition to the well-established chromatographic techniques, liquid–liquid extractions offer several advantages, namely their technological simplicity and low cost, as well as the capability to provide high yields, improved purification factors, enhanced selectivity and a good combination between the recovery and purification steps [14, 53, 54]. Aiming at avoiding the use of organic solvents in liquid-liquid extraction, in 1958, Albertson introduced the ATPS concept for the separation of (bio)molecules by their partitioning between two liquid aqueous phases [55]. ATPS have shown to be an alternative, efficient, and clean approach for the separation and purification of a broad array of (bio)molecules [56]. ATPS consist of two aqueous-rich phases typically formed by polymer/polymer, polymer/ salt, or salt/salt combinations [56]. The basis of separation of (bio)molecules in ATPS is a direct result of their selective distribution between the two distinct aqueous phases [57]. On the whole, both phases are composed of approximately 70-90 wt % of water, which means that (bio)molecules are not easily denatured, constituting therefore an important advantage when the goal is to extract proteins and/or enzymes [58, 59]. Moreover, a high extractive performance can be achieved by the manipulation of the affinity of the specific compound for each of the aqueous-rich phases.

Besides the typical and largely studied polymer-polymer and polymer-salt ATPS [55], in recent years, Gutowski et al. [60] demonstrated that ATPS can also be formed by the addition of inorganic salts to aqueous solutions of hydrophilic ILs (imidazolium-based). These IL-rich systems were proposed as viable alternatives to polymeric ones with a set of important advantages: low viscosity, quick phase separation, and high and tailored extraction efficiency [56].

In the past decade, a large number of studies regarding the phase behaviour of ternary systems composed of ILs + water + inorganic salts has been reported [56, 58, 61-66]. One of these studies showed that the influence of the inorganic ions in the liquid-liquid demixing seems to be well described by the Hofmeister series (ions classification based on their salting-out/-in ability) [67]. Generally, it is accepted that the inorganic/organic salts of high charge density lead to the salting-out of the IL for a second liquid and aqueous phase [67]. In addition, it was also demonstrated that IL-based ATPS can be formed either with carbohydrates, polymers or amino acids [56]. Despite the determination of the ternary phase diagrams of IL-based ATPS, some researchers evaluated the potential of these systems for the extraction of the most distinct added-value compounds and/or biomolecules [56]. The extractive potential of biomolecules using IL-based ATPS was already shown for testosterone and epitestosterone [63], alkaloids [68], antibiotics [64], amino acids [61, 62], proteins [69], aromatic and phenolic compounds [70, 71], among others. In some of these works it was possible to demonstrate that a proper choice of the IL and salting-out agent could lead to the complete extraction of the target solute and concentration factors up to 100 times [68, 72].

ATPS were mostly studied at a laboratory scale, but their scale-up was already confirmed with a number of proteins being already purified by this process at an industrial level [57].

2. Extraction of dyes using IL-based ATPS

2.1. Introduction

Based on the tailoring ability of ILs, either for the solvation of a wide array of compounds or to extract the most diverse biomolecules from aqueous media [73], in this work, IL-based ATPS were studied to extract and remove dyes typically discharged by the textile industry foreseeing their potential application in the treatment of aqueous effluents. Recent investigations reported the use of ILs in the extraction of dyes from water-rich phases [3, 18-20, 74-76]. Nevertheless, in these studies, hydrophobic ILs, *i.e.* non water-miscible ILs at temperatures close to room temperature, were employed [3, 18-20, 74-76]. Furthermore, most of the investigated hydrophobic ILs contain fluorinated ions which are environmentally less benign and some of them even tend to be unstable in aqueous media (leading to the release of fluoridic acid [77]). Fluorinated ILs also tend to be more expensive than halogen-based counterparts. The toxicity of ILs mainly depends on their hydrophobicity and hydrophilic ILs are recognized as more environmentally friendly compounds than the hydrophobic ones [78]. Thus, IL-based ATPS or aqueous systems composed of hydrophilic ILs should constitute a "greener" and more benign option since they are also mainly composed of water (*ca.* 40-50 wt % in the overall system) [56]. On the other hand, IL-based ATPS can lead to complete extractions and high concentration factors of a variety of compounds by a proper tailoring of the IL chemical structure and modification of the salting-out agent [56, 68, 72].

To assess the potential of IL-based ATPS to extract/remove textile dyes from aqueous effluents, different ATPS composed of several ILs and two distinct salts were investigated. The selected combinations of IL/salt allow the evaluation of the influence of the IL structural features, the nature and salting-out ability of the salt employed and the effect of the pH of the aqueous medium through the extraction performance of the studied ATPS. The partition coefficients and extraction efficiencies of three current textile dyes, sudan III, indigo blue and chloranilic acid (Figure 2.1) for the IL-rich phase were experimentally determined at 298 K. The main physicochemical properties of the dyes investigated are listed in Table 2.1.

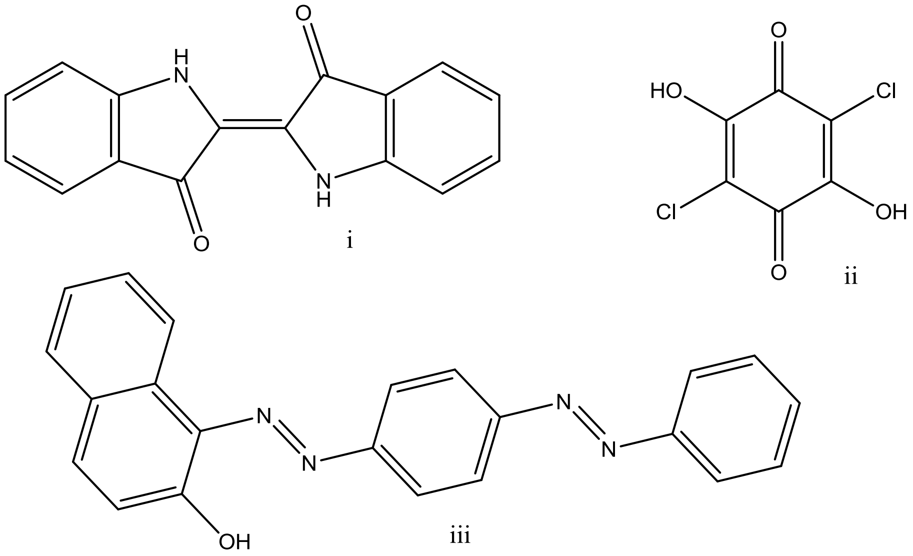

Figure 2.1. Chemical structures of the dyes studied: (i) Indigo blue; (ii) chloranilic acid and (iii) sudan III.

Table 2.1. Thermophysical properties of the investigated dyes [79].

	Chloranilic Acid	Indigo Blue	Sudan III
Molecular weight ($g \cdot mol^{-1}$)	208.98	262.26	352.39
Solubility in water at 298 K	Moderate	Insoluble	Insoluble
$\text{Log}(K_{OW})$	0.76	2.65	7.74
pK_{a1}/pK_{a2} at 298 K	5.22/9.41	8.18/8.44	0.22/11.34

2.2. Experimental section

2.2.1. Chemicals

The ILs studied in this work were: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[C_2mim][CF_3SO_3]$ (purity of 99 wt %); 1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[C_4mim][CF_3SO_3]$ (purity of 99 wt %); 1-butyl-3-methylimidazolium tosylate, $[C_4mim][Tos]$ (purity of 98 wt %); 1-butyl-3-methylimidazolium dicyanamide, $[C_4mim][N(CN)_2]$ (purity > 98 wt %); tetrabutylphosphonium bromide, $[P_{4444}]Br$ (purity of 95 wt %); tributylmethylphosphonium methylsulfate, $[P_{4441}][CH_3SO_4]$ (purity of 96-98 wt %); tri(isobutyl)methylphosphonium tosylate, $[P_{i(444)1}][Tos]$ (purity of 98 wt %); and tetrabutylphosphonium chloride, $[P_{4444}]Cl$ (purity of 97 wt %). The chemical structures of the investigated ILs are depicted in Figure 2.2. The phosphonium-based ILs were kindly supplied by Cytec Industries Inc., whereas imidazolium-based ILs were purchased from Iolitec. Before use, all

ILs were purified and dried for a minimum of 24 h, under constant agitation, at moderate temperature (≈ 353 K) and under vacuum (to reduce their volatile impurities to negligible values). After this step, the purity of each IL was also confirmed by ^{1}H and ^{13}C NMR spectra and found to be in accordance with the purity levels given by the suppliers.

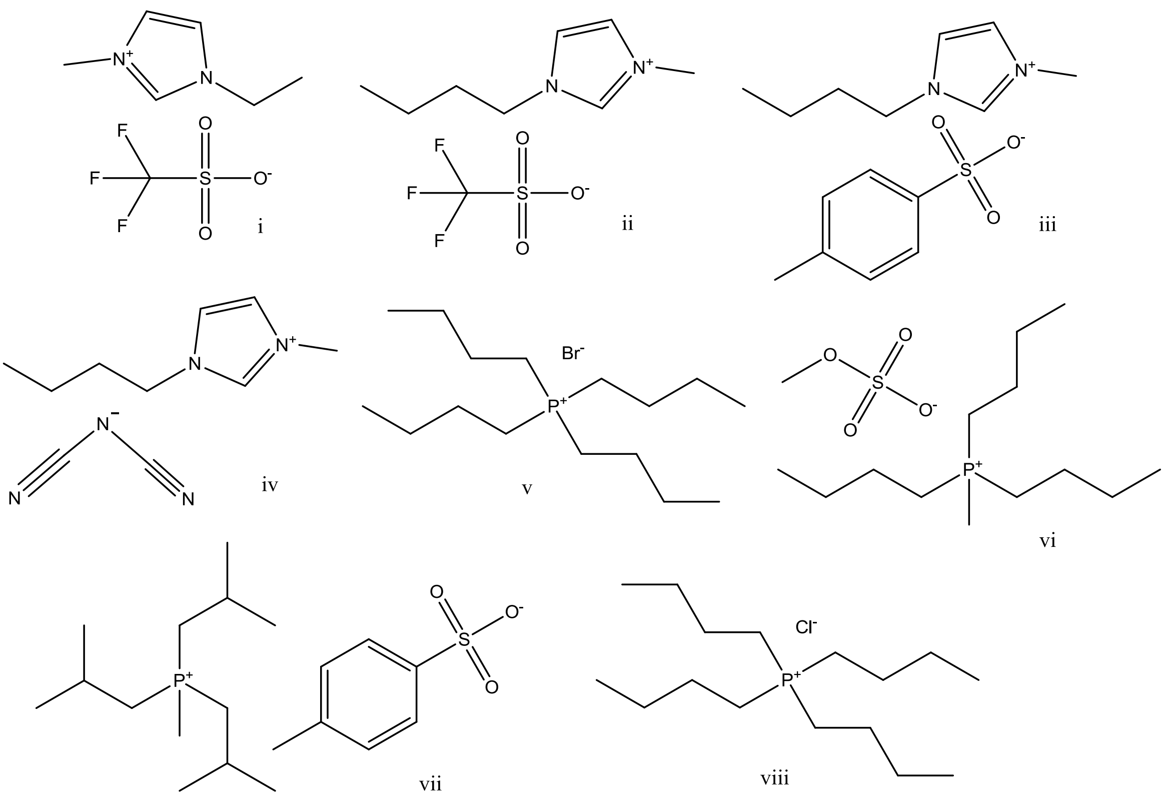

Figure 2.2. Chemical structures of the ILs investigated: (i) [C$_2$mim][CF$_3$SO$_3$]; (ii) [C$_4$mim][CF$_3$SO$_3$]; (iii) [C$_4$mim][Tos]; (iv) [C$_4$mim][N(CN)$_2$]; (v) [P$_{4444}$]Br; (vi) [P$_{4441}$][CH$_3$SO$_4$]; (vii) [P$_{i(444)1}$][Tos] and (viii) [P$_{4444}$]Cl.

The salts used were the inorganic salt aluminium sulphate, Al$_2$(SO$_4$)$_3$ (≥ 98.0 wt % pure), and the organic salt potassium citrate (tribasic monohydrated), K$_3$C$_6$H$_5$O$_7$·H$_2$O (≥ 99 wt % pure), acquired from Himedia and from Sigma–Aldrich, respectively.

The water employed was ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment.

The dyes used were sudan III and chloranilic acid (> 99 wt % pure), both from Merck, and indigo blue (> 95 wt % pure) acquired from Sigma-Aldrich.

2.2.2. Experimental procedure

2.2.2.1. Phase diagrams and tie-lines (TLs)

Some of the ATPS used here for the extraction studies were prepared based on compositions falling within the biphasic region and assessed from the respective ternary phase diagrams already reported in the literature [80, 81]. Nonetheless, novel ternary phase diagrams were also determined in this work to expand the study on the ILs and salts influence on the extraction efficiencies of the three dyes. The ILs investigated for the creation of ATPS comprise imidazolium- and phosphonium-based compounds whereas the salts used include an inorganic and an organic salt, $Al_2(SO_4)_3$ and $K_3C_6H_5O_7$, respectively. The novel ternary phase diagrams (IL + salt + water) were determined at 298 K and atmospheric pressure with the organic salt for the following ILs: $[C_2mim][CF_3SO_3]$, $[C_4mim][Tos]$, $[P_{4444}]Br$, $[P_{4441}][CH_3SO_4]$ and $[P_{i(444)1}][Tos]$.

The binodal curves of the ternary phase diagrams were determined through the cloud point titration method at (298 ± 1) K and atmospheric pressure [82, 83]. Aqueous solutions of $K_3C_6H_5O_7$ and aqueous solutions of the different hydrophilic ILs at variable concentrations were prepared gravimetrically, and used for the determination of the binodal curves. Drop-wise addition of the aqueous organic salt solution to each IL aqueous solution, or vice-versa, was carried out until the detection of a cloudy solution (biphasic region), followed by the drop-wise addition of ultra-pure water until the detection of a clear and limpid solution (monophasic region). The ternary system compositions were determined by the weight quantification of all components added within $\pm 10^{-4}$ g (using an analytical balance, Mettler Toledo Excellence XS205 DualRange).

The tie-lines (TLs), which allow the inspection on the coexisting phases' compositions, were determined by a gravimetric method originally described by Merchuk et al. [84]. In this method, a mixture at the biphasic region was gravimetrically prepared (IL + salt + water) within $\pm 10^{-4}$ g, vigorously stirred, and left for at least 12 h at (298 ± 1) K to reach the complete separation and equilibration of the coexisting phases. After separation, both top and bottom phases were weighed. The experimental binodal curves were fitted using Equation 1 [84],

$$[\mathrm{IL}] = Aexp[(B[\mathrm{Salt}]^{0.5}) - (C[\mathrm{Salt}]^{3})] \tag{1}$$

where $[\mathrm{IL}]$ and $[\mathrm{Salt}]$ are the IL and salt weight fractions percentages, respectively, and A, B and C are fitted constants obtained by least-squares regression.

Each individual TL was determined by a weight balance approach through the relationship between the top weight phase composition and the overall system composition. For the determination of TLs the following system of four equations (Equations 2 to 5) was used to estimate ($[\mathrm{IL}]_{\mathrm{IL}}$, $[\mathrm{IL}]_{\mathrm{Salt}}$, $[\mathrm{Salt}]_{\mathrm{IL}}$ and $[\mathrm{Salt}]_{\mathrm{Salt}}$) [84]:

$$[\mathrm{IL}]_{\mathrm{IL}} = Aexp\left[\left(B[\mathrm{Salt}]_{\mathrm{IL}}^{0.5}\right) - \left(C[\mathrm{Salt}]_{\mathrm{IL}}^{3}\right)\right] \tag{2}$$

$$[\mathrm{IL}]_{\mathrm{Salt}} = Aexp\left[\left(B[\mathrm{Salt}]_{\mathrm{Salt}}^{0.5}\right) - \left(C[\mathrm{Salt}]_{\mathrm{Salt}}^{3}\right)\right] \tag{3}$$

$$[\mathrm{IL}]_{\mathrm{IL}} = \frac{[\mathrm{IL}]_{\mathrm{M}}}{\alpha} - \left(\frac{1-\alpha}{\alpha}\right)[\mathrm{IL}]_{\mathrm{Salt}} \tag{4}$$

$$[\mathrm{Salt}]_{\mathrm{IL}} = \frac{[\mathrm{Salt}]_{\mathrm{M}}}{\alpha} - \left(\frac{1-\alpha}{\alpha}\right)[\mathrm{Salt}]_{\mathrm{Salt}} \tag{5}$$

where the subscripts IL, Salt designate the top and bottom phases, respectively, and M is the initial mixture composition. The parameter α is the ratio between the top weight and the total weight of the mixture. The solution of this system provides the concentration (wt %) of the IL and salt in the top and bottom phases, and thus the, TLs can be easily represented.

For the calculation of the tie-line lengths (TLLs) Equation 6 was applied.

$$\mathrm{TLL} = \sqrt{([\mathrm{Salt}]_{\mathrm{IL}} - [\mathrm{Salt}]_{\mathrm{Salt}})^2 \mp ([\mathrm{IL}]_{\mathrm{IL}} - [\mathrm{IL}]_{\mathrm{Salt}})^2} \tag{6}$$

2.2.2.2. pH measurements

The pH values (± 0.02) of both the IL-rich and salt-rich aqueous phases were measured at (298 ± 1) K using a Mettler Toledo S47 SevenMulti$^{\mathrm{TM}}$ dual meter pH/conductivity equipment.

2.2.2.3. Partition coefficients and extraction efficiencies of the dyes

The ternary mixtures compositions used in the partitioning experiments were chosen based on the phase diagrams determined before or based on literature data [80, 81]. A ternary mixture with a common composition, and within the biphasic region, was prepared with 10 wt % of salt, 45 wt % of IL and 45 wt % of water (Figure 2.3). Only for the system composed of $[P_{4441}][CH_3SO_4]$ and the citrate-based salt a different composition (19 wt % of salt, 35 wt % of IL and 46 wt % of water) was used due to the smaller biphasic region obtained with this IL. In each system, a small amount of dye, ≈ 0.30 mg, was added to glass tubes containing the

Figure 2.3. Chloranilic acid extraction with an ATPS formed by IL + $K_3C_6H_5O_7$ + H_2O.

ternary compositions with a total weight of 5 g. Each mixture was vigorously stirred and left to equilibrate for at least 12 h, at (298 ± 1) K, to achieve a complete dye partitioning between the two phases.

In the studied ATPS, the top phase corresponds to the IL-rich aqueous phase, while the bottom phase is mainly composed of salt and water. The only exception was observed with the [C_4mim][CF_3SO_3]-based systems [80, 81] and with the system composed of [C_2mim][CF_3SO_3] and the organic salt. The higher density of the fluorinated ILs is the main reason behind this inversion of the phases' densities [85].

After a careful separation of both phases, the quantification of each dye in the two phases was carried by UV-spectroscopy, using a Shimadzu UV-1700, Pharma-Spec Spectrometer, at a wavelength of 348 nm for sudan III, 335 nm for indigo blue and 321 nm for chloranilic acid. The maximum wavelengths observed here are in close agreement with those reported in literature [86, 87]. At least three individual experiments were performed in order to determine the average in the partition coefficient and extraction efficiency, as well as the respective standard deviations. The interference of the salts and ILs with the quantification method was also ascertained and blank control samples were always used.

The partition coefficient of the studied dyes, K_{Sud} for sudan III, K_{IB} for indigo blue, and K_{CA} for chloranilic acid, are defined as the ratio of the concentration of each dye in the IL-rich to that in the salt-rich aqueous phase according to Equation 7,

$$K_{\mathrm{Dye}} = \frac{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}}}{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}}} \tag{7}$$

where $\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}}$ and $\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}}$ are the absorbance of each dye at the maximum wavelength, adjusted by the respective dilution factor, in the IL-rich and in the salt-rich aqueous phases, respectively.

The percentage extraction efficiency of each dye, $EE_{\mathrm{Sud}}\%$ for sudan III, $EE_{\mathrm{IB}}\%$ for indigo blue and $EE_{\mathrm{CA}}\%$ for chloranilic acid, is defined as the percentage ratio between the amount of dye in the IL-rich aqueous phase to that in the total mixture, and is defined according to Equation 8,

$$EE_{\mathrm{Dye}}\% = \frac{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times w_{\mathrm{IL}}}{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times w_{\mathrm{IL}} + \mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}} \times w_{\mathrm{Salt}}} \times 100 \tag{8}$$

where $w_{\mathrm{IL}}$and w_{Salt} are the weight of the IL-rich phase and the weight of the salt-rich phase, respectively.

2.3. Results and discussion

The development of more efficient, economic and environmentally-friendly processes to remove and recover dyes from wastewaters is highly important. In this work, the choice of $Al_2(SO_4)_3$ was due to its strong salting-out aptitude [88], and its current use in water treatment processes [4]. However, common inorganic salts lead to environmental concerns due to their high charge density and formation of aqueous solutions of high ionic strength [81]. Since organic salts tend to be biodegradable and nontoxic [89-91] an organic salt, $K_3C_6H_5O_7$, was also tested.

The new phase diagrams for the ILs [C_2mim][CF_3SO_3], [C_4mim][Tos], [P_{4444}]Br, [P_{4441}][CH_3SO_4] and [$P_{i(444)1}$][Tos] combined with the organic salt are illustrated in Figure 2.4. The ternary phase diagrams previously reported for [P_{4444}]Cl, [C_4mim][CF_3SO_3] and [C_4mim][$N(CN)_2$] with $K_3C_6H_5O_7$ [81] are also included for comparison purposes. In addition, the phase diagrams for the salt $Al_2(SO_4)_3$ [80] are also shown in Figure 2.4. The detailed experimental weight fraction data of each phase diagram are presented in Appendix A (Table A.1.1. to Table A.1.4).

From the analysis of Figure 2.4, it is visible that the solubility curves show a strong dependency on the IL chemical nature. The solubility curves give the minimum weight fraction composition to form a specific ATPS and separate the monophasic from the biphasic region. The larger the monophasic region the higher is the amount of IL and/or salt needed to induce the ATPS formation. From the gathered data, for a fixed concentration of 10 wt % of salt, the tendency of the ILs to form ATPS by the addition of $Al_2(SO_4)_3$ follows the order: [P_{4444}]Br > [C_4mim][CF_3SO_3] > [P_{4444}]Cl ≈ [P_{4441}][CH_3SO_4] > [$P_{i(444)1}$][Tos] > [C_4mim][$N(CN)_2$] > [C_2mim][CF_3SO_3] ≈ [C_4mim][Tos]. At the same concentration of the organic salt, the ability of the ILs to undergo liquid-liquid demixing follows the rank: [C_4mim][CF_3SO_3] > [P_{4444}]Br > [C_4mim][$N(CN)_2$] > [P_{4444}]Cl ≈ [$P_{i(444)1}$][Tos] > [C_2mim][CF_3SO_3] ≈ [C_4mim][Tos]. Albeit small differences in the ranking order of the ILs are observed it seems that, in general, ILs tend to closely follow the same order for a wide variety of salts. These small differences can be derived from purity levels of the IL or mainly from pH-derived effects [85, 92].

In general, the higher the hydrophobicity of the IL, the higher is the ability of such IL to undergo liquid-liquid demixing in the presence of a given salt. An increase in the cation/anion alkyl side chain length leads to an increase in the IL hydrophobicity and thus to a higher phase separation ability. This trend can be seen with the ILs pair [C_2mim][CF_3SO_3]/[C_4mim][CF_3SO_3].

Furthermore, the four aliphatic chains present in phosphonium-based ILs also confer a higher hydrophobicity to the IL and a consequent higher ability for phase separation. On the other hand, it was already demonstrated that the ability of ILs to create ATPS is largely dependent on their hydrogen-bond basicity values [71]. The hydrogen-bond basicity is a measure of the ability of the solvent to accept a proton (or donate an electron pair) in a solute-solvent hydrogen-bond. From the data presented in Figure 2.4 (the respective phase diagrams in molality units are presented in Appendix B in Figure B.1.1) it can be seen that a decrease in the hydrogen-bond basicity of the IL anion promotes the formation of ATPS, and in agreement with previous literature data [71]. Therefore the triflate-based ILs which present a lower ability to hydrogen-bond with water are more prone to be salted-out by conventional salts in aqueous media.

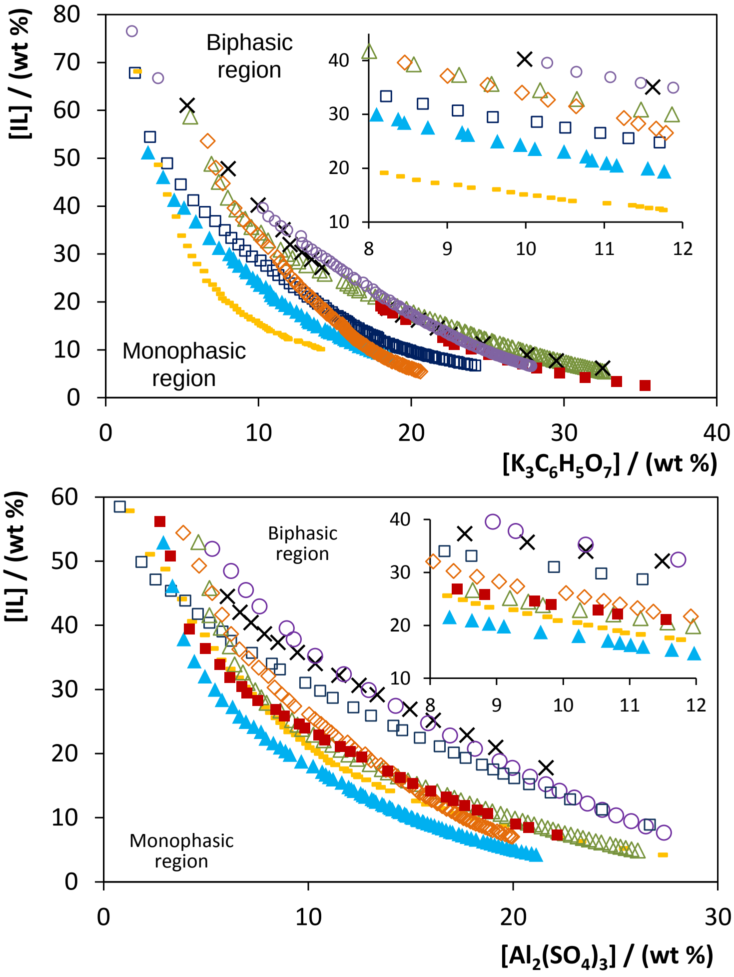

Figure 2.4. Ternary phase diagrams for systems composed of IL + salt + water at 298 K and atmospheric pressure: (×) [C_2mim][CF_3SO_3], (–) [C_4mim][CF_3SO_3], (☐) [C_4mim][N(CN)$_2$], (○) [C_4mim][Tos], (△) [P_{4444}]Cl, (▲) [P_{4444}]Br, (■) [P_{4441}][CH_3SO_4] and (◇) [$P_{i(444)1}$][Tos].

For the studied systems, the experimental binodal data were further fitted by the empirical relationship described by Equation 1 [84]. The regression parameters were estimated by least-squares regression, and their values and corresponding standard deviations (*σ*) are provided in Table 2.2. In general, good correlation coefficients were obtained for all systems, indicating that these fittings can be used to predict data in a given region of the phase diagram where no experimental results are available. The experimental TLs, along with their respective length (TLL), are reported in Tables 2.3 and 2.4, for the citrate- and sulphate-based systems, respectively, as well as the initial composition of each system used for the extraction studies and respective pH values.

Table 2.2. Correlation parameters used to describe the experimental binodal data by Equation 1.

IL + $K_3C_6H_5O_7$ + water	$A \pm \sigma$	$B \pm \sigma$	$10^5(C \pm \sigma)$	R^2
$[P_{4444}]Br$	108.6 ± 2.0	-0.442 ± 0.008	13.5 ± 0.46	0.9987
$[P_{4441}][CH_3SO_4]$	480.0 ± 73.3	-0.733 ± 0.039	1.99 ± 0.02	0.9993
$[P_{i(444)1}][Tos]$	223.7 ± 8.3	-0.550 ± 0.013	15.0 ± 0.40	0.9982
$[C_2mim][CF_3SO_3]$	207.6 ± 8.7	-0.522 ± 0.015	2.07 ± 0.29	0.9980
$[C_4mim][Tos]$	119.8 ± 0.6	-0.330 ± 0.002	5.55 ± 0.04	0.9994

Table 2.3. Experimental data for TLs and TLLs of IL + $K_3C_6H_5O_7$ ATPS, initial mixture compositions ($[IL]_M$ and $[salt]_M$), and pH values of the coexisting phases.

IL	Weight fraction composition / wt %								TLL
	$[IL]_{IL}$	$[Salt]_{IL}$	pH_{IL}	$[IL]_M$	$[Salt]_M$	$[IL]_{Salt}$	$[Salt]_{Salt}$	pH_{Salt}	
$[P_{4444}]Cl$	52.07	5.95	8.19	44.56	10.16	6.86	31.31	7.87	51.83
$[P_{4444}]Br$	84.16	0.33	7.44	44.69	10.48	4.19	20.90	7.01	82.57
$[P_{4441}][CH_3SO_4]$	60.26	7.94	7.01	34.71	19.01	3.75	32.42	6.85	61.59
$[P_{i(444)1}][Tos]$	58.55	5.69	5.86	44.96	10.08	1.91	23.97	5.85	59.51
$[C_2mim][CF_3SO_3]$	57.10	6.07	7.11	44.73	10.03	20.29	17.87	6.87	38.65
$[C_4mim][CF_3SO_3]$	81.75	1.28	7.30	44.51	10.56	20.52	4.48	7.16	79.63
$[C_4mim][N(CN)_2]$	63.19	2.18	7.28	44.47	10.43	2.23	29.05	7.10	66.62
$[C_4mim][Tos]$	55.78	5.26	8.24	44.75	9.94	9.96	24.78	7.92	49.81

Table 2.4. Experimental data for TLs and TLLs of IL + $Al_2(SO_4)_3$ ATPS, initial mixture compositions ($[IL]_M$ and $[Salt]_M$), and pH values of the coexisting phases.

IL	Weight fraction composition / wt %								TLL
	$[IL]_{IL}$	$[Salt]_{IL}$	pH_{IL}	$[IL]_M$	$[Salt]_M$	$[IL]_{Salt}$	$[Salt]_{Salt}$	pH_{Salt}	
$[P_{4444}]Cl$	55.44	2.9	1.41	44.85	10.00	1.01	39.42	1.30	65.55
$[P_{4444}]Br$	63.40	1.69	1.41	44.94	9.97	1.37	29.51	1.26	67.98
$[P_{4441}][CH_3SO_4]$	58.34	2.21	1.49	44.95	9.97	2.81	34.38	1.35	64.18
$[P_{i(444)1}][Tos]$	56.15	3.53	1.42	45.16	9.93	0.10	36.17	1.385	64.86
$[C_2mim][CF_3SO_3]$	56.80	2.56	1.93	44.96	9.96	6.26	34.19	1.76	59.62
$[C_4mim][CF_3SO_3]$	73.51	0.47	1.95	44.97	9.96	4.49	23.43	1.90	72.74
$[C_4mim][N(CN)_2]$	58.66	0.69	4.76	45.09	9.94	40.04	0.95	4.65	69.85
$[C_4mim][Tos]$	53.57	4.84	3.16	45.05	10.63	0.82	40.67	3.00	63.77

After the complete characterization of the studied ATPS by the determination of their phase diagrams, TLs and TLLs, they were further evaluated in their ability to extract textile dyes. Figure 2.5 to Figure 2.7 depict the results obtained for the partition coefficients of the three dyes in the several IL-based ATPS at 298 K. It should be noted that when *K* equals ∞ it means that the complete extraction was reached (no detection of dye in the salt-rich phase).

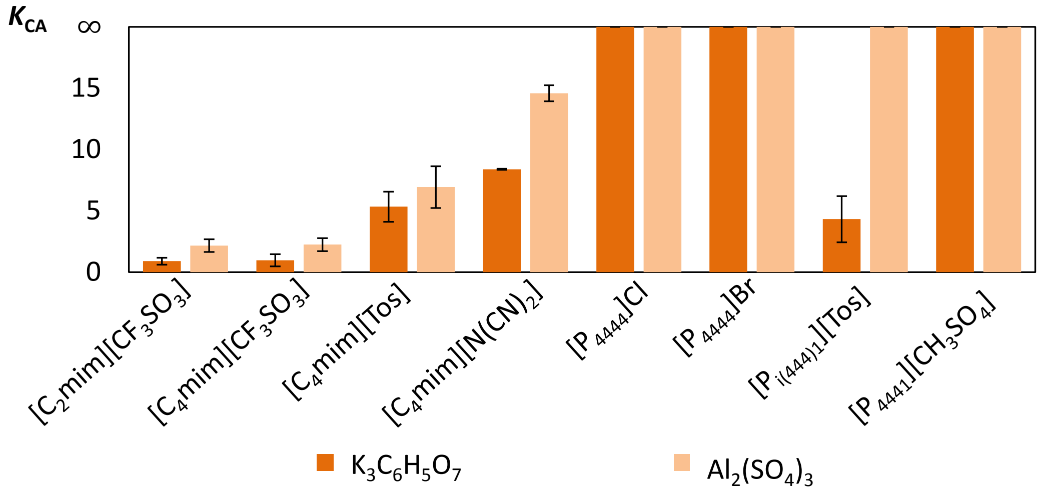

Figure 2.5. Partition coefficients of choranilic acid in the studied ATPS at 298 K.

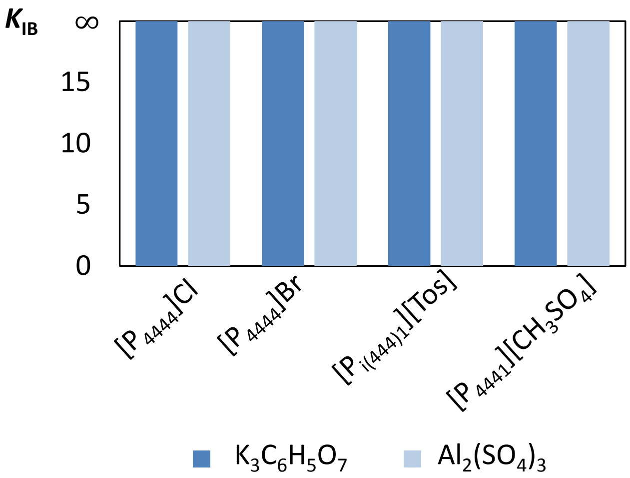

Figure 2.6. Partition coefficients of indigo blue in the studied ATPS at 298 K.

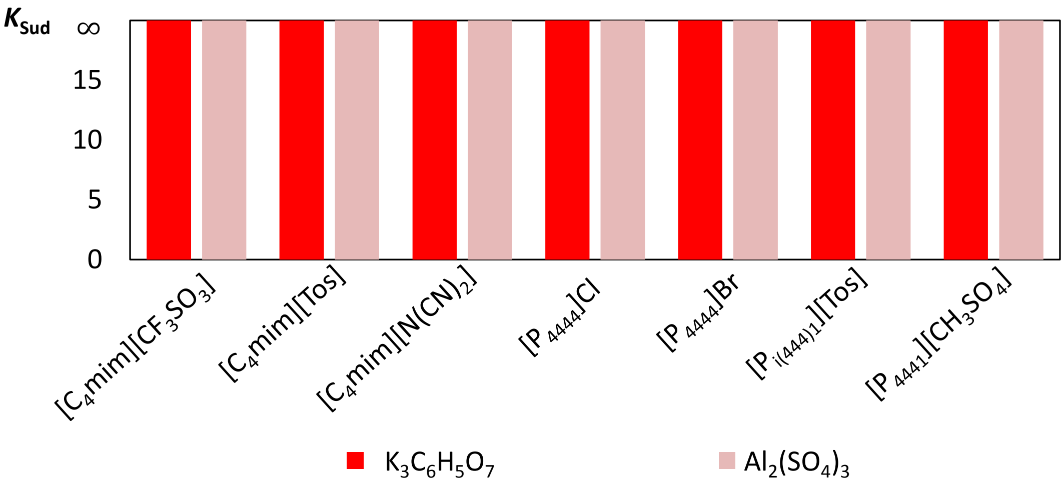

Figure 2.7. Partition coefficients of sudan III in the studied ATPS at 298 K.

Outstanding results were obtained for sudan III and indigo blue with the complete extraction of the dyes for the IL-rich phase either by using the organic or the inorganic salt. Only chloranilic acid displays a partitioning trend more dependent on the IL nature with partition coefficient values ranging between 0.89 to the complete extraction, for the organic salt, and from 2.17 to the complete extraction, with the inorganic salt. Besides the salting-out ability of the two salts, this behaviour is also a consequence of the pH of the aqueous media. The pH values of both phases in each ATPS are given in Tables 2.3 and 2.4. The pH values of the systems composed of IL + $K_3C_6H_5O_7$ + H_2O are in the neutral/alkaline region (pH ≈ 6 - 8) whereas the systems composed of IL + $Al_2(SO_4)_3$ + H_2O are more acidic (pH ≈ 1 - 5). The main differences observed in the pH values of the aqueous solutions are a direct consequence of the speciation of the salts investigated. At pH values ranging from 1 to 8, the indigo blue and sudan III are predominantly in a non-charged form - the respective dissociation curves are shown in Appendix B (Figure B.1.2, B.1.3 and B.1.4). However, the negatively charged form of chloranilic acid occurs at lower pH values (pK_{a1} = 5.22) [79]. Thus, chloranilic acid is the most affected dye by the pH variations and is negatively charged in the systems composed of the organic salt. This dye speciation can explain the lower partition coefficients observed with chloranilic acid for the IL-rich phase with the ATPS based on potassium citrate. In fact, and as previously confirmed with other molecules, charged species tend to migrate to less hydrophobic and more ionic and hydrated rich phases [38, 93]. However, lower partition coefficients for chloranilic acid were also observed in the aluminium-based ATPS where the pH values are below the dye pK_{a1}. Therefore, besides the pH effect, the IL chemical structure is also playing a fundamental role. In general, the more hydrophobic phosphonium-based ILs lead to higher partition coefficients of chloranilic acid when compared with the imidazolium-based counterparts. This trend is a main consequence of the low affinity of the organic and more hydrophobic dyes for water and their preferential partitioning to organic-rich phases. The reported log(K_{OW}) (octanol-water partition coefficient) of chloranilic acid, indigo blue and sudan III are 0.76 [79], 2.65 [79] and 7.47 [79], respectively. Thus, the lower partition coefficient obtained with chloranilic acid seems to be further justified.

Amongst the studied ILs the phosphonium-based ILs are in general more efficient in the extraction/removal of textile dyes from aqueous media. Indeed, the imidazolium-based ILs are not able to extract indigo blue - the reason why the respective data are not presented in Figure 2.6. With the imidazolium-based ATPS it was always observed the precipitated dye at the interface, while phosphonium-based ILs completely remove and dissolve the dye from the opposite saline aqueous phase. This pattern reveals that indigo blue cannot be dissolved by any of the aqueous phases of the imidazolium-based systems. Nevertheless, it should be highlighted that this precipitation pattern can also be seen as treatment method itself for the removal of dyes from aqueous media and as previously attempted by other authors [94].

It should be remarked that both salts are strong salting-out agents according to the Hofmeister series (high-charge density anions with an improved ability to create hydration complexes) [47] and are able to further induce the partitioning of the dyes to the IL-rich phase. Depending on the purpose and specific application either an inorganic salt used in water-treatment processes or a biodegradable and less toxic organic salt can be chosen.

For an easier interpretation of the partitioning data and to ascertain on the potential of the investigated ATPS for scale-up, the extraction efficiencies of the three dyes in the investigated systems are depicted in Figure 2.8 to Figure 2.10. It should be noted that a high partition coefficient does not necessarily corresponds to high extraction efficiency, or *vice-versa,* since the first is dependent on the volume/weight of the coexisting phases. The percentage extraction efficiencies (*EE*%) are defined as the percentage ratio between the amount of dye in the ionic-liquid-rich phase to that in the total mixture.

The extraction efficiencies of the three dyes, in all ATPS investigated, are always higher than 50 %. Moreover, in most of the systems evaluated, the extraction efficiencies reach 100 % (complete extraction in a single-step procedure).

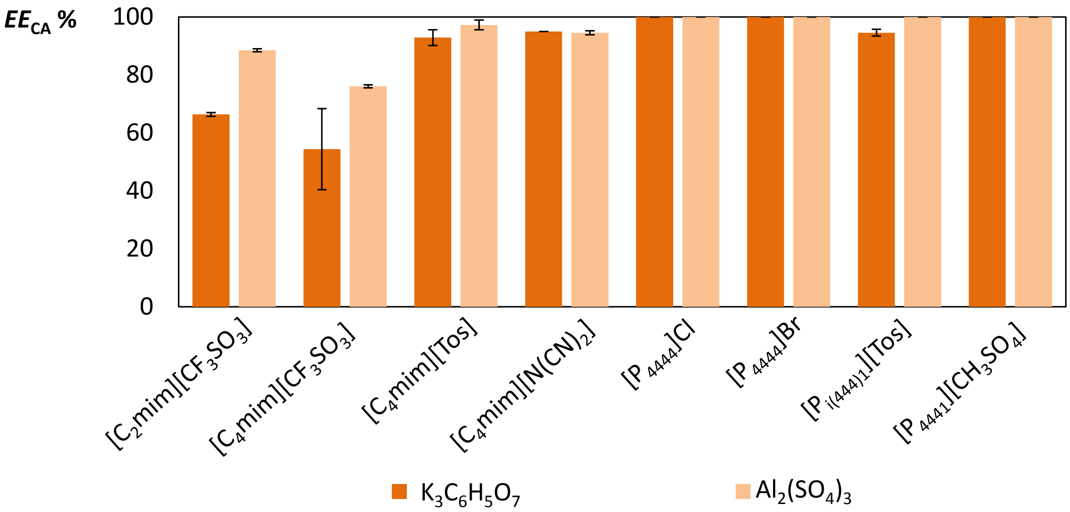

Figure 2.8. Percentage extraction efficiencies of chloranilic acid, EE_{CA}%, in different ATPS at 298 K.

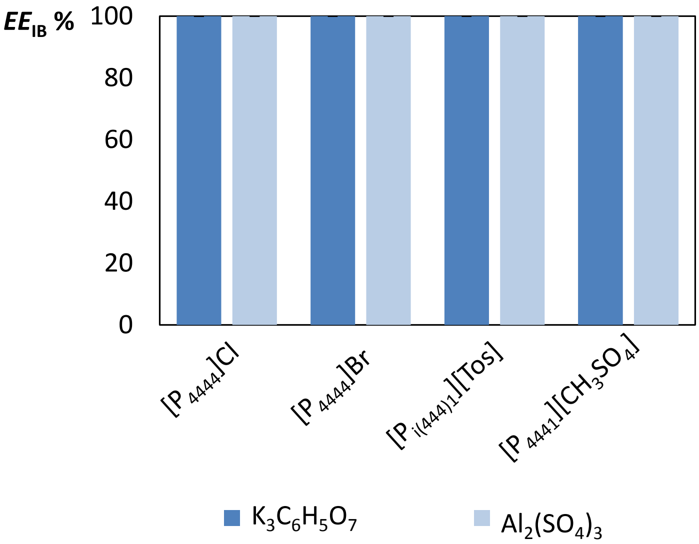

Figure 2.9. Percentage extraction efficiencies of indigo blue, EE_{IB}%, in different ATPS at 298 K.

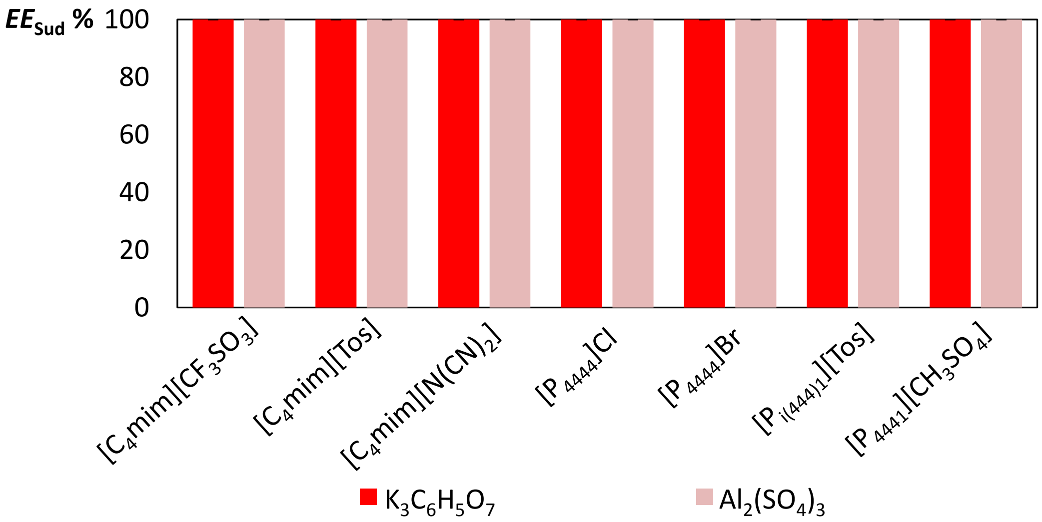

Figure 2.10. Percentage extraction efficiencies of sudan III, EE_{sud}%, in different ATPS at 298 K.

To the best of our knowledge, we report here, for the first time, the remarkable ability of IL-based ATPS to extract textile dyes in a single-step procedure with extraction efficiencies up to 100 %. Although some data regarding the extraction of dyes are already reported in the literature [3, 18-20, 74] with extraction efficiencies ranging from 60-98 % for the IL-rich phase, the extraction efficiencies achieved here are larger and were attained with aqueous systems. It should be further remarked that the higher extraction efficiencies previously reported in literature were achieved by multiple extractions steps [18], by the optimization of additional parameters, such as temperature, pH and addition of inorganic salts [19, 74], by coupling volatile and toxic solvents [20] or by adding crown ethers with strong complexation abilities with metal ions [3]. Furthermore, the ILs used in the literature are usually fluorinated, and thus more expensive, toxic and non-water stable [46, 77, 78]. For instance, tetrabutylammonium bromide in a methylene chloride solution was employed for the liquid-liquid extraction of anionic dyes with a maximum extraction efficiency of 98 % (from a 50 mg·dm^{-3} dye aqueous solution) [20]. Under the optimized conditions, 85-99 % of methyl orange, almost 100 % of eosin yellows, and 69% of orange G were transferred from an aqueous phase to hexafluorophosphate- and tetrafluoroborate-based water-immiscible ILs [74]. Improved results were also obtained with the hydrophobic methyltrioctylammonium thiocyanate with extraction efficiencies of 89 % and 64 % for methyl orange and methylene blue, respectively [19]. Using the water immiscible *N*-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide extraction efficiencies up to 95 % for azo dyes were achieved; yet, requiring two to three cycles of fresh IL [18]. Therefore, the novel approach proposed here, based on ATPS composed of hydrophilic ILs, reveals a higher performance in the extraction of textile dyes, while being more environmentally friendly, and should be considered as a promising route for wastewater treatment processes.

Finally, the use of phosphonium-based ILs to create ATPS aiming at extracting dyes from aqueous media is recommended since they allow higher extraction efficiencies than the imidazolium-based compounds. Figure 2.11 depicts one example of the visual identification of the complete extraction behaviour observed with the studied systems. Most studies comprising IL-based ATPS have been focused on imidazolium fluids [56]. Nevertheless, phosphonium-based ILs display additional advantages over the imidazolium-based counterparts: they are less expensive and thermally more stable [95, 96]. Phosphonium-based ILs are being industrially produced by Cytec, are available in a multi-ton scale and have been used in industrial processes [95, 96]. In addition, and unlike most ILs, phosphonium-based ILs are less dense than water facilitating therefore the use of conventional units designed for systems that require the aqueous phase decantation [97, 98]. Based on the results demonstrated here and on the additional phosphonium-based ILs advantages, they are particularly recommended for the extraction/removal of textile dyes from wastewaters.

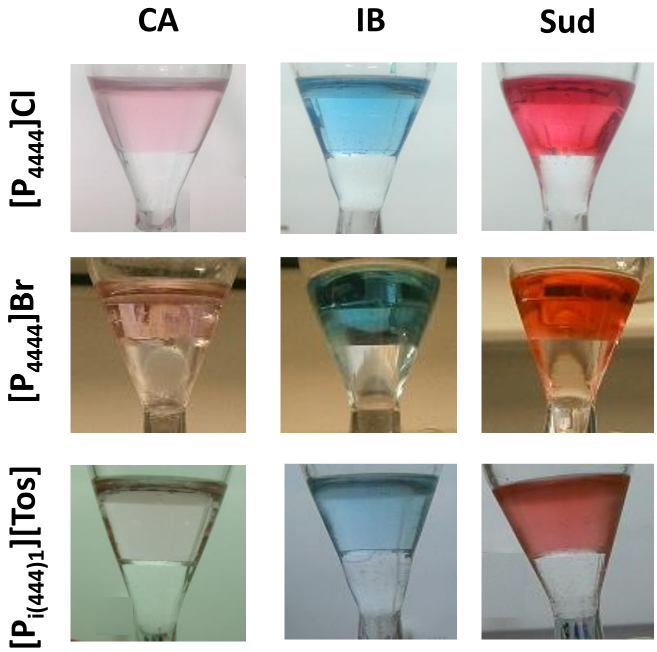

Figure 2.11. Extraction of (CA) choranilic acid, (IB) indigo blue and (Sud) sudan III using ATPS composed of different ILs and the salt potassium citrate at 298 K.

2.4. Conclusions

In this work, the extraction of three textile dyes (chloranilic acid, sudan III and indigo blue) from aqueous media using IL-based ATPS was investigated. Besides the IL and salt effects, a slight pH-dependent effect on the partitioning behaviour, in particular for chloranilic acid, was also observed. Higher extraction efficiencies are reached at low pH values due to the predominance of non-charged dyes. In general, phosphonium-based ATPS lead to higher partition coefficients and extraction efficiencies when compared with imidazolium-based compounds. Extraction efficiencies up to 100 %, *i.e.* the complete removal of dyes from aqueous solutions, were obtained in a single-step procedure by a proper choice of the IL and salt nature. These results suggest that IL-based ATPS could be developed into alternative processes for the treatment of wastewaters contaminated with textile dyes.

3. Selective separation of dyes using IL-salt reversible ATPS

3.1. Introduction

Recently, a large interest has been devoted to the exploitation of less usual dynamic and reversible biphasic systems constituted by ILs [99]. More specifically, it was already demonstrated that mixtures involving ILs and other solvents can be adjusted between the homogeneous regime and a two-phase system either by a temperature-driven phenomenon or by adding CO_2/N_2 [100]. Some IL/solvent mixtures display an upper critical solution temperature (UCST) [18, 94, 101-106] whereas others present a lower critical solution temperature (LCST) [100, 107-114]. These temperature-dependent phase transitions have shown to be advantageous in the selective separation of proteins [113] and metals [111]. However, some UCST and LCST in systems involving ILs only occur at temperatures well above the room temperature and a high energy input is required to trigger their reversibility. Moreover, these systems are usually composed of an IL-rich phase (typically with hydrophobic characteristics) and a molecular solvent-rich phase (usually water [100, 101, 104-106, 108-120], alcohols [94, 102, 103, 116] or hydrocarbons [18]). On the other hand, reversible liquid-liquid systems have also been achieved with molecular solvents that react with CO_2 forming salts and/or ILs [121-125]. These systems have been used in the separation of aliphatic and aromatic amines [124, 125]. However, these reversible systems require the addition of high-cost gases and the use of specific equipment that can be seen as their major disadvantages [121-125].

Actually, the research in liquid–liquid extractions using ILs has been focused on two different approaches: the direct use of hydrophobic ILs and non-miscible aqueous or organic solvents (and where the reversible temperature- and CO_2/N_2-dependent systems fall within) and the use of ATPS composed of ILs and organic/inorganic salts [56]. Besides all the advantages previously mentioned regarding the high performance of IL-based ATPS, their reversible behaviour was not hitherto attempted. Therefore, the major goal of this work is to show, for the first time, the reversibility behaviour of IL-based ATPS triggered by a pH-dependent phenomenon and their potential application in the selective separation of textile dyes, more specifically, sudan III and pigment blue 27 (PB27). In Figure 3.1 the chemical structure of PB27 is presented. Its main physicochemical properties are presented in Table 3.1.

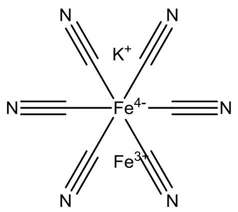

Figure 3.1. Chemical structure of PB27.

Table 3.1. Physicochemical properties of PB27 [79].

Molecular weight	306.89	$g\cdot mol^{-1}$
Solubility in water at 298 K	10	$mg\cdot cm^{-3}$
$Log(K_{OW})$	-0.26	
pK_a at 298 K	---	

3.2. Experimental section

3.2.1. Chemicals

The ATPS studied in this work were established by using the organic salt potassium citrate (tribasic monohydrated), $K_3C_6H_5O_7\cdot H_2O$ (≥ 99 wt % pure), purchased from Sigma-Aldrich, monohydrate citric acid, $C_6H_8O_7\cdot H_2O$ (100 wt % pure) from Fisher Scientific, and potassium hydroxide (100 wt % pure) from Pronolab. The ILs studied were: 1-butyl-3-methylimidazolium chloride, $[C_4mim]Cl$ (99 wt %); 1-butyl-3-methylpyridinium chloride, $[C_4mpy]Cl$ (> 98 wt %); 1-butyl-1-methylpiperidinium chloride, $[C_4mpip]Cl$ (99 wt %); tetrabutylphosphonium chloride, $[P_{4444}]Cl$ (98 wt %); 1-butyl-3-methylimidazolium bromide, $[C_4mim]Br$ (99 wt %); 1-butyl-2,3-dimethylimidazolium chloride, $[C_4C_1mim]Cl$ (98 wt %). The chemical structures of the investigated ILs are depicted in Figure 3.2. All imidazolium-, pyridinium-, and pyrrolidinium-based ILs were purchased from Iolitec. The $[P_{4444}]Cl$ was kindly supplied by Cytec Industries Inc. Before use all the ILs were dried for a minimum of 24h, at moderate temperature (353 K) and vacuum under constant agitation. After this procedure, the purity of each IL was further confirmed by ^1H and ^{13}C NMR spectra.

The water used was ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus.

For the extraction of dyes it was used sudan III from Merck, and PB27 acquired from Daicolor.

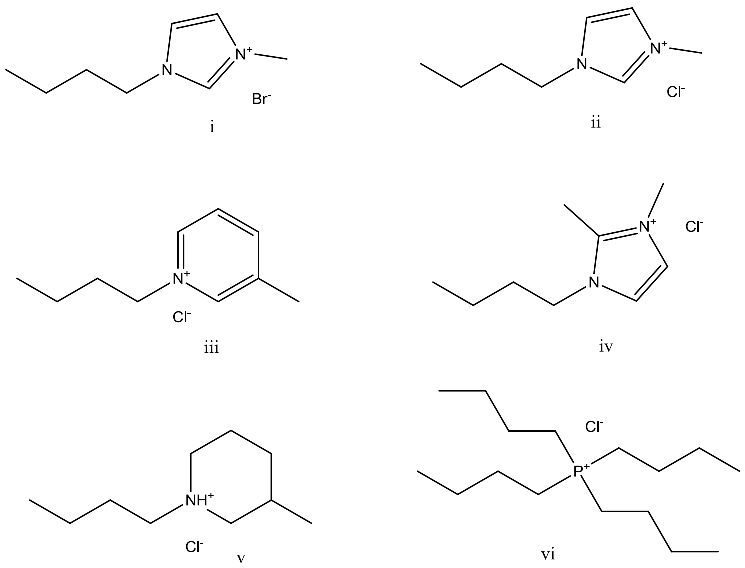

Figure 3.2. Chemical structures of the ILs used to form ATPS: (i) [C$_4$mim]Br, (ii) [C$_4$mim]Cl, (iii) [C$_4$mpy]Cl, (iv) [C$_4$C$_1$mim]Cl, (v) [C$_4$mpip]Cl and (vi) [P$_{4444}$]Cl.

3.2.2. Experimental procedure

3.2.2.1. Phase diagrams and TLs

New phase diagrams for the ILs at several pH values, namely [C$_4$C$_1$mim]Cl in the range from pH 9 to 7, [C$_4$mpip]Cl from pH 8 to 6, [C$_4$mpyp]Cl from pH 8 to 6, [C$_4$mim]Cl at pH 8, [P$_{4444}$]Cl at pH values of 8, 6 and 5, and [C$_4$mim]Br from pH 8 to 5 were determined in this work. Other phase diagrams were already reported and were taken from literature [81, 89], such as [C$_4$mpip]Cl at pH 9, [C$_4$mpyr]Cl at pH 9, [C$_4$mim]Cl at pH 9 and 7, [P$_{4444}$]Cl at pH 9 and 7, and [C$_4$mim]Br at pH 9. Nevertheless, the results attained in this work were compared with literature data [81, 89] and are in close agreement.

The ternary phase diagrams were determined for each of the water-soluble IL, water and $K_3C_6H_5O_7$ or $K_3C_6H_5O_7/C_6H_8O_7$ mixtures. The latter mixture was used in different molar ratios as buffer solutions to maintain the pH of the overall ATPS at the desired value. The experimental procedure adopted was similar to the one described in Section 2.2.2. The ternary phase diagrams were determined through the cloud point titration method [81, 83] at (298 ± 1) K and atmospheric pressure, using aqueous solutions of salt at around 50 wt % and aqueous solutions of the different hydrophilic ILs (with concentrations ranging from 60 wt % to 90 wt %). The ternary system compositions were determined by weight quantification within ± 10^{-4} g.

The TLs were determined by the gravimetric method described by Merchuk et al. [84] and presented in Section 2.2.2.

The pH of both IL and organic salt aqueous phases was measured at 298 K using a Mettler Toledo S47 SevenMulti^{TM} dual meter pH/conductivity equipment within ± 0.02.

3.2.2.2. pH-triggered reversibility experiments

Aiming at studying the possibility of moving from monophasic to biphasic regimes in IL-based ATPS, by a proper tailoring of the pH the aqueous media, an initial ternary mixture region was chosen based on the phase diagrams determined before. A common ternary mixture, within the biphasic region, was prepared with $K_3C_6H_5O_7$ (35 wt %) + IL (45 wt %) + water (45 wt %) and allowed for the phases separation for at least 3 h. The only exception was [C_4mim]Br (32 wt % of salt and 35 wt % of IL) because with this IL the initial mixture point falls within the biphasic region for all the studied pH values. At the initial mixture compositions the pH values of the aqueous media is *circa* to 9. In order to move to the monophasic regime, an aqueous solution of citric acid at 50 wt % was drop wise added under constant agitation until the mixture became homogeneous (monophasic). Then, an aqueous solution of potassium hydroxide at 50 wt % was added, under agitation, to attain the initial pH value of ≈ 9. It should be remarked that the pH of the aqueous solutions was experimentally measured in all of the addition steps.

3.2.2.3. Partition coefficients and extraction efficiencies of the dyes

The ternary mixtures compositions used in the partitioning experiments were the same used in the study of the pH-triggered reversibility studies. In each system, a small amount of sudan III and PB27 (≈ 0.30 mg of each dye) was added to glass tubes containing the ternary compositions with a total weight of 5 g. Each mixture was vigorously stirred and left to equilibrate for at least 3 h, at (298 ± 1) K, to achieve the complete dye partitioning between the two phases.

In the studied ATPS, the top phase corresponds to the IL-rich aqueous phase, while the bottom phase is mainly composed of salt.

After a careful separation of both phases, the quantification of the dyes in each phase was carried by UV-spectroscopy, using a Shimadzu UV-1700, Pharma-Spec Spectrometer, at a wavelength of 348 nm for sudam III and 636 nm for PB27. At least three individual samples of each phase were quantified in order to determine the average in the partition coefficient and extraction efficiency and the respective standard deviations. The interferences of the salts and ILs with the analytical method were investigated and blank control samples were always used.

The percentage extraction efficiency of sudan III for the IL-rich phase, $EE_{\mathrm{Sud}}\%$, was determined according to Equation 8 described in Section 2.2.2. On the other hand, the percentage extraction efficiency of PB27, $EE_{\mathrm{PB27}}\%$ is defined as the percentage ratio between the amount of pigment in the salt-rich aqueous phase to that in the total mixture, and according to Equation 9,

$$EE_{\mathrm{PB}}\% = \frac{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}} \times \mathrm{w}_{\mathrm{Salt}}}{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times \mathrm{w}_{\mathrm{IL}} + \mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{Salt}} \times \mathrm{w}_{\mathrm{Salt}}} \tag{9}$$

where w_{IL} and w_{Salt} are the weight of the IL-rich phase and the weight of the salt-rich phase, respectively.

3.3. Results and discussion

Aiming at studying the possibility of moving from monophasic to biphasic regimes in IL-based ATPS, by a proper tailoring of the pH the aqueous media, the liquid-liquid ternary phase diagrams were determined for different hydrophilic ILs, as well as their reversibility behaviour, namely [C_4mim]Cl, [C_4C_1mim]Cl, [C_4mpip]Cl, [C_4mpy]Cl, [C_4mim]Br and [P_{4444}]Cl using combinations of potassium citrate ($K_3C_6H_5O_7$) and citric acid ($C_6H_8O_7$).

The ternary phase diagrams for the systems composed of water + organic salt + ILs at different pH values, are illustrated in Figure 3.3 (the respective phase diagrams in molality units are presented in Appendix B in Figure B.2.1). The experimental weight fraction data of each phase diagram are depicted in Appendix A (Table A.2.1. to Table A.1.8). It should be remarked that the phase diagrams at pH ≈ 8 and pH ≈ 6 with [C_4mim]Br have already been reported by Zafarani-Moattar and Hamzehzadeh [89], and the results obtained here show a good agreement with literature data [89]. The respective comparisons are provided in Appendix B (Figure B.1.2). For the studied systems at pH 9, the experimental binodal data were further fitted by the empirical relationship described by Equation 1 and their values and corresponding standard deviations (σ) are provided in Table 3.2. The experimental binodal data obtained lead to improved correlation coefficients indicating that these fittings can be used to predict data in a given region of the phase diagram where no experimental results are available. The experimental TLs, along with their respective length (TLL), are reported in Table 3.3, as well as the composition of each system used in the extraction and respective pH values.

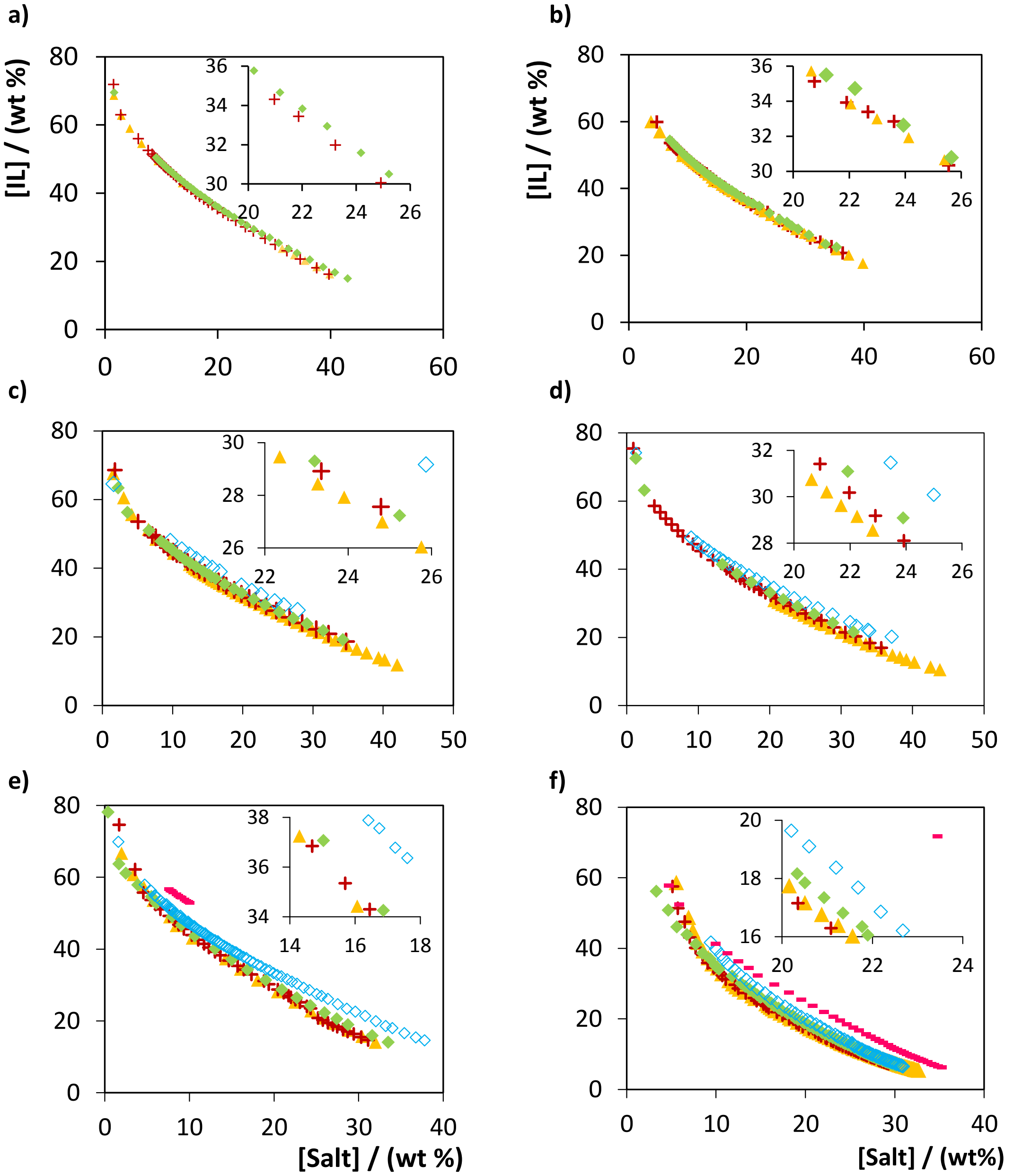

Figure 3.3. Evaluation of the pH effect in ternary phase diagrams composed of IL + water + $K_3C_6H_5O_7$/ $C_6H_8O_7$ at (▲) pH ≈ 9, (+) pH ≈ 8, (♦) pH ≈ 7, (◊) pH ≈ 6 and (—) pH ≈ 5. The ILs are: (a) [C_4mim]Cl, (b) [C_4C_1mim]Cl, (c) [C_4mpip]Cl, (d) [C_4mpy]Cl, (e) [C_4mim]Br and (f) [P_{4444}]Cl. Some phase diagrams have been reported by other authors and are included here for comparison purposes [81, 89, 126].

Table 3.2. Correlation parameters obtained from the fitting of the experimental binodal data by Equation 1.

IL	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$	R^2
$[C_4C_1mim]Cl$	92.3 ± 0.5	-0.198 ± 0.002	0.68 ± 0.01	0.9998
$[C_4mim]Cl$ [81]	86.0 ± 0.5	-0.180 ± 0.003	0.84 ± 0.03	0.9998
$[C_4mim]Br$ [81]	92.4 ± 0.6	-0.228 ± 0.003	1.87 ± 0.06	0.9997
$[C_4mpip]Cl$ [81]	87.1 ± 0.3	-0.210 ± 0.001	0.85 ± 0.01	0.9997
$[C_4mpy]Cl$ [81]	94.3 ± 0.4	-0.232 ± 0.001	0.80 ± 0.01	0.9996
$[P_{4444}]Cl$ [81]	170.0 ± 5.7	-0.484 ± 0.011	1.64 ± 0.14	0.9944

Table 3.3. Weight fraction percentage (wt %) for the coexisting phases of IL + potassium citrate + H_2O, and respective values of tie-line length (TLL) and pH values of each phase.

IL	**Weight fraction composition / wt %**								**TLL**
	$[IL]_{IL}$	$[salt]_{IL}$	pH_{IL}	$[IL]_M$	$[salt]_M$	$[IL]_{salt}$	$[salt]_{salt}$	pH_{salt}	
$[C_4mim]Cl$	53.04	7.13	9.32	25.25	35.03	5.77	54.58	9.30	66.98
$[C_4C_1mim]Cl$	47.88	10.76	8.93	25.02	34.90	9.78	51.00	8.67	55.42
$[C_4mpip]Cl$	55.91	4.46	9.26	25.13	34.75	4.40	55.15	9.34	72.27
$[C_4mpy]Cl$	55.74	5.13	8.44	24.62	35.47	4.39	55.19	8.16	71.71
$[C_4mim]Br$	76.93	0.65	8.93	35.08	32.04	0.42	58.03	8.92	95.64
$[P_{4444}]Cl$	72.93	3.06	9.34	24.97	35.03	0.58	51.29	9.14	86.95

Figure 3.4 (the respective phase diagrams in molality units are presented in Appendix B in Figure B.2.3) shows that ILs with a higher hydrophobicity, achieved either with longer and more aliphatic moieties or with anions with improved hydrogen-bond basicity [71], are capable of forming ATPS at lower pH values. Such examples at work can be seen with $[P_{4444}]Cl$ and $[C_4mim]Br$ that form ATPS even at a pH of 5. Furthermore, at a fixed pH, the IL ability to form ATPS follows the order: $[P_{4444}]Cl$ > $[C_4mim]Br$ > $[C_4mpy]$ Cl ≈ $[C_4mpip]Cl$ > $[C_4C_1mim]Cl$ ≈ $[C_4mim]Cl$ (Figure 3.4). This trend follows the hydrophobic sequence of the IL cations and anions. The phosphonium-based IL investigated is highly hydrophobic due to its four butyl chains which favour its ability to undergo the liquid-liquid demixing even at acidic pH. Piperidinium-based ILs are 6-sided ring cations and are more able to induce ATPS when compared with the smaller 5-sided rings of imidazolium. Furthermore, it should be noted that the substitution of the most acidic proton in the imidazolium ring, from $[C_4mim]^+$ to $[C_4C_1mim]^+$, has no significant influence on the ILs ability to form ATPS. This trend was already verified and discussed by Freire et al. [127] in ATPS composed

of ILs and K_3PO_4. The effect of the anion nature on the ATPS phase behaviour was also investigated with ILs containing the common $[C_4mim]^+$ cation, while combined with two anions (Cl^- and Br^-). $[C_4mim]Br$ is more prone to form ATPS than $[C_4mim]Cl$ in the presence of a fixed salt, and which is in agreement with results with other salts [81].

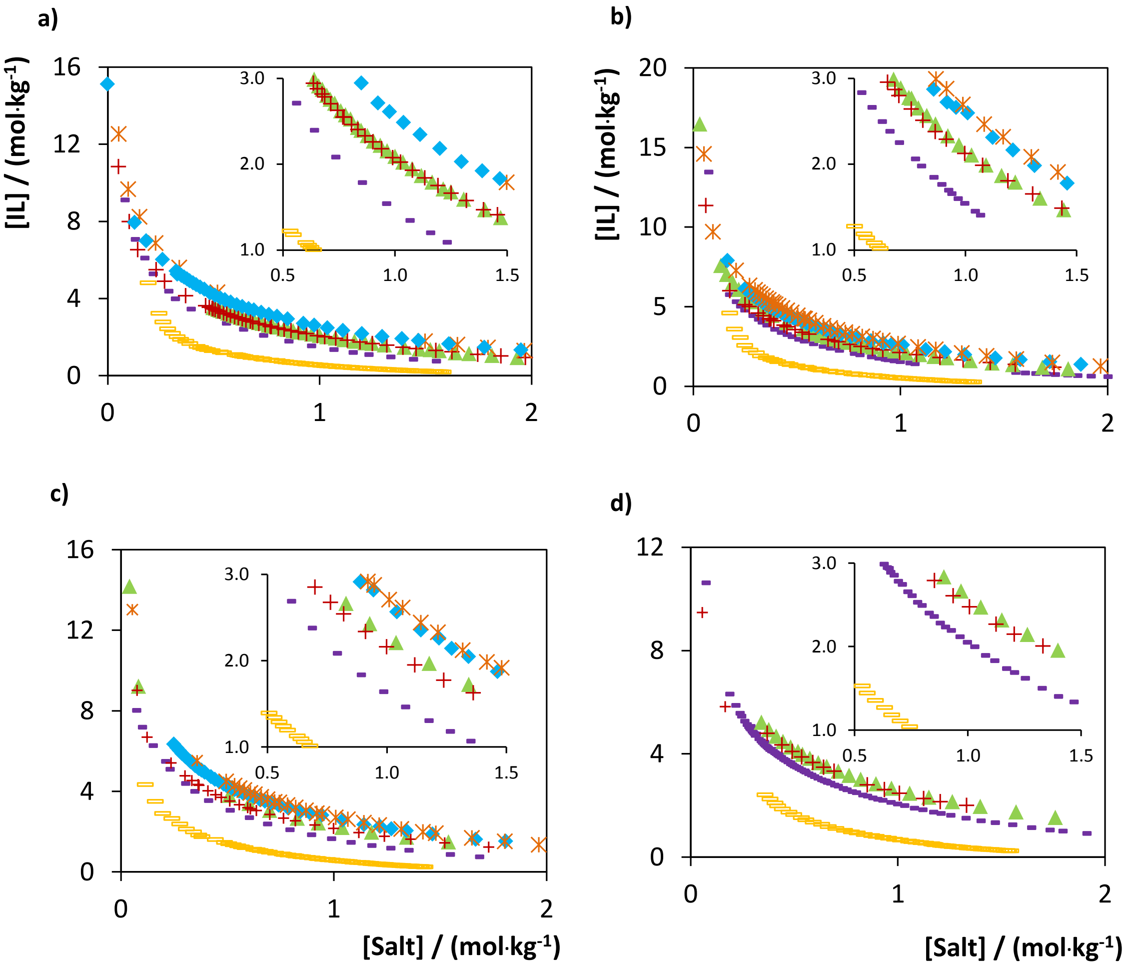

Figure 3.4. Phases diagrams for the different ILs at fixed pH. Phase diagrams of ATPS composed of IL + water + $K_3C_6H_5O_7$ at (a) pH ≈ 9 and ATPS composed of IL + water + $K_3C_6H_5O_7/C_6H_8O_7$ at (b) pH ≈ 8, (c) pH ≈ 7 and (d) pH ≈ 6. The ILs used are: (✳) $[C_4mim]Cl$, (♦) $[C_4C_1mim]Cl$, (+) $[C_4mpip]Cl$, (▲) $[C_4mpy]Cl$, (▬) $[C_4mim]Br$ and (▭) $[P_{4444}]Cl$.

In general, and for all ILs, there is a decrease on the ability for ATPS formation with the pH reduction, e.g., the higher the pH of the aqueous medium the larger is the biphasic region. These results are summarized in Table 3.4.

Table 3.4. Identification of the systems able (✓) or not able (×) to form two-phase systems at different pH values.

pH	9	8	7	6	5
$[C_4mim]Cl$	✓	✓	✓	×	×
$[C_4C_1mim]Cl$	✓	✓	✓	×	×
$[C_4mpip]Cl$	✓	✓	✓	✓	×
$[C_4mpy]Cl$	✓	✓	✓	✓	×
$[C_4mim]Br$	✓	✓	✓	✓	✓
$[P_{4444}]Cl$	✓	✓	✓	✓	✓

In general, the ability for ATPS formation as a function of pH is strongly related with the speciation behaviour or citric acid or potassium citrate. Figure B.2.4 in Appendix B shows the speciation curves of citric acid. Table 3.5 presents the pK_a values of citric acid. At pH values below 3.05 the non-charged citric acid is mainly present. At pH values above 4.67 and 5.39 there is the prevalence of the divalent and trivalent charged hydrogenocitrate and citrate anions, respectively. Therefore, it seems that the most hydrophobic ILs such as $[C_4mim]Br$ and $[P_{4444}]Cl$ are still able to form ATPS with a large amount of hydrogenocitrate in solution (a weaker salting-out species if compared with the trivalent citrate anion).

Table 3.5. pK_a values of citric acid at 298 K [79].

pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
3.05	4.67	5.39	13.92

After the determination of the ternary phase diagrams, the understanding of the pH effect, and at which pH the systems do not undergo the liquid-liquid demixing, the reversible IL-based ATPS behaviour was further evaluated by the addition of citric acid and potassium hydroxide. These compounds were chosen to be able to change the pH of the aqueous medium while maintaining the initial ionic species in all the liquid-liquid systems. Figure 3.5 depicts the summary of the described reversible process, and also represents the differences in the compositions of the two phases before and after the addition of citric acid and KOH. The differences in the phases' compositions are in fact small, since a short amount of each aqueous solution (± 0.6 wt %) is enough to trigger the reversibility behaviour.

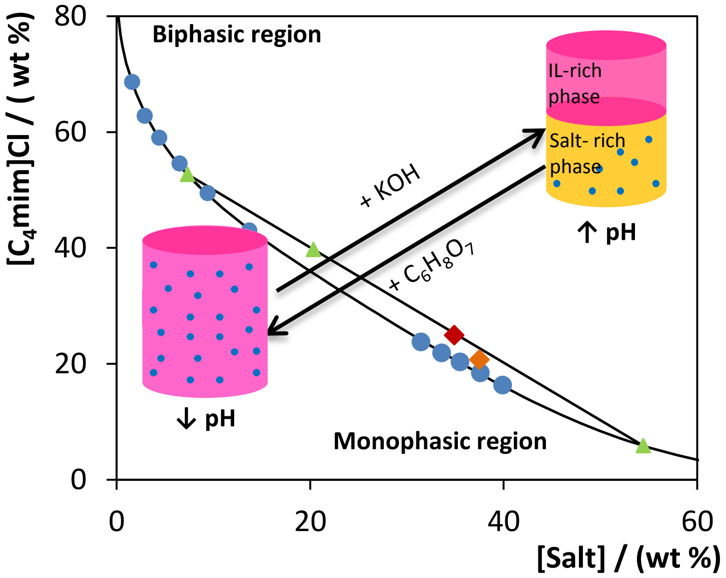

Figure 3.5. Ternary phase diagram of the systems composed of [C_4mim]Cl + water + $K_3C_6H_5O_7$ at (●) pH ≈ 9, (▲) tie-line data, (◆) initial biphasic mixture and(◆) final biphasic mixture (after the citric acid and KOH addition).

The pH-driven reversibility was proved with the ILs [C_4mim]Cl, [C_4C_1mim]Cl, [C_4mpip]Cl, [C_4mpy]Cl, [C_4mim]Br and [P_{4444}]Cl. In summary, it is possible to have reversible IL-based ATPS playing around with the speciation behaviour of the organic salt employed. In addition, the cyclic reversibility was also proved with the [C_4mim]Cl-based ATPS, at least for 3 times, with no significant changes in the phases' composition. Moreover, this reversible scenario occurs at room temperature and is achieved with low cost compounds. Therefore, these novel systems can be envisaged as potential alternatives to the more complex reversible systems that require high energy inputs [100, 101, 104-106, 108-120] or the addition of high-cost gases and specific equipment [121-125]. Their reversible nature is a crucial advantage on liquid-liquid extractions and to perform selective separations as demonstrated hereinafter.

The investigated IL-based reversible ATPS were also investigated in what concerns their ability for the selective separation (migration for opposite phases) of mixtures of dyes and pigments usually found in textile effluents, more specifically of sudan III and PB27. The mixture of both dyes exists in the monophasic and homogenous mixture than can be selectively separated by the creation of an appropriate IL-based ATPS. Figure 3.6 depicts the macroscopic appearance of the selective separation achieved by manipulating the pH of the system composed of [C_4mim]Cl at 298 K, whereas Figure 3.7 depicts the extraction efficiencies (*EE*%) of each dye in each aqueous-rich phase. The extraction efficiencies are defined as the percentage ratio between the amount of each dye in one of phases to that in the total mixture considering the weight/volume of the coexisting phases.

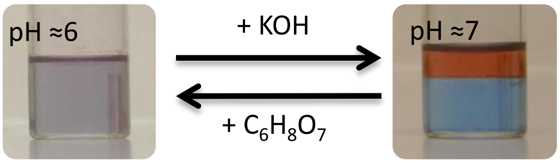

Figure 3.6. Selective separation of sudan III and PB27 from their initial monophasic mixture using the ATPS composed of [C_4mim]Cl.

From the results illustrated in Figure 3.6, it is clear that sudan III preferentially migrates for the IL-rich phase while PB27 partitions for the citrate-rich phase. Indeed, this trend reflects the behaviour displayed by their octanol-water partition coefficients (K_{ow}): log(K_{ow}) of sudan III is 7.47 and log(K_{ow}) of PB27 is -0.26 [79].Thus, sudan III has a less-polar character and preferentially migrates for the more hydrophobic IL-rich phase while the pigment favourably partitions to the more charged and polar phase. Note that, the selective extraction with the ATPS composed of [C_4mim]Br or [P_{4444}]Cl was not studied because these systems only reach the monophasic at lower pH values, namely pH 4 and pH 3, respectively. For both situations a higher amount of acidic solution is required when compared with the remaining ILs becoming thus less economically viable.

The extraction efficiencies and the selective extraction of sudan III and PB27 for opposite phases is highly dependent on the IL cation (Figure 3.7). The selective partition of both compounds for the opposite phases follows the order: [C_4mpy]Cl < [C_4mpip]Cl < [C_4C_1mim]Cl < [C_4mim]Cl. Remarkably, the extraction efficiencies of sudan III and PB27 with the ATPS constituted by [C_4mim]Cl are close to 100 % meaning that this system is completely able to separate both dyes into opposite aqueous phases. In addition, amongst the studied fluids, these remarkable selective separations are achieved with a low cost and low toxic IL [43].

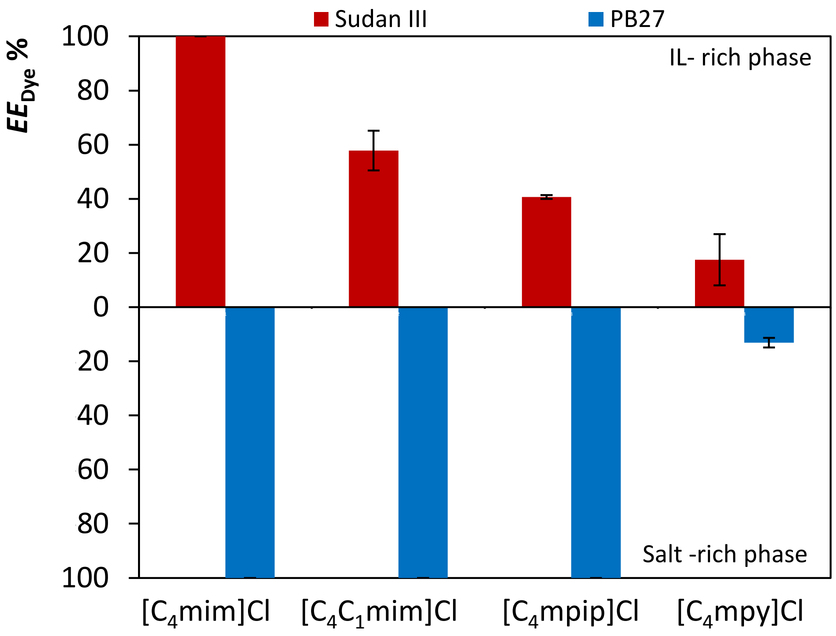

Figure 3.7. Percentage extraction efficiencies of sudan III and PB27, EE_{Dye}%, in the different ATPS at 298 K.

3.4. Conclusions

The novel evidences demonstrated here clearly confirm that low-cost and easily reversible ATPS composed of ILs can be achieved by the use of organic salts. For the first time, the reversible nature of IL-based ATPS was demonstrated. In addition, these systems have shown to be highly valuable and efficient for the selective separation of compounds with different hydrophobic nature albeit present in the same aqueous medium. Therefore, the use of the proposed reversible systems for use in the separation of the most diverse compounds in straightforwardly envisaged.

4. Selective separation of dyes using IL-polymer reversible ATPS

4.1. Introduction

Over the last decade, IL-based ATPS have gained a high recognition in the separation field due to their high extraction efficiencies for the most diverse compounds [56]. However, some ILs have been classified as less “green” solvents due to their high/moderate toxicity and poorly biodegradable nature, and these include imidazolium-, pyridinium-, piperidinium-, pyrrolidinium-, and phosphonium-based cations combined with several anions, such as halogens, or more complex fluorinated anions [128-130]. Actually, the main reason behind the “green” nature associated to ILs relays on their negligible volatility; and so, atmospheric pollution is avoided [131]. However, either in academia or at an industrial scale there will be the loss of ILs into water ecosystems causing aquatic environmental concerns. In addition, and when dealing with conventional salt-IL-based ATPS, the high concentrations of inorganic salts typically used produce a great amount of highly salty water leading also to related environmental problems. In this context, it is important to design more environmentally friendly IL-based ATPS for the development of cleaner manufacturing and/or separation processes.

An alternative scenario for the most studied and moderately toxic ILs consists on the synthesis and use of non-toxic and more environmentally benign ILs. Cholinium chloride (also known as 2-hydroxyethyltrimethyl ammonium chloride or vitamin B4), is known to be non-toxic, biodegradable and is a water soluble essential nutrient which supports several biological functions [132]. However, cholinium chloride falls within the category of common salts due to its high melting point (575 K). Recent advances have demonstrated the synthesis of novel cholinium-based ILs combined with more complex and organic anions which lead to the decrease of their melting temperatures [133]. Most of these anions either are amino-acid-based or derived from carboxylic acids and present a high biodegradability pattern and low toxicity, and therefore are more environmentally benign [134].

Poly(alkylene glycols), such as polyethylene or polypropylene glycols, PEGs or PPGs, respectively, are widely used as phase-forming components of ATPS [135-137]. These polymers display high biodegradability, low toxicity, low cost, relatively low melting points, and low volatility [138]. These are the main advantages which have contributed for their wide interest [138].

Taking into account all the benefits of cholinium-based salts and PPGs, the development of more environmentally friendly ATPS can be anticipated by the combination of both solutes. Therefore, in this work, the phase diagrams, TLs and TLLs of novel systems composed of PPG 400 and cholinium-based ILs were determined at 298 K. These ternary phase diagrams were also evaluated according to their pH-dependent behaviour by the combination of cholinium hydroxide and the corresponding acid of the IL anion. Finally, the extractive performance and the reversibility behaviour of the proposed ATPS were evaluated through their application on the selective extraction of textile dyes, namely sudan III, PB27 and pigment blue 29 (PB29). The chemical formula of PGB29 and the respective physicochemical properties are presented in Table 4.1, as well as, the chemical structure of PB29 is presented Figure 4.1. The physicochemical properties and chemical structure of sudan III and PB27 were previously presented in Table 2.1 and Table 3.1 and Figure 2.1 and Figure 3.1.

Table 4.1. Physicochemical properties of PB29 [139].

Chemical formula	$Na_6(Al_6Si_6O_{24}S_4).2NaS_3$	
Molecular weight	994.54	$g{\cdot}mol^{-1}$
Solubility in water at 298 K	Insoluble in cold water	

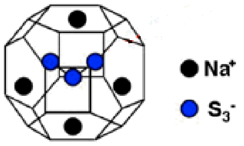

Figure 4.1. Chemical structure of PB29 [139].

4.2. Experimental section

4.2.1. Chemicals

The ILs studied in this work were cholinium ((2-hydroxyethyl)trimethylammonium) chloride, [Ch]Cl (99 wt % pure), from Sigma-Aldrich, and cholinium acetate, [Ch][Ac] (98 wt % pure), purchased from Iolitec. The following ILs were also studied and were synthetized in our lab according to standard protocols [140, 141], namely cholinium propionate, [Ch][Pro]; cholinium glycolate, [Ch][Gly]; cholinium butanoate, [Ch][But]; cholinium lactate, [Ch][Lac]; and cholinium hexanoate, [Ch][Hex]. It should be remarked that [Ch]Cl does not fall within the IL category due to its higher melting point. However, it is included in the cholinium-based ILs group in all the results and discussions presented thereinafter for comparison purposes.

Before use, all the ILs were purified and dried for a minimum of 24 h at constant agitation, at moderate temperature (≈ 353 K) and under vacuum (to reduce their volatile impurities to negligible values). After this step, the purity of each IL was confirmed by ^1H and ^{13}C NMR spectra and found to be > 98 wt %. The polymer used was polypropylene glycol of average molecular weight 400 $g{\cdot}mol^{-1}$, PPG 400, and was supplied by Aldrich and used as received. The chemical structures of the investigated ILs and of PPG 400 are depicted in Figure 4.2.

The ATPS studied at different pH values were established by using the hydrochloric acid (37 wt % in aqueous solution) and glycolic acid (99 wt % pure), both purchased from Sigma-

Aldrich; acetic acid (≥ 99.5 wt % pure), purchased from José Manuel Gomes dos Santos; propanoic acid (99 wt % pure), acquired from Merck; and butanoic acid (99 wt % pure) and lactic acid (88-92 wt % pure), both purchased from Riedel-de-Haën.

The water employed was ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment.

For the extraction of dyes it used sudan III from Merck, and the pigments PB27 and PB29 acquired from Daicolor and Holliday Pigments, respectively.

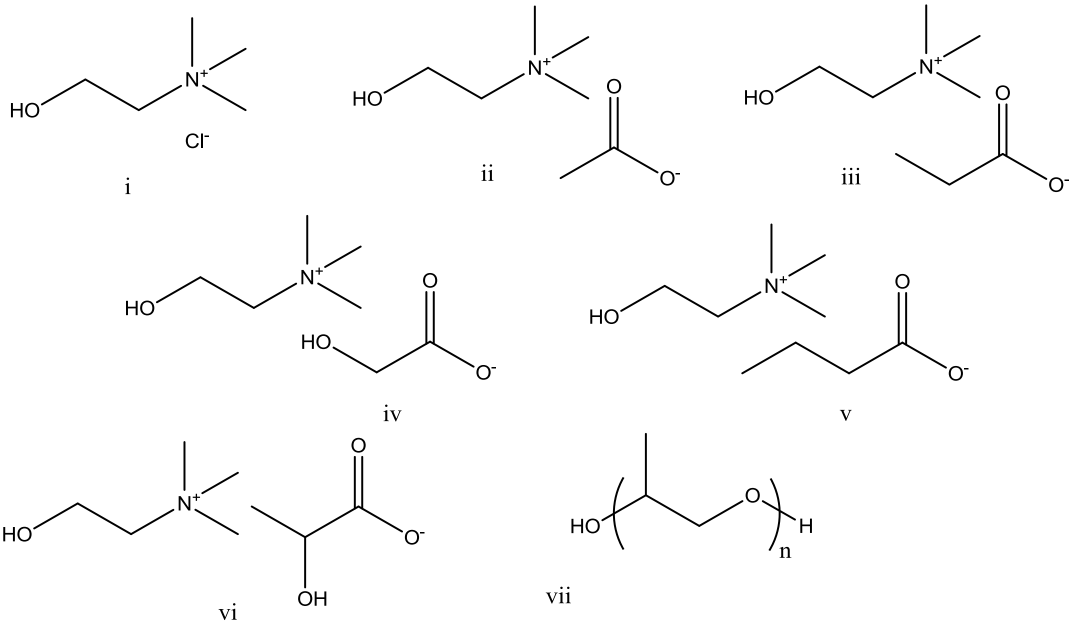

Figure 4.2. Chemical structures of the ILs and polymer investigated: (i) [Ch]Cl; (ii) [Ch][Ac]; (iii) [Ch][Pro]; (iv) [Ch][Gly]; (v) [Ch][But], (vi) [Ch][Lac], and (vii) PPG.

4.2.2. Experimental procedure

4.2.2.1. Phase diagrams and tie-lines

The ternary phase diagrams (PPG 400 + IL + water) were determined at several pH values with the following ILs: [Ch]Cl (from pH 5 to 0), [Ch][Ac] (from pH 9 to 5), [Ch][Pro] (from pH 8 to 5), [Ch][Gly] (from pH 7 to 4), [Ch][But] (from pH 8 to 5), [Ch][Lac] (from pH 7 to 4).

The ternary phase diagrams were determined for each of the water-soluble ILs, water and PPG. The phase diagrams at different pH values were attained using the acid which corresponds to the precursor of the IL anion studied. The acid was used in different molar ratios in respect to the IL to maintain the pH of the overall ATPS at the desired value. Note that the acid is added to the initial aqueous solution of each IL. The experimental procedure adopted was similar to the one described in Section 2.2.2. The ternary phase diagrams were determined through the cloud point titration method [81, 83] at (298 ± 1) K and atmospheric pressure. Aqueous solutions of PPG 400 at $\approx$ 65 wt % and aqueous solutions of the different hydrophilic ILs at variable concentrations (from 60 wt % to 80 wt %) were prepared gravimetrically and used for the determination of the binodal curves. Drop-wise addition of each aqueous IL solution to a PPG 400 aqueous solution was carried out until the detection of a cloudy solution (biphasic region), followed by the drop-wise addition of ultra-pure water until the detection of a clear and limpid solution (monophasic region). Whenever necessary, the addition of the PPG solution to the IL was also carried out to complete the phase diagrams. The ternary system compositions were determined by weight quantification within ± 10^{-4} g.

The TLs were determined by the gravimetric method described by Merchuk et al. [84] and presented in Section 2.2.2.

The pH of both the IL- and polymer-rich aqueous phases was measured at 298 K using a Mettler Toledo S47 SevenMulti$^{\text{TM}}$ dual meter pH/conductivity equipment within ± 0.02.

4.2.2.2. Extraction efficiencies of the dyes

The ternary mixtures compositions used in the partitioning experiments were chosen based on the phase diagrams determined here for each PPG 400-IL-water system. A ternary mixture with a common composition, and within the biphasic region, was prepared with 34 wt % of PPG 400, 13 wt % of IL and 53 wt % of water. In each system, a small amount of the two dyes, ≈ 0.30 mg of each, was added to glass tubes containing the ternary compositions with a total weight of 3 g. Each mixture was vigorously stirred and left to equilibrate for at least 3 h, at (298 ± 1) K.

In the studied ATPS, the top phase corresponds to the PPG-rich aqueous phase while the bottom phase is mainly composed of IL and water.

After a careful separation of both phases, the quantification of each dye in the two phases was carried by UV-Visible spectroscopy, using a Shimadzu UV-1700, Pharma-Spec Spectrometer, at a wavelength of 348 nm for sudan III, 636 nm for PB27 and 725 nm for PB27. 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 salts and ILs with the quantification method was also taken into account and blank control samples were always employed.

The percentage extraction efficiency of sudan III for the PPG-rich phase, $EE_{\text{Sud}}\%$, was determined according to Equation 10,

$$EE_{\mathrm{Dye}}\% = \frac{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{PPG}} \times w_{\mathrm{PPG}}}{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{PPG}} \times w_{\mathrm{PPG}} + \mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times w_{\mathrm{IL}}} \times 100 \tag{10}$$

where w_{PPG} and w_{IL} are the weight of the PPG-rich phase and the weight of the IL-rich phase, respectively. On the other hand, the percentage extraction efficiency of PB27, $EE_{\mathrm{PB27}}\%$ or the percentage extraction efficiency of PB29, $EE_{\mathrm{PB29}}\%$, was determined according to Equation 11.

$$EE_{\mathrm{PB}}\% = \frac{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times \mathrm{w}_{\mathrm{IL}}}{\mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{PPG}} \times \mathrm{w}_{\mathrm{PPG}} + \mathrm{Abs}_{\mathrm{Dye}}^{\mathrm{IL}} \times \mathrm{w}_{\mathrm{IL}}} \tag{11}$$

4.3. Results and discussion

Aiming at studying the possibility of moving from monophasic to biphasic regimes in IL-based ATPS by a proper tailoring of the aqueous media pH, the liquid-liquid ternary phase diagrams of different hydrophilic ILs, namely [Ch][But], [Ch]Cl, [Ch][Pro], [Ch][Lac], [Ch][Ac] and [Ch][Gly], were determined making use of the corresponding acids. These compounds were chosen to be able to change the pH of the aqueous medium while maintaining the initial ionic species in all the liquid-liquid systems. In summary, the reversibility behaviour is reached by the speciation of the IL anion. The experimental phase diagrams at the initial pH of the various ternary systems are graphically presented in Figure 4.3 (the phase diagrams in molality are presented in Appendix B in Figure B.3.1), and their detailed experimental weight fraction data are provided in Appendix A (Table A.3.1. to Table A.3.7). Some phase diagrams at the initial pH of the solution, *e.g.* with no control of the pH value of the ATPS, were already reported by Li et al. [131] and the results attained in this work are in close agreement with literature data.

It should be stressed that the ability of [Ch][Hex] to form liquid-liquid aqueous phases was also tested; however, it was not possible to detect the formation of two liquid phases with this IL.

According to the data depicted in Figure 4.3, the ability of ILs to form a biphasic system follows the rank: [Ch][But] < [Ch]Cl < [Ch][Pro] < [Ch][Lac] < [Ch][Ac] < [Ch][Gly]. Considering the fact that all ILs share the same cation, yet combined with different anions, the phase-forming aptitude of these ILs is only determined by the nature of their anions. Actually, the salting-out aptitude of an anion is directly related to its hydration capacity [131]. Anions with higher charge densities have stronger hydration capacities than those with lower charge densities, resulting in the decrease in the number of water molecules available to hydrate the polymer in a given ATPS. Therefore, ILs composed of more charged anions or anions with shorter alkyl side chains are more able to form two aqueous phases with a highly hydrophobic polymer such as PPG. This trend can be seen at work with the ILs comprising the anions acetate, propanoate and butanoate. Indeed, the longest alkyl side chain IL anion, [Ch][Hex], is not able to form ATPS with PPG 400. Furthermore, the addition of extra –OH groups, for instance comparing the [Ch][Ac]/[Ch][Gly] and [Ch][Pro]/[Ch][Lac] pairs, leads to an improved ILs performance to create ATPS. The introduction of –OH groups enhances the affinity of the ILs for water, and thus their hydration aptitude, leading to an easier separation of the polymer for the opposite phase. This trend was already observed [62], yet with ABS composed of imidazolium-based ILs and inorganic salts and where the –OH group was introduced at the longest alkyl chain of the IL cation.

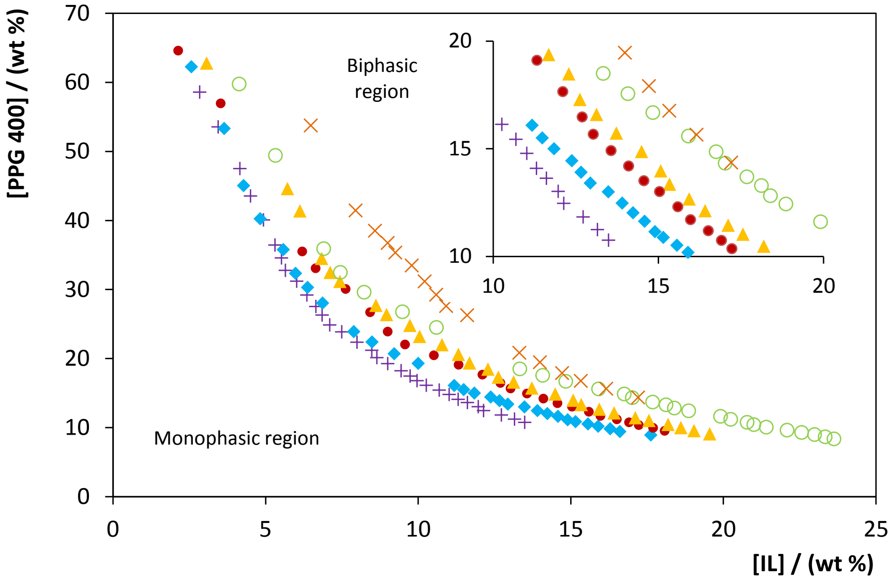

Figure 4.3. Ternary phase diagrams for systems composed of PPG 400 + IL + water at 298 K and atmospheric pressure. The ILs studied were: (×) [Ch][But], (○) [Ch]Cl, (▲) [Ch][Pro], (●) [Ch][Lac], (◆) [Ch][Ac] and (+) [Ch][Gly].

For the studied systems, the experimental binodal data were further fitted by the empirical relationship described by Equation 1. The regression parameters were estimated by the least-squares regression method, and their values and corresponding standard deviations (σ) are provided in Table 4.2. In general, good correlation coefficients were obtained for all systems. The experimental TLs, along with their respective length (TLL), are reported in Table 4.3 for IL-based systems, as well as the composition of each system used in the selective extraction of dyes (shown later) and respective pH values.

Table 4.2. Fitting parameters obtained from the description of the experimental binodal data by Equation 1.

IL	$A \pm \sigma$	$B \pm \sigma$	$10^6 (C \pm \sigma)$	R^2
[Ch]Cl	229.5 ± 14.9	-0.679 ± 0.030	0.10 ± 6.85	0.9913
[Ch][Ac]	222.0 ± 7.7	-0.778 ± 0.017	0.10 ± 11.4	0.9970
[Ch][Pro]	213.8 ± 10.2	-0.688 ± 0.020	18.6 ± 10.5	0.9938
[Ch][But]	452.9 ± 33.6	-0.840 ± 0.028	0.10 ± 11.2	0.9984
[Ch][Gly]	261.4 ± 10.6	-0.861 ± 0.019	18.2 ± 17.7	0.9962
[Ch][Lac]	233.4 ± 9.5	-0.747 ± 0.017	0.10 ± 9.19	0.9972

Table 4.3. Weight fraction percentage (wt %) of the coexisting phases of IL + PPG 400 + H_2O, and respective values of tie-line length (TLL), and pH values of each phase.

IL	Weight fraction composition / wt %								TLL
	$[PPG]_{PPG}$	$[IL]_{PPG}$	pH_{PPG}	$[PPG]_M$	$[IL]_M$	$[PPG]_{IL}$	$[IL]_{IL}$	pH_{IL}	
[Ch]Cl	42.18	6.23	3.11	33.91	13.13	3.36	38.62	3.03	50.56
[Ch][Ac]	43.79	4.35	6.72	33.99	13.14	1.39	42.40	6.70	56.97
[Ch][Pro]	44.33	5.21	3.02	34.13	13.29	0.89	39.62	2.95	55.42
[Ch][Gly]	46.66	4.00	5.24	33.97	13.29	0.49	37.82	5.19	57.23
[Ch][But]	40.74	8.22	6.74	34.00	13.30	2.44	38.59	6.65	48.88

Aiming at exploring the reversibility behaviour of the systems shown in Figure 4.3, the phase diagrams for each IL, PPG 400 and water at several pH values, achieved by the addition of the anion corresponding acid, were determined at 298 K. The phase diagrams at the several pH values are shown in Figure 4.4 (the respective phase diagrams in molality units are presented in Appendix B in Figure B.3.2). In addition, Table 4.4 presents the summary on the ability or non-ability of a given IL to form ATPS at a specific pH value.

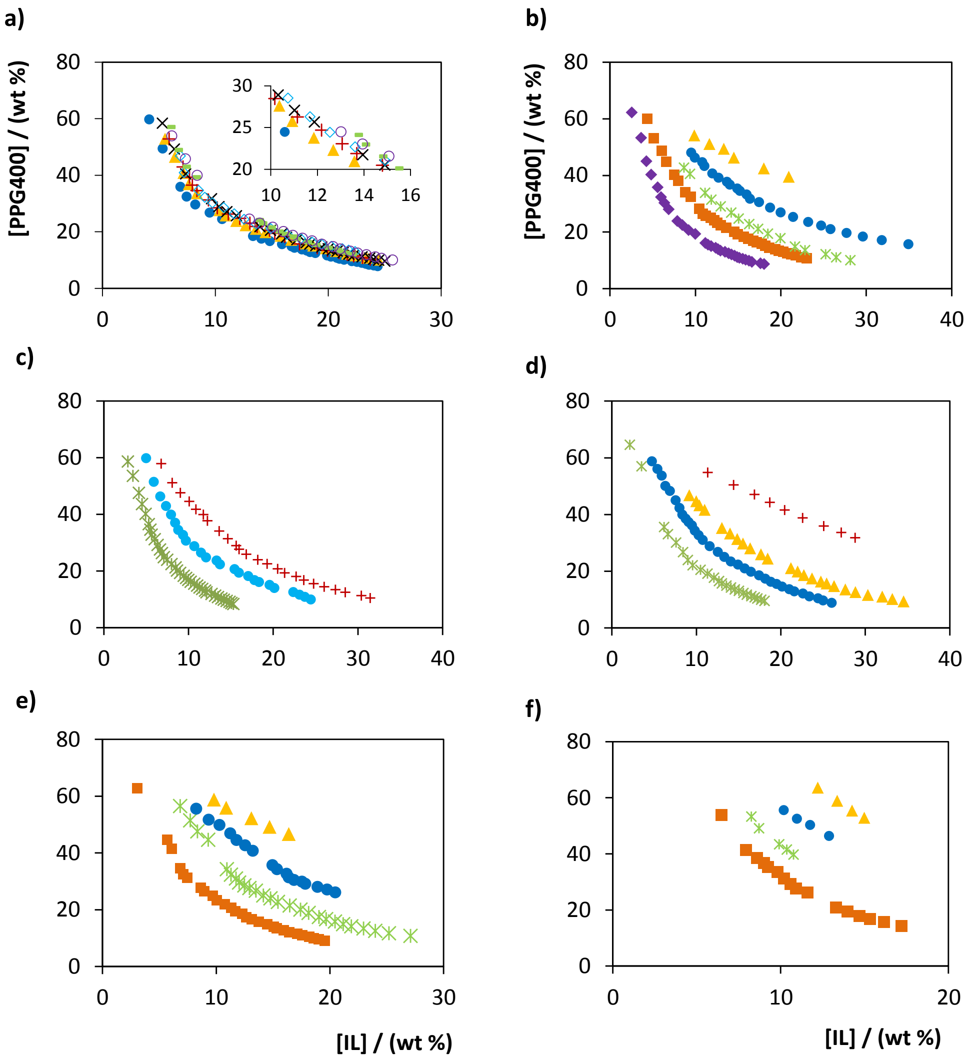

Figure 4.4. Evaluation of the pH effect in ternary phase diagrams composed of PPG 400 + water + IL at (♦) pH ≈ 9, (■) pH ≈ 8, (✳) pH ≈ 7 , (●) pH ≈ 6, (▲) pH ≈ 5, (+) pH ≈ 4, (×) pH ≈ 3, (◊) pH ≈ 2, (—) pH ≈ 1 and (○) pH ≈ 0. The ILs are: (a) [Ch]Cl, (b) [Ch][Ac], (c) [Ch][Gly], (d) [Ch][Lac], (e) [Ch][Pro], and (f) [Ch][But].

From the gathered results there are clear evidences that the decrease on the pH is not favourable for the formation of ATPS. The lower the overall pH value of the aqueous solution the smaller is the biphasic region of a given ATPS. The ATPS composed of [Ch]Cl is the less affected by a pH-driven phenomenon. This fact is a direct result of the non-speciation of the chloride anion. In this type of system the [Ch]Cl is always present at all pH values, although with a higher amount of HCl in solution which inherently means a less concentrated [Ch]Cl system. This difference in the pH can also have some influence on the amount of dissociated ions in aqueous media [142] and can justify the slightly decrease in the ability for ATPS formation with [Ch]Cl as the pH moves towards the acidic region.

Table 4.4. Identification of the systems able (✓) or not able (✗) to form two-phase systems at different pH values.

pH	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**	**0**
[Ch]Cl					✓	✓	✓	✓	✓	✓
[Ch][Ac]	✓	✓	✓	✓	✓	✗	✗	✗	✗	✗
[Ch][Gly]			✓	✓		✓	✗	✗	✗	✗
[Ch][Lac]			✓	✓	✓	✓	✗	✗	✗	✗
[Ch]Prop]		✓	✓	✓	✓	✗	✗	✗	✗	✗
[Ch][But]		✓	✓	✓	✓	✗	✗	✗	✗	✗

In general, and for all ILs studied, the ability for ATPS formation apparently is related to the pK_a of the acid corresponding to IL anion (Table 4.5). In fact, ILs constituted by the anions $[Ac]^-$, $[Pro]^-$ and $[But]^-$ are those that are only able to form ATPS up to a pH value of 5 due to their higher pK_a values. On the other hand, ILs with $[Gly]^-$ and $[Lac]^-$ can go further and down to a pH value of 4 since their pK_a values are smaller and, therefore, there is a larger amount of ionic species at this low pH value.

Table 4.5. pK_a of acids used in this study at 298 K [79].

Acid	**pK_{a1}**	**pK_{a2}**
hydrochloric acid	---	---
acetic acid	4.54	---
propanoic acid	4.75	---
butanoic acid	4.91	---
lactic acid	14.59	3.78
glycolic acid	14.78	3.53

After the proper evaluation of the pH-triggered reversibility of IL-PPG-based ATPS by the proper speciation of the IL anion, the investigated IL-based ATPS were further evaluated in what concerns their ability for the selective separation (migration for opposite phases) of mixtures of dyes and pigments usually found in textile effluents, more specifically, of sudan III, PB27 and

PB29. In this type of systems, two selective separations were attempted, namely the sudan III/PB27 and sudan III/PB29 pairs.

Figure 4.5 depicts the macroscopic appearance of the selective separation achieved with the system composed of [Ch][Ac], whereas Figure 4.6 and Figure 4.7 present the extraction efficiencies (*EE*%) of each dye for the IL- or PPG-rich phases.

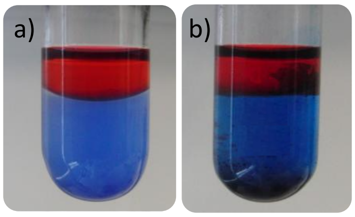

Figure 4.5. Selective separation of sudan III and (a) PB27 or (b) PB29 using ATPS composed of [Ch][Ac].

From the results illustrated in Figure 4.5, it is clear that sudan III preferentially migrates for the PPG-rich phase while PB27 or PB29 partition for the IL-rich phase. Outstandingly, this type of systems are able to separate two pairs of dyes (trend not accomplished with the systems reported in Section 3 since with PB29 it was always observed the precipitation of the pigment that was not able to dissolve at the salt-rich phase). In addition, suddan III now migrates for the PPG-rich phase whereas the inorganic pigments partition for the IL-rich phase. In the previous Section 3.3, where the IL-salt-based ATPS were ascertained, sudan III migrated for the IL-rich phase and the pigment for the salt-rich phase. The trend observed reflects the behaviour displayed by the octanol-water partition coefficients of each dye and as previously discussed in Section 3.3. Sudan III has a less-polar character and preferentially migrates to the more hydrophobic phase, which is now the PPG-rich phase, while the inorganic pigment partitions preferentially to the more charged and polar phase, that in PPG-IL-based ATPS corresponds to the IL-rich phase.

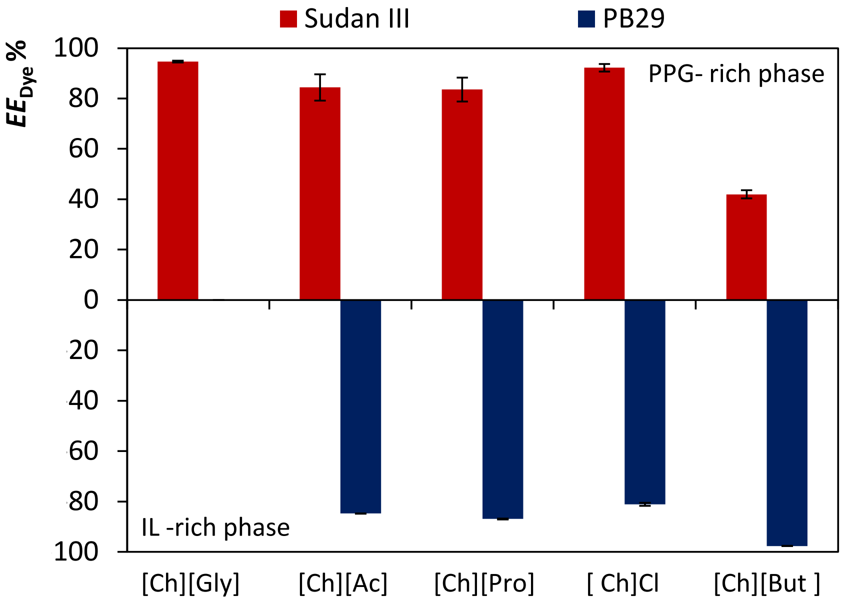

Figure 4.6. Percentage extraction efficiencies of sudan III and PB29, EE_{Dye}%, in the different ATPS at 298 K.

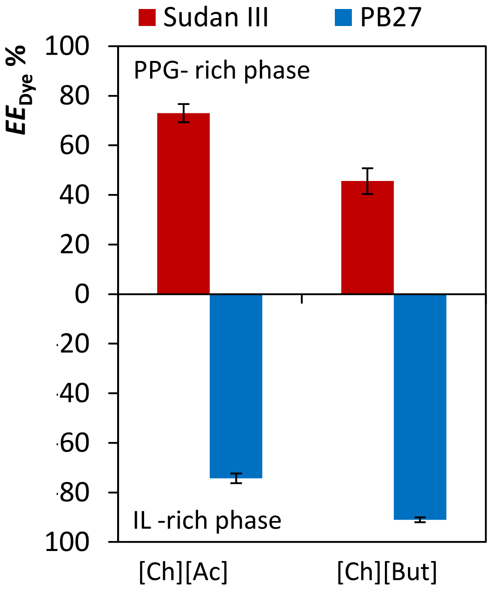

Figure 4.7. Percentage extraction efficiencies of sudan III and PB27, EE_{Dye}%, in the different ATPS at 298 K.

According to the data provided in Figure 4.6 and Figure 4.7, the extraction efficiencies and the selective extraction of sudan III and PB27/PB29 for opposite phases is highly dependent on the IL anion. The selective partitioning of both compounds for the opposite phases, and independently of the inorganic dye, follows the order: [Ch][But] <[Ch][Pro] ≈ [Ch][Ac] < [Ch]Cl. Remarkably, the extraction efficiencies of sudan III and PB29 are higher than 80 % (in both phases) for the systems composed of [Ch][Ac], [Ch][Pro] and [Ch]Cl. The ATPS composed of [Ch][Gly] gives rise to the precipitation of the inorganic dye at the interface and thus no extraction efficiencies are presented. This is the most hydrophilic IL investigated and seems to be unable to dissolve PB29. However, this trend can be seen as a separation method itself since both dyes are in fact separated. This type of separation approach was already shown by Maroof Ali et al. [94] with the precipitation of methylene blue and safranine O from aqueous media using imidazolium-based ILs [94]. For the systems with sudan III and PB27, the selective separation and respective extraction efficiency for both phases are slightly lower. This can be a main result of the structural differences between the pigments used.

The pH-triggered ATPS proposed here can represent a novel approach for the selective separation of textile dyes commonly found in wastewaters. In addition, this type of systems are even able to separate two pairs of dyes, namely sudan III/PB27 and sudan III/PB29. Finally, these selective separations were achieved with less aggressive ILs and PPG that tend to be non-toxic and biodegradable.

4.4. Conclusions

For the first time, the reversible nature of IL-polymer ATPS was demonstrated. This pH-driven phenomenon was achieved with the speciation of [Ch]-based ILs.

Aiming at exploring their possible application, these novels reversible ATPS were applied in the selective extraction/separation of textile dyes, namely sudan III and PB27 or sudan III and PB29. Selective extraction efficiencies higher than 80 % for sudan III and PB29 with the ATPS composed of [Ch][Ac], [Ch][Prop] and [Ch]Cl were achieved. On the other hand, lower extraction efficiencies were observed with the selective separation of sudan III and PB27 although higher than those observed with the ATPS composed of ILs and salts. These results reveal that IL-polymer ATPS are of a reversible nature and can be envisaged as a more environmentally-benign option for the treatment of wastewaters contaminated with textile dyes.

5. Final remarks

5.1. Conclusions

In this work it was demonstrated that IL-based ATPS are a potential alternative for the treatment of wastewaters contaminated with textile dyes.

As a first approach, the ability of more conventional IL-based ATPS for the extraction of three textile dyes (chloranilic acid, indigo blue and sudan III) was evaluated. The results obtained reveal that the complete extraction of the dyes, extraction efficiencies up to 100 %, can be obtained in a single-step procedure by a proper tailoring of the IL and salt nature. In general, phosphonium-based ATPS lead to higher partition coefficients and extraction efficiencies than their imidazolium-based counterparts.

After establishing the high ability of IL-based ATPS to remove dyes from aqueous media, it was demonstrated the reversibility behaviour of IL-salt-based ATPS, at least for three times, and their outstanding capacity to selectively separate two dyes (sudan III and PB27) for opposite phases. The reversibility behaviour was achieved by a pH-driven phenomenon through the manipulation of the speciation of the organic salt used.

Finally, the selective efficiency of IL-polymer ATPS on the extraction of sudan III, PB27 and PB29 was studied. The results obtained reveal that these systems are reversible by the speciation of the IL anion and the respective acid and are able to selectively separate two pairs of dyes: sudan III/PB27 and sudan III/PB29. For the first set of dyes extraction efficiencies for opposite phases higher than 80 % where obtained for most of the systems evaluated.

The novel evidences demonstrated here clearly confirm that low-cost and low toxic reversible ATPS composed of ILs can be formed with high potential for the selective separation of dyes from the wastewaters of textile industries.

5.2. Future work

Based on the results gathered in this work it will be interesting to further explore and to continue the study on the development of novel reversible ATPS composed of ILs. These can be achieved with other salts, other polymers and even with protic ILs where the speciation trend is also easy to attain. Moreover, their potential applicability in the selective separation of other added-value compounds, besides the textile dyes studied here, is of outmost importance. In particular, their particular application in the separation of biopharmaceuticals or natural compounds from more complex matrices seems to be the step to follow.

Finally, and to further support the sustainable character of the ATPS investigated, it will be important to ascertain on the phase-forming components recovery and reusability.

6. References

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- A. M. Ferreira, A. F. M. Cláudio, J. A. P. Coutinho, A. M. Fernandes and M. G. Freire*, pH-triggered reversible aqueous biphasic systems composed of ionic liquids and organic salts*, (in preparation).
- A. M. Ferreira, J. A. P. Coutinho, A M Fernandes and M. G. Freire, *Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems*, Sep. Purif. Technol. (2013) (Submitted for publication).
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Appendix A

Experimental binodal data

A.1. Experimental binodal data for systems composed of IL + salt + H_2O used in the extraction of dyes

Table A.1.1. Experimental weight fraction data for the system composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O (3) at 298 K and at atmospheric pressure.

$[P_{4444}]Br$					
$M_w = 339.3350$					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
51.2054	2.7774	22.1335	10.7752	13.3589	14.9436
46.0250	3.7720	21.3909	10.8461	12.9051	15.2856
41.2637	4.5008	20.8937	11.0318	12.5616	15.3901
39.6199	5.1429	20.4987	11.1598	12.2666	15.6394
36.7642	5.9195	19.9260	11.5587	11.9834	15.7520
33.3185	6.8030	19.3560	11.7659	11.5868	16.0676
31.2465	7.4340	18.6758	12.0712	11.2310	16.3761
29.9311	8.1018	17.9083	12.5040	10.7738	16.5972
29.0453	8.3757	17.1944	12.8168	10.5388	16.8678
28.4225	8.4537	16.5369	13.1794	10.2420	17.0877
27.5378	8.7553	15.9963	13.2846	9.9183	17.3378
26.5969	9.1913	15.7280	13.3633	9.6669	17.5626
26.1587	9.2654	15.3466	13.6447	9.3651	17.8264
24.9759	9.6407	14.8970	13.8781	8.9408	18.2411
24.3121	9.9300	14.2094	14.3895	8.6094	18.5469
23.5626	10.1176	13.8656	14.5471		
23.0361	10.4889	13.6138	14.6947		

Table A.1.2. Experimental weight fraction data for the system composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O (3) at 298 K and at atmospheric pressure.

$[P_{i(444)1}][Tos]$ $M_w = 385.5220$					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
53.5336	6.6908	15.9723	15.0872	9.6285	17.5388
47.9469	7.2178	15.7041	15.1619	9.4927	17.6061
44.7024	7.6756	15.2515	15.5076	9.3383	17.7529
39.5386	8.4601	14.9748	15.5536	9.1646	17.7972
37.0977	9.0046	14.6917	15.5992	8.9972	17.8805
35.3901	9.5142	14.4536	15.6645	8.8580	18.0122
33.9527	9.9528	14.2367	15.7347	8.6934	18.0595
32.6468	10.2838	14.0002	15.7746	8.5321	18.1443
31.4171	10.6446	13.7826	15.8239	8.3893	18.2275
29.2493	11.2542	13.5388	15.8467	8.2866	18.3061
28.2339	11.4356	13.4026	15.9878	8.0969	18.4345
27.2772	11.6635	13.1972	16.0699	7.9045	18.5259
26.5128	11.7871	12.9837	16.0865	7.7340	18.6723
25.0733	12.1510	12.8104	16.1394	7.6074	18.7141
24.3185	12.4134	12.6293	16.1943	7.4897	18.7605
23.5845	12.5445	12.4917	16.3085	7.3528	18.9741
22.9763	12.7841	12.3345	16.2466	7.1900	19.1161
22.4133	12.9515	12.2070	16.3762	7.0357	19.1880
21.8546	13.1370	12.0277	16.4137	6.8939	19.2861
21.3143	13.2322	11.9084	16.5287	6.7686	19.4435
20.9475	13.4843	11.7270	16.5626	6.6502	19.4365
20.4430	13.6008	11.5662	16.6102	6.5296	19.5608
19.9234	13.7892	11.4402	16.7279	6.4029	19.6444
19.4655	13.9128	11.2921	16.7607	6.2875	19.7288
19.0260	14.0292	11.1794	16.8581	6.1782	19.8506
18.5666	14.1352	11.0141	16.8688	6.0216	20.0598
18.2528	14.3779	10.8014	17.0319	5.8555	20.1627
17.8730	14.4621	10.6733	17.0914	5.7535	20.2380
17.4661	14.5013	10.4387	17.1533	5.6672	20.3351
17.2202	14.6845	10.3083	17.1602	5.5517	20.4874
16.8790	14.7872	10.1256	17.2967	5.4060	20.6199
16.5103	14.8551	9.9421	17.4456		
16.2908	15.0240	9.7436	17.5355		

Table A.1.3. Experimental weight fraction data for the system composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O (3) at 298 K and at atmospheric pressure.

[C_4mim][Tos]					
M_w = 310.4220					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
76.5364	1.7167	17.3671	20.1048	10.0371	24.7323
66.6935	3.4220	17.1566	20.1787	9.8975	24.7863
39.5795	10.2758	16.9401	20.2928	9.7399	24.9172
37.8640	10.6455	16.7293	20.3712	9.6410	25.0299
36.8974	11.0812	16.5399	20.4496	9.5210	25.0885
35.8420	11.4687	16.3434	20.5496	9.4179	25.2076
34.9614	11.8804	16.0837	20.7798	9.2782	25.2471
33.7284	12.7914	15.9116	20.8635	9.1837	25.3436
32.3024	12.8622	15.7479	20.9802	9.0736	25.4666
31.5806	13.1822	15.5970	21.0076	8.9864	25.5550
30.9180	13.5003	15.3721	21.1829	8.8697	25.5939
30.2660	13.7923	15.0401	21.3313	8.7863	25.6823
29.6230	14.1261	14.8038	21.5665	8.6951	25.7984
29.0006	14.4361	14.5077	21.7351	8.5937	25.8591
28.4889	14.6829	14.2219	21.8147	8.5124	25.9590
27.8921	14.9202	13.9545	22.1280	8.4412	26.0258
27.3948	15.1332	13.6924	22.2400	8.3622	26.1054
26.8600	15.3835	13.4673	22.3534	8.2633	26.1390
26.3859	15.5781	13.2886	22.5063	8.1869	26.2296
25.9518	15.8069	13.0485	22.5811	8.1156	26.3101
25.0385	16.2305	12.8811	22.7379	8.0356	26.4110
24.6547	16.3592	12.6524	22.8889	7.9167	26.4923
24.0378	16.8543	12.4787	23.0254	7.8031	26.5793
23.3250	17.0801	12.2878	23.1503	7.6937	26.6945
22.6259	17.4918	12.1608	23.1324	7.5946	26.8220
21.9862	17.6853	12.0137	23.2741	7.4922	26.9018
21.4000	17.9221	11.9088	23.3237	7.4110	27.0323
21.0743	18.0687	11.7768	23.4442	7.3090	27.0971
20.7226	18.2482	11.6844	23.4780	7.1935	27.2235
20.2985	18.5919	11.5438	23.6264	7.0959	27.3142
19.7411	18.8027	11.3640	23.7045	6.9552	27.4941
19.4646	18.9148	11.2260	23.8437	6.8731	27.5463
19.0746	19.1983	11.0672	23.9120	6.7814	27.6329
18.8377	19.3017	10.8510	24.1155	6.7299	27.6898
18.5878	19.3819	10.7165	24.2165	6.6774	27.7537
18.3624	19.4835	10.5078	24.3981	6.6292	27.8071

Table A.1.4. Experimental weight fraction data for the systems composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O (3) at 298 K and at atmospheric pressure.

$[C_2mim][CF_3SO_3]$ M_w = 260.2260		$[P_{4441}][CH_3SO_4]$ M_w = 358.5200	
100 w_1	100 w_2	100 w_1	100 w_2
60.9879	5.3370	19.0878	18.0162
47.7790	8.0288	18.6400	18.1830
40.1960	9.9859	18.2238	18.3045
35.0475	11.6191	17.6277	18.7794
31.9615	12.0822	16.3075	19.6538
30.3081	12.8534	12.5893	22.0649
28.8209	13.4909	11.7742	22.4587
27.1495	14.1739	11.1081	22.8166
18.5898	18.5102	10.1293	23.9271
17.2233	19.4502	9.0064	25.0558
16.1300	20.4838	7.7989	26.3301
14.5170	21.7256	6.9569	27.3046
13.1816	22.5504	6.1678	28.2098
11.2206	24.7092	5.2036	29.7303
8.8396	27.5867	4.2707	31.3776
7.6313	29.5087	3.4033	33.4308
6.1529	32.5501	2.5234	35.3110

A.2. Experimental binodal data for the reversible IL-based ATPS systems composed of IL + salt + H_2O

Table A.2.1. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

$[C_4C_1mim]Cl$							
M_w = 188.6998							
pH ≈ 9				pH ≈ 8			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
17.5639	39.8362	41.8435	15.1113	22.4236	35.3274	43.5522	13.9208
20.0557	37.4146	42.6419	14.5066	23.3368	33.4880	44.0532	13.5694
21.6310	35.2678	43.1248	14.0310	26.1175	30.6571	44.7276	13.0196
23.6885	33.0411	43.9949	13.4263	27.8648	28.8437	45.1257	12.7364
25.6583	31.0179	44.7581	12.8835	28.7956	27.7530	45.7717	12.2850
26.5884	29.8473	45.8031	12.2799	29.9169	26.9052	46.4527	11.7919
27.6666	28.4244	46.4520	11.8184	30.7609	25.6530	47.1620	11.3652
29.1333	26.8809	47.0710	11.3796	32.6215	23.9410	48.2544	10.6519
30.6602	25.3975	47.5449	11.0071	34.7080	22.2041	48.7955	10.2831
31.9121	24.1263	48.1635	10.6226	35.4705	21.1840	49.1995	9.9937
32.9990	22.9993	48.6019	10.3021	36.1866	20.3259	49.8791	9.5702
33.8364	22.0619	49.0689	9.9799	37.4028	19.2026	50.7905	9.0487
35.7135	20.6511	49.5037	9.6697	38.4585	18.3004	51.9121	8.4121
36.7707	19.6852	50.0581	9.3561	39.3304	17.5438	52.5663	7.9932
37.4674	18.9073	50.5745	9.0419	39.8576	16.9852	53.2454	7.6860
38.2935	18.1959	49.8258	9.1656	40.3881	16.5001	53.7612	7.4004
39.1099	17.4737	53.1731	7.3481	41.2282	15.8913	54.4843	7.0120
39.6331	16.9411	56.8969	5.3008	41.7614	15.4316	59.8442	4.8006
40.3374	16.3041	59.9870	3.7771	42.5672	14.7401	80.7466	1.5373
40.9630	15.7582			43.0529	14.3983		

Table A.2.2. Experimental weight fraction data for the systems composed of IL (1) + salt (2) + H_2O (3) at 298 K and at atmospheric pressure.

$[C_4C_1mim]Cl$					
M_w = 188.6998					
pH ≈ 7					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
22.4236	35.3274	39.3304	17.5438	47.1620	11.3652
23.3368	33.4880	39.8576	16.9852	48.2544	10.6519
26.1175	30.6571	40.3881	16.5001	48.7955	10.2831
27.8648	28.8437	41.2282	15.8913	49.1995	9.9937
28.7956	27.7530	41.7614	15.4316	49.8791	9.5702
29.9169	26.9052	42.5672	14.7401	50.7905	9.0487
30.7609	25.6530	43.0529	14.3983	51.9121	8.4121
32.6215	23.9410	43.5522	13.9208	52.5663	7.9932
34.7080	22.2041	44.0532	13.5694	53.2454	7.6860
35.4705	21.1840	44.7276	13.0196	53.7612	7.4004
36.1866	20.3259	45.1257	12.7364	54.4843	7.0120
37.4028	19.2026	45.7717	12.2850		
38.4585	18.3004	46.4527	11.7919		

Table A.2.3. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

$[C_4mpip]Cl$					
M_w = 191.7410					
pH ≈ 8		pH ≈ 7		pH ≈ 6	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
18.5918	34.7445	19.1288	34.2900	27.7645	27.8446
20.8318	32.2317	21.7665	31.4809	29.1664	25.8716
22.1675	30.4867	23.7906	29.1489	30.3075	24.5749
24.0414	28.4860	25.3628	27.2222	32.1771	22.5954
25.6902	26.6967	27.2252	25.2342	33.3385	21.3135
27.5645	24.7879	29.2963	23.1948	34.8580	19.8117
28.9116	23.3592	30.9309	21.5805	38.9572	16.7164
30.4896	21.8523	32.7478	19.8526	40.0301	15.6677
31.2913	20.9193	33.9099	18.7602	41.2147	14.5968
32.4779	19.8362	35.3521	17.4506	42.6312	13.4330
33.6068	18.7931	36.9450	16.1302	43.9236	12.4418
34.9018	17.6500	37.9718	15.2572	45.4226	11.3171
36.1462	16.5798	39.0318	14.3832	47.8643	9.6811
38.5627	14.5789	40.3601	13.3873	52.7397	4.6158
39.4598	13.8450	41.5498	12.4932	64.4868	1.6150
40.5345	13.0524	42.3966	11.8384		
41.7785	12.1531	43.5867	11.0112		
44.0910	10.6062	45.2099	9.9857		
44.7628	10.0927	46.5449	9.1533		
45.9167	9.3553	47.7960	8.3586		
46.8941	8.7397	50.9636	6.6636		
48.9936	7.6139	56.2140	3.5958		
49.5723	7.0979	63.3822	2.2685		
53.5122	5.0866				
68.5290	1.7860				

Table A.2.4. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[C_4mpy]Cl M_w = 185.6940						[C_4mim]Cl M_w = 174.6550	
pH ≈ 8		pH ≈ 7		pH ≈ 6		pH ≈ 8	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w1	100 w2
16.9273	35.6444	21.5771	31.7416	22.2059	33.7680	16.2015	39.7620
18.2660	34.0265	24.2457	28.8622	24.4832	31.2751	18.0449	37.5680
20.2400	32.0472	26.7603	26.2502	26.6514	28.8265	20.6275	34.6616
21.3891	30.6210	29.0774	23.9020	28.4713	26.7850	23.0347	32.3024
22.9234	29.0184	31.0846	21.9179	30.0789	24.9885	24.9579	30.2246
24.9414	27.2426	33.0890	20.0474	31.4671	23.4530	26.6832	28.3980
25.7217	26.2342	36.1432	17.4650	33.1138	21.9288	28.7878	26.3575
26.9441	25.0526	38.6748	15.4201	34.4902	20.5712	30.0575	24.9217
28.0943	23.9309	41.3471	13.3668	35.8826	19.2143	31.9690	23.2300
29.1787	22.9104	31.9968	20.1813	36.9922	18.1436	33.4293	21.8732
30.1656	21.9762	37.4888	15.6438	38.1765	17.1090	34.3020	20.9736
31.4095	20.9305	40.8707	13.1594	39.4551	15.9860	35.3888	19.9772
32.2430	20.1809	45.7972	9.8627	40.4175	15.1589	36.5283	19.0168
33.0047	19.4386	48.1307	8.5136	41.5049	14.2939	37.2610	18.3318
34.0095	18.5780	50.9816	6.9487	42.4770	13.5260	38.2071	17.5459
34.8891	17.8234	53.4026	5.8067	43.1374	13.0487	39.0233	16.8121
35.6641	17.1577	63.1170	2.4657	44.2086	12.2774	39.8134	16.1412
36.4912	16.5136	72.4823	1.2649	45.4020	11.4464	41.0238	15.3058
37.2162	15.9302			46.4700	10.6942	41.9017	14.6291
38.0505	15.2839			47.8241	9.8384	42.7254	14.0282
38.9771	14.8442			49.2084	9.0043	43.6995	13.3455
39.4575	14.4938			74.1362	1.2936	44.7233	12.6910
40.0736	13.9930					45.3943	12.1682
42.6186	12.0720					46.1959	11.6223
45.2390	10.4137					46.8467	11.1724
47.2672	9.2799					47.3296	10.8433
49.6622	7.8588					48.0030	10.4235
51.2425	7.1413					48.6208	10.0248
53.0469	6.2975					49.1136	9.7075
54.7933	5.4977					49.7471	9.3290
56.6343	4.6807					50.2986	9.0019
58.4954	3.8956					50.7863	8.7038
75.3583	0.9345					51.3774	8.3611
						62.9106	2.7942
						71.8110	1.5504

Table A.2.5. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

$[P_{4444}]Cl$

M_w = 294.8840

pH ≈ 8

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.5547	5.1133	21.9022	16.7962	11.3907	25.1182
51.3753	5.7210	21.0825	17.4168	11.1177	25.4472
47.5050	6.4933	20.0351	18.1653	10.8229	25.6632
43.0923	7.0668	18.9056	18.9747	10.5643	25.9218
40.1382	7.7242	18.4039	19.2313	10.2648	26.2606
38.2240	8.4985	17.8655	19.6852	10.0261	26.4734
35.8977	9.0434	17.1444	20.3577	9.8045	26.7087
34.5148	9.7294	16.2847	21.0846	9.5972	26.8828
33.2760	10.2711	15.2364	21.7508	9.1832	27.2877
32.3099	10.6881	14.7070	22.2491	9.0141	27.4496
31.2601	11.0874	14.4866	22.3586	8.8087	27.6920
29.6716	12.1152	13.9772	22.8716	8.4320	28.1528
28.6393	12.4888	13.6519	23.0838	8.3148	28.2237
27.3283	13.2994	13.2699	23.4331	8.2061	28.2859
25.9506	14.2791	13.0134	23.6562	7.9859	28.5354
25.1962	14.5425	12.7424	23.8372	7.7987	28.7652
24.1979	15.3099	12.3581	24.1644	7.6536	28.9181
23.6382	15.6013	12.0469	24.5081	7.4963	29.1136
23.1173	15.8606	11.7097	24.8224	7.3494	29.2819

Table A.2.6. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[P_{4444}]Cl					
M_w = 294.8840					
pH ≈ 6					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
41.5610	9.4338	17.6874	21.6882	10.0606	27.3306
39.8025	10.0148	16.8498	22.1895	9.8021	27.5614
38.1769	10.5583	16.2087	22.6783	9.5076	27.8837
36.8672	10.8672	15.4576	23.3484	9.3654	28.0262
35.4010	11.3902	15.0291	23.6087	9.1816	28.1641
33.8517	12.0940	14.5723	23.9605	9.0279	28.3228
32.6151	12.6011	14.0916	24.3544	8.9228	28.3978
31.0253	13.4039	13.5857	24.7420	8.6930	28.6809
29.8230	13.8782	13.0761	25.2134	8.4773	28.8730
28.5100	14.6504	12.9396	25.2058	8.3147	29.0162
27.1956	15.4978	12.6996	25.3586	8.1654	29.1964
25.8070	16.1369	12.4731	25.4425	7.9760	29.3996
24.6101	16.8965	12.2056	25.4959	7.7789	29.5979
23.4508	17.7110	11.8010	25.8939	7.6032	29.7881
22.3471	18.3558	11.5617	26.0623	7.3574	30.0296
21.4818	18.8986	11.2675	26.3211	7.1839	30.2386
20.5104	19.5391	11.0216	26.4946	6.9413	30.4722
19.6346	20.2063	10.7197	26.7594	6.7763	30.6786
19.1031	20.6049	10.4980	26.9721	6.6610	30.7860
18.3677	21.1999	10.2920	27.1530	6.5208	30.9234

Table A.2.7. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[P$_{4444}$]Cl					
M_w = 294.8840					
pH ≈ 5					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.7084	4.1732	18.3660	24.0994	9.9574	30.8217
52.3413	5.3498	17.4716	24.8313	9.6061	31.1558
41.1731	9.4540	16.5868	25.4299	9.2556	31.4689
38.4940	10.7645	15.6178	26.2426	8.9596	31.7383
36.2354	11.9482	14.8823	26.7742	8.6081	32.1045
34.3652	13.0916	14.1684	27.3257	8.3384	32.3654
32.2713	14.1512	13.6598	27.7164	8.0661	32.6489
29.5863	15.9934	13.0798	28.1534	7.5930	33.1546
27.3230	17.6217	12.4625	28.7098	7.1679	33.5836
25.3565	18.9943	12.0134	29.0412	6.8786	33.8693
23.5731	20.2839	11.5925	29.3615	6.5060	34.3004
21.8258	21.5693	11.1492	29.7298	6.1373	34.7029
20.5767	22.5930	10.7012	30.1348	5.7658	35.1614
19.4395	23.3356	10.3057	30.4901		

Table A.2.8. Binodal weight fraction data for IL (1) + salt (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[C$_4$mim]Br							
M_w = 219.1220							
pH ≈ 8				pH ≈ 6			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
74.6692	1.7071	14.7402	31.1274	13.1289	40.9277	42.5059	13.0330
62.2292	3.5899			14.6369	37.8062	42.8610	12.7617
55.7952	4.5687			15.4353	36.7627	43.2331	12.5204
53.7379	5.4895			16.6319	35.4319	43.5518	12.2803
52.4385	6.0282			18.0233	34.0131	43.9026	12.0745
51.1184	6.5971			18.6667	33.2197	44.2004	11.8618
49.2717	7.6222			19.9499	32.0458	44.6306	11.5841
47.9687	8.3090			21.4402	30.7913	45.0522	11.3258
46.8307	8.7596			22.6211	29.6228	45.3365	11.1196
45.6325	9.3666			23.4683	28.6192	45.8005	10.8714
43.9663	10.2978			24.7265	27.5343	46.1277	10.6633
42.5776	11.0643			26.1772	26.3980	46.4046	10.4826
41.4969	11.7464			26.9795	25.6396	46.6931	10.2876
40.4967	12.3258			27.5439	25.0612	46.9333	10.1271
39.2647	13.0520			28.6331	24.2187	47.2513	9.9269
38.3023	13.6647			29.3257	23.5222	47.4015	9.7540
36.8416	14.6905			30.4280	22.7180	47.7184	9.5641
35.3456	15.7034			30.9947	22.1325	48.0615	9.3802
34.2934	16.4524			31.6755	21.5690	48.3586	9.2140
33.0183	17.3642			32.4393	20.8683	48.6681	9.0465
31.1062	18.8453			32.8501	20.4090	48.9684	8.8754
30.2517	19.3823			33.3331	19.9721	49.2857	8.7043
28.7960	20.4784			34.0746	19.4849	49.6341	8.5348
27.8623	21.1637			34.4802	19.0562	50.0614	8.2920
27.0973	21.7318			35.3174	18.4711	50.8046	7.8751
26.6466	22.0029			35.6522	18.0907	51.1411	7.7314
25.9514	22.5344			36.3547	17.6037	51.3609	7.6091
25.2505	23.0745			36.7720	17.2347	51.6497	7.4731
24.1415	23.9091			37.5590	16.7515	52.0009	7.3234
23.5451	24.3393			37.8739	16.4092	52.2130	7.2098
20.8741	25.2211			38.4874	16.0096	52.5221	7.0811
20.2310	25.7807			38.7591	15.6990	52.9099	6.8869
19.5592	26.3928			39.2165	15.3895	53.5474	6.5863
18.3783	27.4884			40.0778	14.7448	54.9257	6.0009
17.0936	28.7205			40.9810	14.0989	56.2662	5.4754
16.3846	29.4266			41.3850	13.8069	58.0126	4.7360
15.5370	30.3036			41.8287	13.5066	69.9374	1.6121

A.3. Experimental binodal data for systems composed of PPG 400 + IL + H_2O

Table A.3.1. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch]Cl M_w = 139.6240							
pH ≈ 6		pH ≈ 5		pH ≈ 4		pH ≈ 3	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
59.7532	4.1395	52.8723	5.5387	52.7824	5.9084	58.3564	5.3205
49.4185	5.3248	46.4150	6.4181	42.9307	7.1386	49.2396	6.3663
35.8966	6.9097	40.7974	7.1892	39.2582	7.7223	40.4128	7.3836
32.4552	7.4524	36.8239	7.6400	36.4770	7.9673	31.6416	9.6679
29.6019	8.2317	33.6122	8.3820	34.5635	8.3681	28.8933	10.3231
26.7506	9.4906	27.6148	10.3735	31.2450	9.3932	27.0617	11.0236
24.4788	10.5980	25.7613	10.9259	28.4750	10.1740	25.6632	11.8768
18.4968	13.3364	23.7786	11.8542	26.2602	11.1482	21.7211	13.9509
17.5558	14.0857	22.2997	12.6928	24.6853	12.1823	20.4996	14.8983
16.6818	14.8366	20.9626	13.5935	23.0535	13.0662	19.2025	15.8738
15.5831	15.9160	19.8542	14.4509	21.8673	13.7015	18.0334	16.3081
14.8640	16.7543	18.5097	15.7845	20.4640	14.8041	17.1847	17.2285
14.3194	17.0226	17.1164	16.7403	19.3719	15.2737	16.0937	18.0482
13.6968	17.6815	15.8749	17.9693	18.2690	16.1415	15.5562	18.3674
13.2829	18.1224	15.1095	18.6685	15.6427	17.4720	15.0386	18.9172
12.8191	18.3980	14.1274	19.8070	14.3531	19.0349	14.5618	19.4484
12.4294	18.8661	13.1325	20.6890	13.3947	19.9554	14.0055	20.0191
0.0000	0.0000	12.2130	21.6637	12.6118	20.9712	13.5096	20.3838
11.6097	19.9104	11.5915	22.4241	11.9627	21.6976	13.1025	20.7967
11.1937	20.2424	10.7515	23.4144	11.4323	22.2675	12.5953	21.3281
10.7458	20.7799	10.0731	24.4786	10.8227	23.0596	12.0384	21.8452
10.4340	21.0027			10.2984	23.7361	11.6476	22.2494
10.0677	21.4114					11.1255	22.9989
9.6171	22.0911					10.6908	23.6781
9.3013	22.5695					10.2762	24.0234
8.9851	22.9893					9.9460	24.4708
8.6572	23.3424					9.5722	25.0197
8.3524	23.6269						
8.0836	24.0514						
7.7731	24.3902						

Table A.3.2. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch]Cl M_w = 139.6240						[Ch][Ac] M_w = 163.2148	
pH ≈ 2		pH ≈ 1		pH ≈ 0		pH ≈ 9	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
46.7755	6.9008	57.0021	5.8068	53.9184	6.1384	62.2434	2.5662
40.8679	7.2435	48.8889	6.4576	45.7955	7.3566	53.3027	3.6444
34.6006	8.5195	43.0007	7.1546	39.9227	8.3976	45.0223	4.2765
32.1922	9.0772	39.2462	8.0611	24.4734	13.0221	40.2374	4.8220
30.1997	9.7495	24.0966	13.6377	23.0218	13.9407	35.7533	5.5826
28.5268	10.7455	22.9697	13.9400	21.5591	15.0802	32.3194	5.9866
26.2866	11.6911	21.5344	14.6861	20.0394	16.0374	30.3054	6.3806
24.4148	12.5483	20.0900	15.3788	18.7397	16.8646	28.0351	6.8690
22.6845	13.6216	19.2542	15.9541	17.7027	17.7139	23.8764	7.8872
21.0476	14.9172	18.2562	16.6517	16.7640	18.5601	22.4079	8.4851
19.0809	16.3731	17.3228	16.9136	15.6210	19.4367	20.7062	9.2137
17.5593	17.5620	16.2446	17.9112	14.7004	20.4285	19.2778	9.9999
16.2876	18.5948	15.2223	18.6531	13.9119	21.0559	16.0776	11.1828
15.5805	19.4104	14.2998	19.7305	13.1692	21.9370	15.4904	11.4911
14.8130	20.2956	13.5687	20.5798	12.4195	22.6066	14.9912	11.8453
14.0085	21.2632	12.8833	20.8624	11.8282	23.3835	14.4345	12.3824
13.4975	21.8212	12.5215	21.2633	11.0677	24.1862	13.8961	12.6638
12.9722	22.3954	12.0080	21.8916	10.5670	24.7267	13.3943	12.9397
				9.9752	25.7119	12.9830	13.4865
						12.4644	13.9071
						12.0131	14.2372
						11.6145	14.5842
						11.1326	14.8984
						10.8677	15.1538
						10.5030	15.5629
						10.1721	15.9009
						9.8193	16.2896
						9.4237	16.6121
						8.9030	17.6248
						8.6957	18.0559

Table A.3.3. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch][Ac] M_w = 163.2148							
pH ≈ 8		pH ≈ 7		pH ≈ 6		pH ≈ 5	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
54.6031	5.0394	56.4943	6.8460	48.0396	9.5022	54.1295	9.8833
48.8655	6.0096	51.4596	7.7135	46.2564	9.9356	51.0816	11.6533
29.9665	11.8524	47.5712	8.3634	44.6495	10.7930	49.3503	13.3356
27.9906	12.7336	44.6179	9.2990	43.3274	11.0511	46.2413	14.5185
26.6476	13.4651	34.2213	10.9544	40.6562	11.9750	42.4865	18.0246
24.7729	13.9703	32.3083	11.2973	39.1273	12.7216	39.4951	20.9362
23.3359	14.6873	30.9894	11.7560	37.7614	13.7091		
22.0874	15.1576	29.4847	12.0318	36.7350	14.0281		
20.6967	15.8834	28.5021	12.4839	35.3484	14.8988		
19.4767	16.8004	27.5649	12.9219	34.5000	15.2042		
18.2613	17.3891	26.6191	13.4923	33.2758	16.0089		
17.3460	17.8304	25.0059	14.1441	31.7019	16.4039		
16.3928	18.4987			30.5723	17.4661		
15.5605	19.0674			28.6270	18.7499		
14.8769	19.3999			26.9100	19.9894		
				25.2884	21.4396		
				23.5715	23.2259		
				22.2588	24.7318		
				20.9626	25.8128		
				19.6128	27.7123		
				18.3490	29.6039		
				17.0761	31.8186		
				15.6422	34.9359		

Table A.3.4. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch][Pro] M_w = 177.2414							
pH ≈ 8		pH ≈ 7		pH ≈ 6		pH ≈ 5	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
44.5952	5.7175	56.4943	6.8460	55.5307	8.2453	61.4200	8.8946
41.3783	6.1279	51.4596	7.7135	51.6542	9.3539	56.8397	11.2466
34.4822	6.8389	47.5712	8.3634	49.8029	10.3037	52.4439	12.9165
32.4571	7.1200	44.6179	9.2990	46.8573	11.2386	50.1136	13.6458
31.1750	7.4391	34.2213	10.9544	44.4757	11.7993	47.5044	15.5158
27.6950	8.6203	32.3083	11.2973	42.6258	12.5584	45.3968	17.0625
26.3713	8.9673	30.9894	11.7560	40.6863	13.2181		
24.7850	9.7275	29.4847	12.0318	35.6820	14.9487		
23.1773	10.0498	28.5021	12.4839	34.2739	15.3597		
21.9820	10.7785	27.5649	12.9219	32.6688	16.1998		
20.5827	11.3181	26.6191	13.4923	31.3793	16.3884		
19.3680	11.6819	25.0059	14.1441	30.4884	16.8421		
18.4598	12.2914	23.9300	14.7874	29.8749	17.5404		
17.2735	12.6296	22.7203	15.4359	29.0650	17.8387		
16.5801	13.1291	21.4602	16.4649	27.9969	18.9169		
15.7179	13.7294	20.0449	17.4179	27.0550	19.7528		
14.8602	14.4935	18.7946	18.1425	26.0586	20.4862		
13.9646	15.0787	17.4092	19.0483				
13.3363	15.3438	16.6174	19.6840				
12.6596	15.9378	15.7684	20.4511				
12.1134	16.4191	14.8904	21.1748				
11.4332	17.1174	14.1233	21.8795				
11.0200	17.5610	13.3370	22.9640				
10.4604	18.1920	12.5012	23.9935				
9.9837	18.6085	11.6981	25.2076				
9.5463	19.0402	10.7417	27.0962				
9.1016	19.5564						

Table A.3.5. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch][But] M_w = 191.2414							
pH ≈ 8		pH ≈ 7		pH ≈ 6		pH ≈ 5	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
53.7438	6.4849	53.2194	8.2470	55.5565	10.1883	63.5970	12.2093
41.4257	7.9477	49.0677	8.7056	52.4686	10.9727	58.8795	13.3721
38.5059	8.5858	43.3820	9.8970	50.2901	11.7508	55.4079	14.2592
36.7404	9.0032	41.4811	10.3504	46.3183	12.8915	52.8001	14.9857
35.3450	9.2535	39.6983	10.7545				
33.4556	9.7941						
31.1496	10.2126						
29.2204	10.5930						
27.5838	10.9168						
26.2754	11.6103						
20.8215	13.3207						
19.4545	13.9915						
17.8966	14.7195						
16.7536	15.3331						
15.6362	16.1611						
14.3498	17.2106						

Table A.3.6. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch][Lac]							
M_w = 193.2408							
pH ≈ 7		pH ≈ 6		pH ≈ 5		pH ≈ 4	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
56.9575	3.5283	58.7605	4.7414	46.7239	9.1828	54.8035	11.3515
0.0000	5.8800	56.0807	5.4008	44.6863	9.9975	50.4094	14.4250
35.5059	6.2014	53.6867	5.8983	43.2509	10.3578	46.9767	16.8815
33.0561	6.6436	50.0782	6.3409	41.5848	10.9828	44.1931	18.7172
30.0739	7.6275	48.2521	6.8630	35.2355	13.0357	41.5404	20.4667
26.6982	8.4305	45.0155	7.5570	33.2873	13.9893	38.7645	22.5816
23.8971	9.0050	42.3031	8.0129	31.2925	14.8492	35.8946	25.0858
22.0381	9.5716	39.8886	8.3647	29.7590	15.5212	33.5717	27.1607
20.4718	10.5160	38.5278	8.7424	27.9996	16.3845	31.7752	28.8225
19.1057	11.3305	37.3275	9.1039	25.9459	17.6506		
17.6568	12.1084	36.1461	9.4873	24.4075	18.4441		
16.4701	12.6995	34.2409	9.8379	21.0115	21.2016		
15.6712	13.0326	32.7047	10.2688	19.8296	21.9969		
14.9078	13.5705	31.0008	10.7548	18.5687	22.7285		
14.1921	14.1030	28.7951	11.5977	17.4251	23.7080		
13.5151	14.5670	26.8138	12.5599	16.2915	24.7439		
13.0089	15.0409	25.0422	13.3312	15.6619	25.4254		
12.3006	15.5938	23.3603	14.0865	14.7127	26.3039		
11.7019	15.9777	22.2641	14.9301	13.5136	27.6597		
11.1916	16.5126	20.9622	15.7390	12.6090	28.8469		
10.7446	16.9131	19.7527	16.4743	11.6030	30.3170		
10.3590	17.2277	18.5438	17.4251	10.9748	32.0263		
9.9392	17.6969	17.2843	18.1701	10.1309	33.1935		
9.5100	18.0761	16.2173	18.8301	9.2899	34.5470		
		15.4649	19.4988				
		14.5479	20.1697				
		13.6239	20.9971				
		12.8825	21.5915				
		12.1359	22.6195				
		11.1002	23.4026				
		10.3702	24.4070				
		9.6582	25.0032				
		8.7701	26.0296				

Table A.3.7. Binodal weight fraction data for PPG 400 (1) + IL (2) + H_2O (3) system at 298 K and at atmospheric pressure.

[Ch][Gly]					
M_w = 179.2142					
pH ≈ 7		pH ≈ 6		pH ≈ 4	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
62.9671	3.1708	59.7877	4.9948	57.8111	6.7937
51.3010	4.0717	51.4078	5.9067	51.0564	8.0817
43.8295	5.1693	46.3200	6.6792	47.5512	9.0382
36.9375	5.7690	42.8885	7.3476	44.5361	10.0949
28.0324	7.2200	39.8920	7.9482	41.6892	10.8792
25.7823	7.6551	37.0065	8.4363	39.8818	11.7668
24.0925	8.1523	34.5014	8.8010	37.6512	12.2464
22.4759	9.0019	32.6456	9.3662	34.0591	13.6205
20.8381	9.6107	30.6550	9.6897	31.3547	14.6370
19.3942	10.3030	28.7295	10.7020	28.8978	15.6352
18.1418	11.0393	26.4707	11.4722	27.6539	15.9857
16.9162	11.7583	24.7902	12.0716	25.8482	16.8336
15.9441	12.3304	23.6134	13.3213	23.9382	18.1751
15.0238	12.7526	22.2632	13.7163	22.4799	19.2959
14.2388	13.4776	20.5797	15.4497	20.7106	20.5423
13.5185	13.7305	19.3834	15.9492	19.2389	21.3595
12.8304	14.3680	18.1396	17.0536	17.9515	22.7080
12.1284	14.8950	16.7612	17.7890	16.6972	23.6229
11.4602	15.6133	16.0667	18.3390	15.4629	24.7914
10.8353	16.0448	15.0440	19.5769	14.4042	26.0293
10.2723	16.6132	13.9212	20.1407	13.3780	27.3638
9.6447	17.1678	12.4944	22.3703	12.4233	28.5322
		11.5647	23.1238	11.2612	30.4304
		10.8146	23.7316	10.3707	31.4536
		9.9253	24.4484		

Appendix B

Additional experimental data

B.1. Additional data for the ATPS composed of ILs and salts

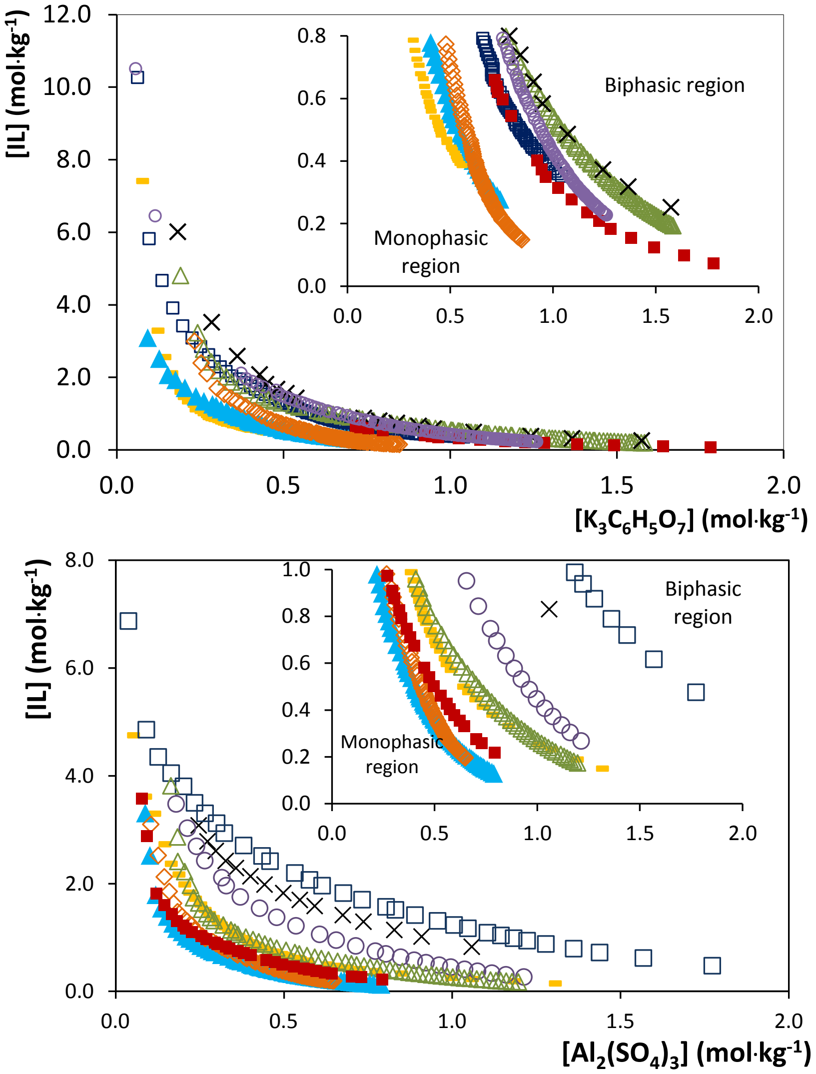

Figure B.1.1. Ternary phase diagrams for systems composed of IL + salt + water at 298 K and atmospheric pressure: (×) [C_2mim][CF_3SO_3], (–) [C_4mim][CF_3SO_3], (□) [C_4mim][$N(CN)_2$], (○) [C_4mim][Tos], (△) [P_{4444}]Cl, (▲) [P_{4444}]Br, (■) [P_{4441}][CH_3SO_4] and (◇) [$P_{i(444)1}$][Tos].

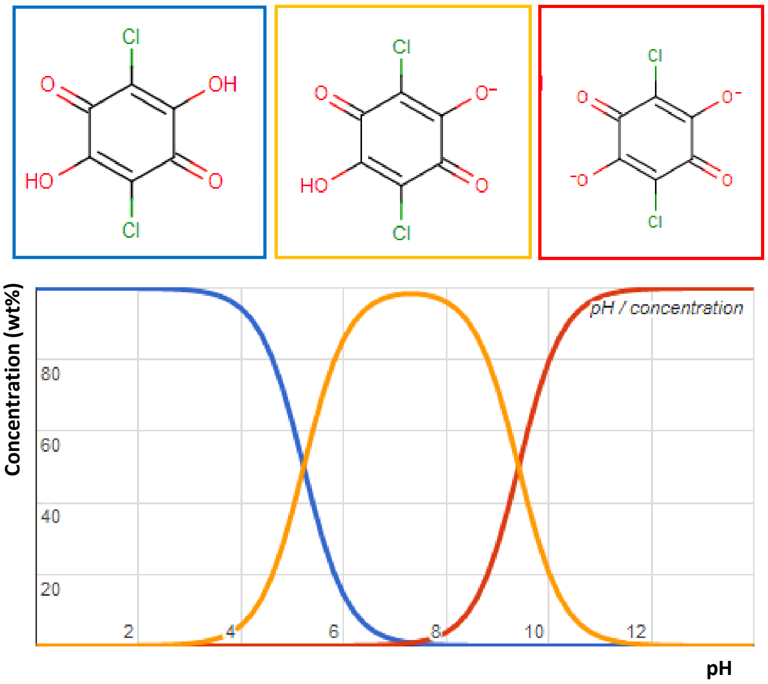

Figure B.1.2. Speciation curve of chloranilic acid as a function of pH [79].

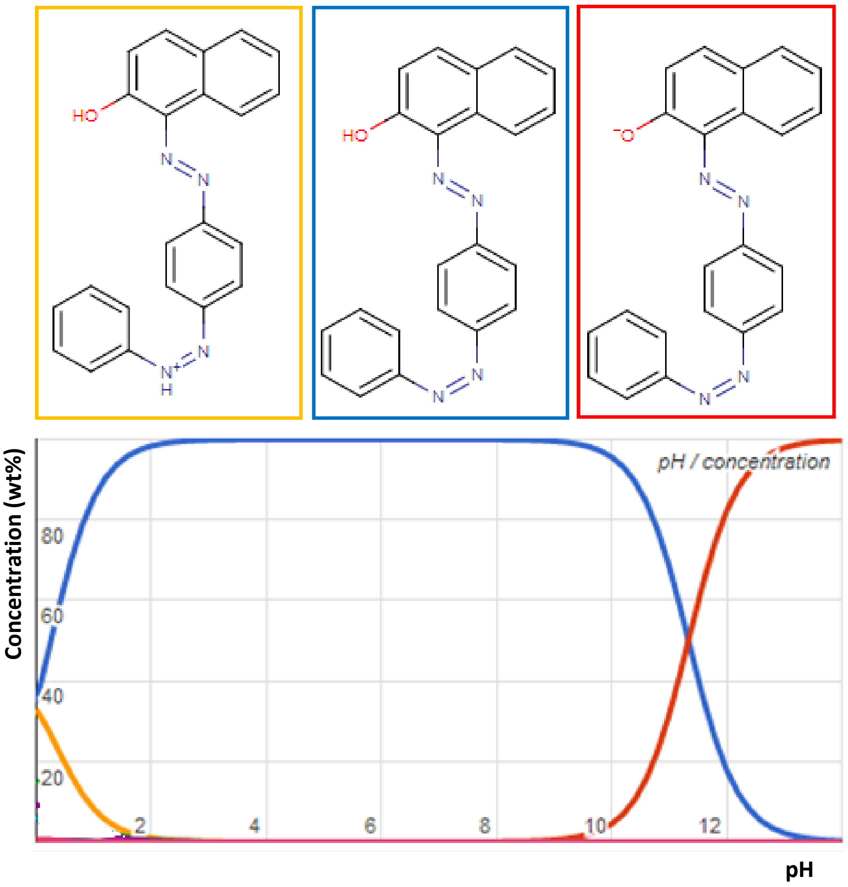

Figure B.1.3. Speciation curve of indigo blue as a function of pH [79].

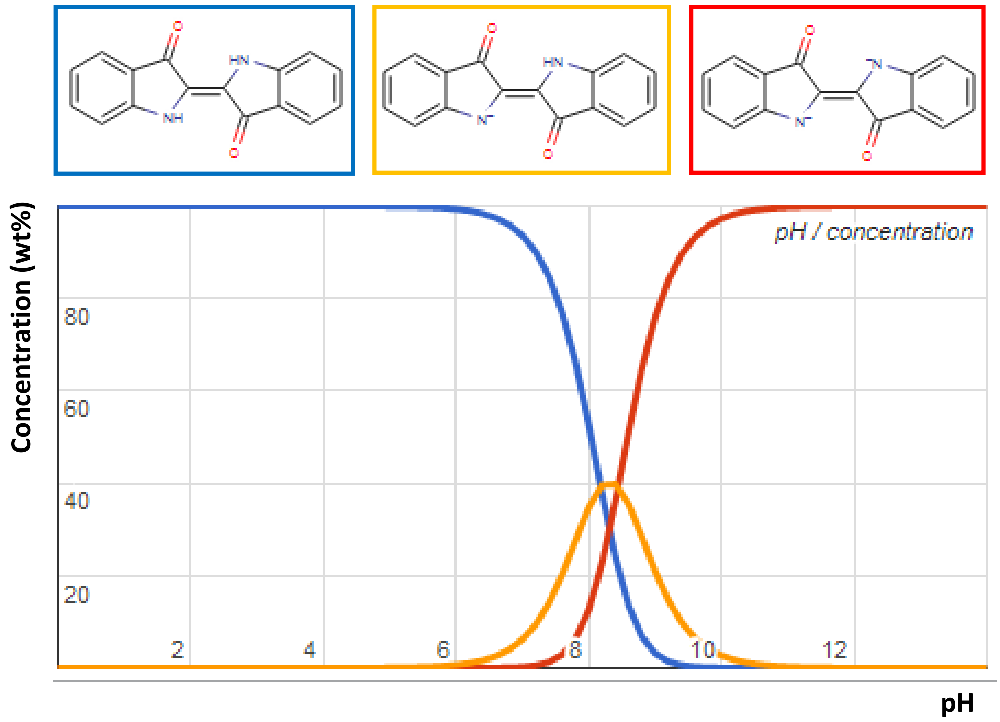

Figure B.1.4. Speciation curve of sudan III as a function of pH [79].

B.2. Additional data for the reversible IL-salt-based ATPS

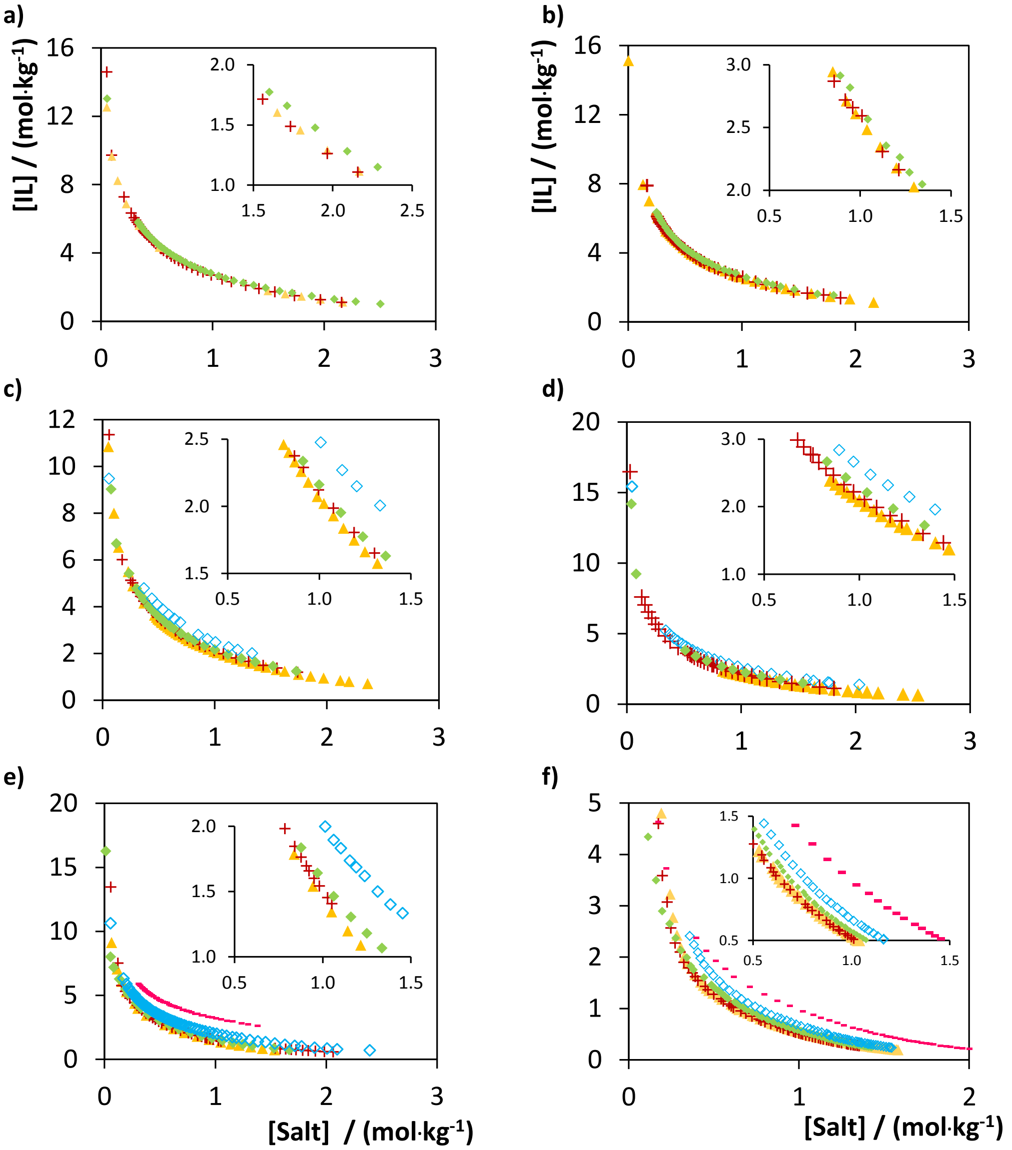

Figure B.2.1. Evaluation of the pH effect in ternary phase diagrams composed of IL + water + $K_3C_6H_5O_7$/ $C_6H_8O_7$ at (▲) pH ≈ 9, (+) pH ≈ 8, (◆) pH ≈ 7, (◇) pH ≈ 6 and (▬) pH ≈ 5. The ILs are: (a) [C_4mim]Cl, (b) [C_4C_1mim]Cl, (c) [C_4mpip]Cl, (d) [C_4mpy]Cl, (e) [C_4mim]Br and (f) [P_{4444}]Cl. Some phase diagrams have been reported by other authors and are included here for comparison purposes [81, 89, 126].

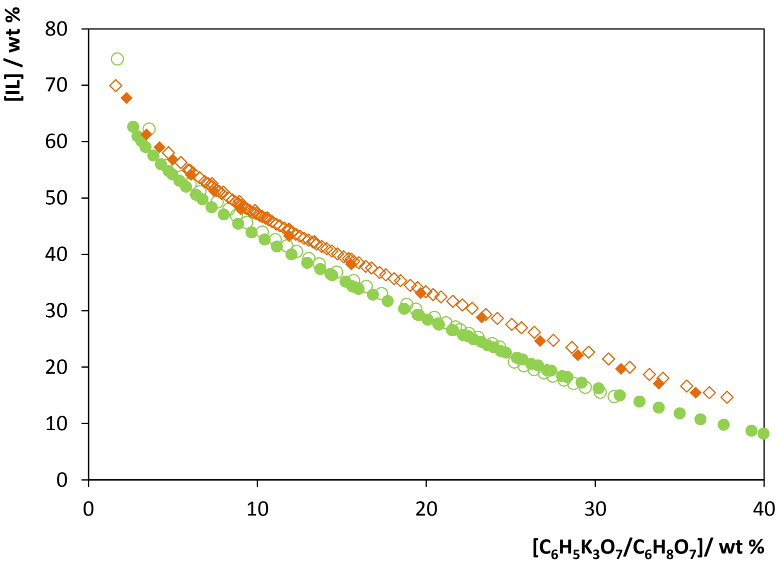

Figure B.2.2. Phase diagram for the ternary system composed of [C_4mim]Br + $K_3C_6H_5O_7$/$C_6H_8O_7$ +H2O, (◇) pH ≈8 and (○) pH ≈6 at 298 K. The full symbols represent the data obtained in this work while the empty symbols correspond to literature data [89].

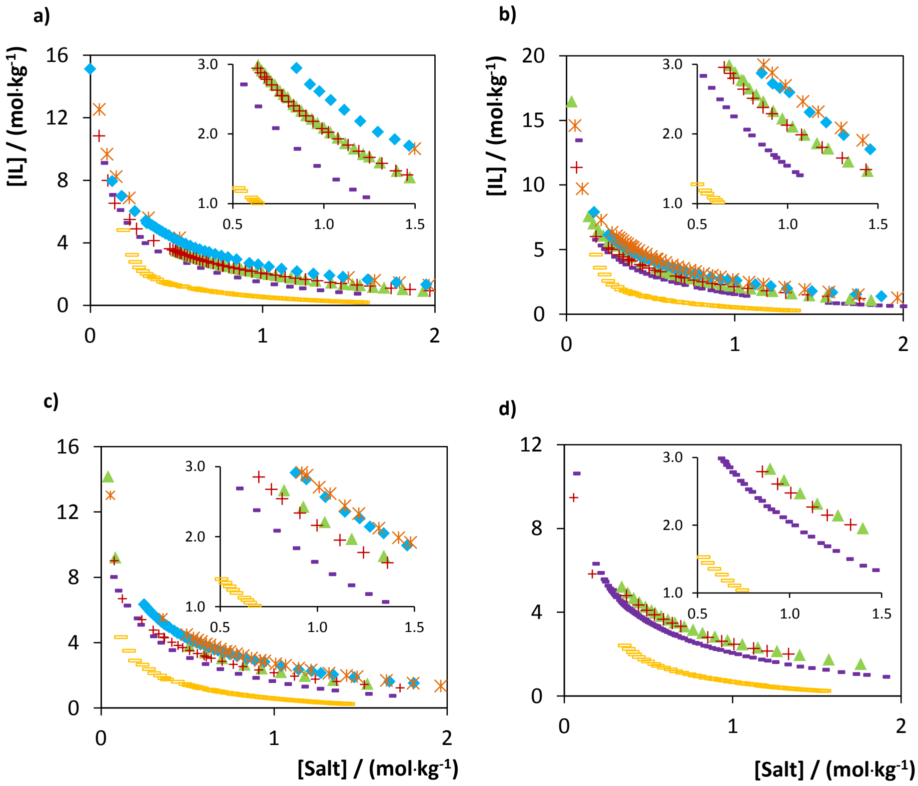

Figure B.2.3. Phases diagrams for the different ILs at fixed pH. Phase diagrams of ATPS composed of IL + water + $K_3C_6H_5O_7$ at (a) pH ≈ 9 and ATPS composed of IL + water + $K_3C_6H_5O_7$/$C_6H_8O_7$ at (b) pH ≈ 8, (c) pH ≈ 7 and (d) pH ≈ 6. The ILs used are: (✳) [C_4mim]Cl, (♦) [C_4C_1mim]Cl, (+) [C_4mpip]Cl, (▲) [C_4mpy]Cl, (▬) [C_4mim]Br and (▭) [P_{4444}]Cl.

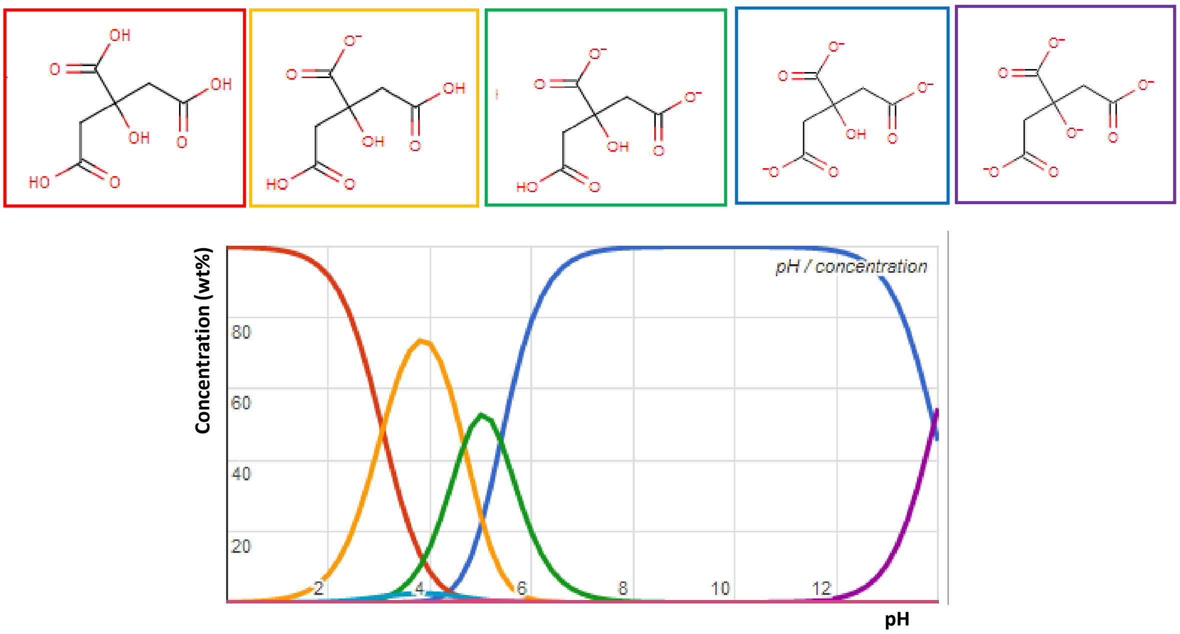

Figure B.2.4. Speciation curve of acid citric as a function of pH [79].

B.3. Additional data for the reversible IL-polymer-based ATPS

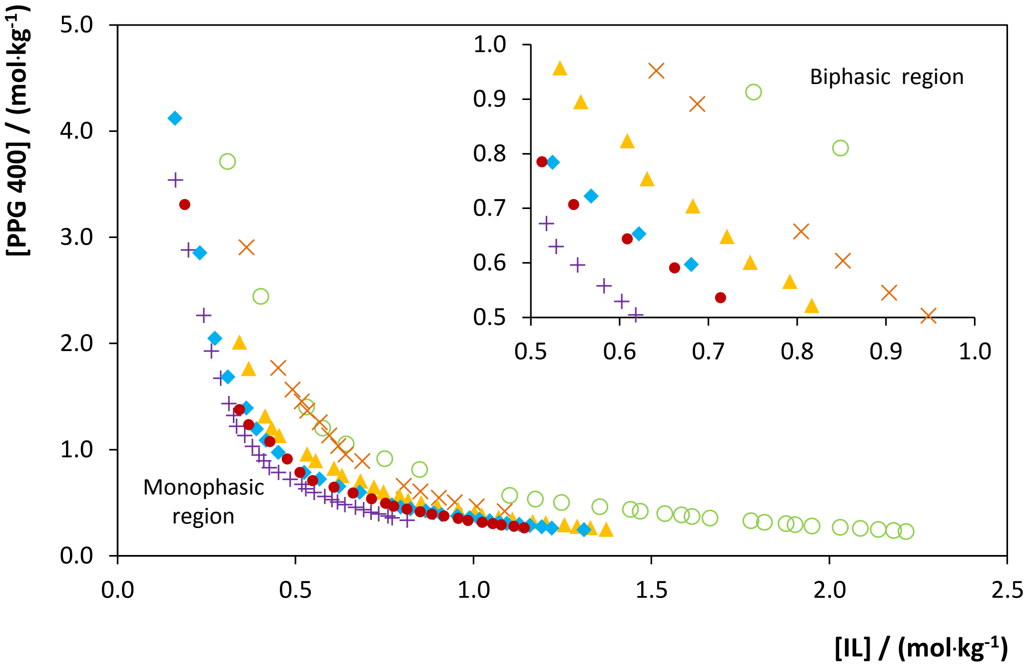

Figure B.3.1. Ternary phase diagrams for systems composed of PPG 400 + IL + water at 298 K and atmospheric pressure. The ILs studied were: (×) [Ch][But], (○) [Ch]Cl, (▲) [Ch][Pro], (●) [Ch][Lac], (◆) [Ch][Ac] and (+) [Ch][Gly].

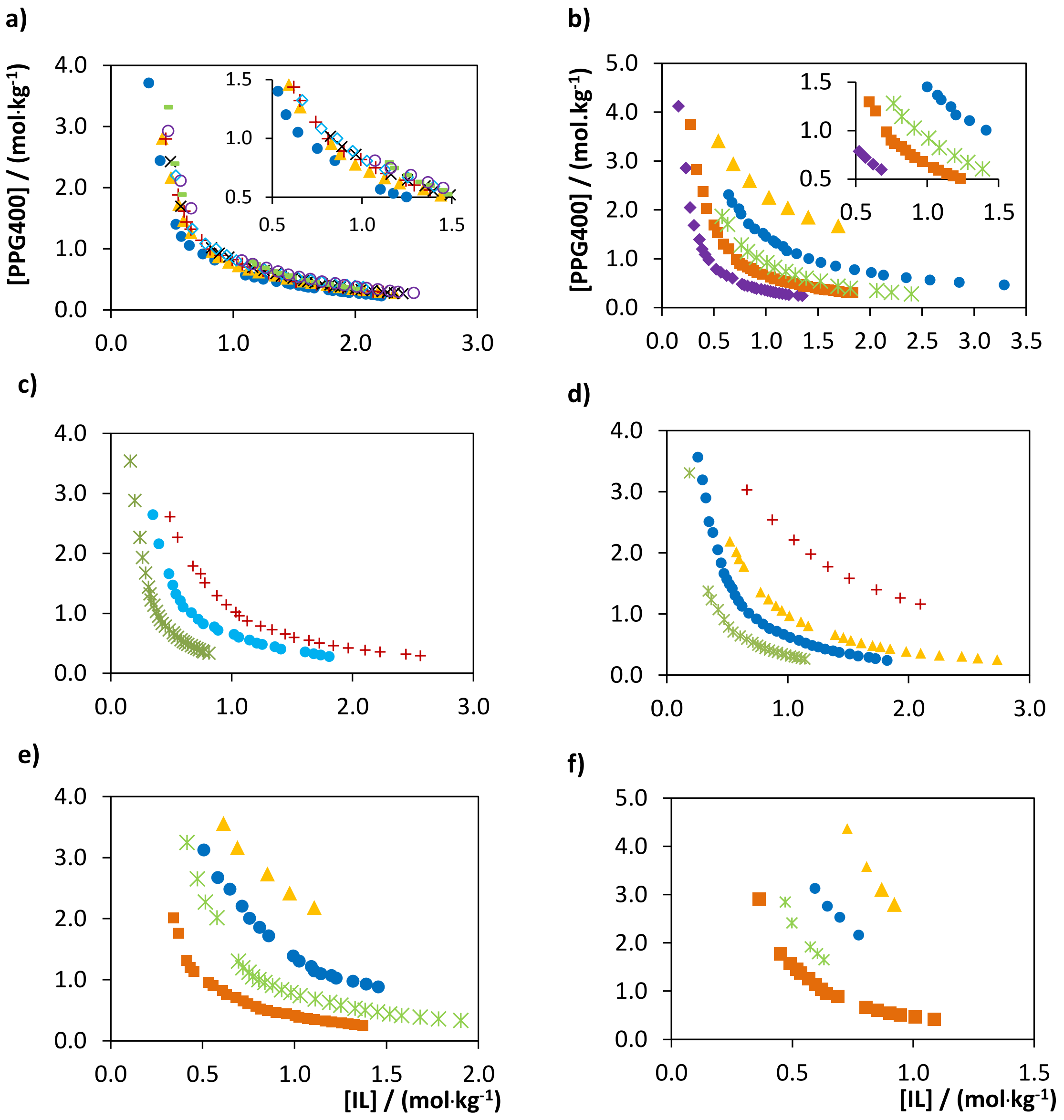

Figure B.3.2. Evaluation of the pH effect in ternary phase diagrams composed of PPG 400 + water + IL at (♦) pH ≈ 9, (■) pH ≈ 8, (✳) pH ≈ 7 , (●) pH ≈ 6, (▲) pH ≈ 5, (✚) pH ≈ 4, (×) pH ≈ 3, (◊) pH ≈ 2, (—) pH ≈ 1 and (○) pH ≈ 0. The ILs are: (a) [Ch]Cl, (b) [Ch][Ac], (c) [Ch][Gly], (d) [Ch][Lac], (e) [Ch][Prop], and (f) [Ch][But].