



Phase diagrams of ionic liquids-based aqueous biphasic systems as a platform for extraction processes



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ABSTRACT

In the past few years, ionic liquid-based aqueous biphasic systems have become the subject of considerable interest as a promising technique for the extraction and purification of several macro/biomolecules. Aiming at developing guidelines for more benign and efficient extraction processes, phase diagrams for aqueous biphasic systems composed of ionic liquids and inorganic/organic salts are here reported. Several combinations of ionic liquid families (imidazolium, pyridinium, phosphonium, quaternary ammonium and cholinium) and salts [potassium phosphate buffer ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ at pH 7), potassium citrate buffer ($\text{C}_6\text{H}_5\text{K}_3\text{O}_7/\text{C}_6\text{H}_8\text{O}_7$ at pH 5, 6, 7 and 8) and potassium carbonate (K_2CO_3 at pH ~ 13)] were evaluated to highlight the influence of the ionic liquid structure (cation core, anion and alkyl chain length), the pH and the salt nature on the formation of aqueous biphasic systems. The binodal curves and respective tie-lines reported for these systems were experimentally determined at (298 ± 1) K. In general, the ability to promote the aqueous biphasic systems formation increases with the pH and alkyl chain length. While the influence of the cation core and anion nature of the ionic liquids on their ability to form aqueous biphasic systems closely correlates with ionic liquids capacity to be hydrated by water, the effect of the different salts depends of the ionic liquid nature and salt valency.

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1. Introduction

Aqueous biphasic systems (ABS) are usually formed as a result of the mutual incompatibility in aqueous solution of two polymers, one polymer and one salt, or two salts above a certain concentration [1]. These systems are mainly composed by water and thereby capable to provide an excellent environment for a large set of cells and biologically active substances. In this way, ABS are commonly investigated for the extraction and purification of distinct (bio)molecules, such as proteins [2–6] and amino-acids [7–12]. They allow a high effectiveness, high yield, improved purity degree, a proper selectivity, technological simplicity and low cost [13]. Furthermore, ABS are considered as environmentally friendly techniques, since volatile organic solvents are not employed in the whole process [14]. The application of polymer-based ABS is well-documented [15–18], nevertheless, most of these aqueous systems present high viscosities, form opaque systems and are considered as limited techniques in terms of the range of polarities of the coexisting phases [19]. There has been, therefore, an effort to find new liquid–liquid alternatives, mainly in the application of distinct and non-polymeric ABS.

In the last decade, the use of ionic liquids (ILs) as a new agent in the formation of ABS has attracted a considerable interest as promising “greener” alternatives to volatile and hazardous organic solvents. This increasing attention is largely justified by their unique properties, such as their negligible vapor pressure, high chemical and thermal stability, their non-flammability, high ionic conductivity, wide electrochemical potential window and high solvation ability. In fact, these ionic compounds are normally known by their tunable properties, which mean that they can be designed for a specific purpose by the selection of the adequate cation/anion combination. Moreover, and allied with their tunable character, the use of ILs in the formation of ABS allows the possibility of tailoring their polarities and affinities by the organization of the ions in the bulk [20].

The use of ILs in the formation of ABS grew steadily [21,22] since in 2003 Rogers and co-workers [23] reported, for the first time, that hydrophilic ILs had the capacity to form ABS in the presence of some inorganic salts. Different lines of research were considered when studying the use of ILs as ABS promoting agents [21,22] namely, the study of the salt type, where phosphate [8–10,23–33], hydrogenophosphate [8,25,26,28,34,35], sulfate [25,27,30,36] and carbonate [8,25,27,32,37,38] and a range of other salts [21,39] were applied, as well as carbohydrates [7,40], polymers [41,42], amino-acids [43,44], and more recently anionic surfactants [45]. Furthermore, recent studies have introduced

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citrate-based salts in the formulation of IL-based ABS because they are more biodegradable and less toxic than most other salts [46–48]. Nevertheless, on most of these liquid–liquid extraction systems, the pH is not adequately controlled, which is a crucial issue regarding the separation or purification of some particular biomolecules, namely proteins [49] and enzymes [50]. Only recently, the inorganic potassium phosphate buffer (K_2HPO_4/KH_2PO_4) and the organic potassium citrate buffer ($C_6H_5K_3O_7/C_6H_8O_7$) solutions (both at pH 7), have been focus of interest among researchers considering not only their ability to form ABS when conjugated with ILs, but also their applicability while extraction and purification systems for several biomolecules [2,6,34,49–54].

Another aspect of major importance when considering the IL-based ABS formation is the study of the impact of the different ILs, not only in what concerns the use of several cations families [21], the imidazolium being one of the most investigated [41,55],

but also considering the effect of the cation alkyl side chain length [8,10,56] and finally, different anions [24,51]. More recently, and since the number of new IL families is increasing, some works concerning the use of new families, such as the acyclic phosphonium, quaternary ammonium and, more recently, the cholinium-based ILs, were reported [9,57–59].

Taking into account the significant extraction efficiencies achieved recently for paracetamol [53] and natural dyes [49] in presence of ammonium compounds, a study on the expansion of the range of ionic liquid-based aqueous biphasic systems (IL-ABS) as a platform for extraction processes is here reported. For that purpose imidazolium-, pyridinium-, phosphonium-, ammonium- and cholinium-based ILs were evaluate toward their ability to form ABS in presence of potassium phosphate buffer (KH_2PO_4/K_2HPO_4), potassium citrate buffer ($C_6H_5K_3O_7/C_6H_8O_7$) and potassium carbonate (K_2CO_3) solutions.

This work is divided into four main sections: (i) the first addresses the pH influence; (ii) the second reports the impact of different cation cores, (iii) the third describes the influence of the cation side alkyl chain length and anion effect, and the (iv) addresses the salt effect. In this context, it was chosen to evaluate one inorganic salt (K_2CO_3 at pH ~ 13) and two buffers with different ionic strength: the organic and benign potassium citrate buffer ($C_6H_5K_3O_7/C_6H_8O_7$ at pH 5, 6, 7 and 8) and the inorganic potassium phosphate buffer (KH_2PO_4/K_2HPO_4 at pH 7).

TABLE 1
Identification and purity of all ILs studied.

Ionic liquids		
Name	Acronym	Purity (wt%)
Tetraethylammonium chloride	[N _{2,2,2,2}]Cl	98
Tetrapropylammonium chloride	[N _{3,3,3,3}]Cl	98
Tetrapropylammonium bromide	[N _{3,3,3,3}]Br	98
Tetrabutylammonium chloride	[N _{4,4,4,4}]Cl	97
Tetrabutylammonium bromide	[N _{4,4,4,4}]Br	98
Choline salicylate	[Ch][Sal]	95
Benzyl dimethyl(2-hydroxyethyl) ammonium chloride	[BCh]Cl	97
Tetrabutylphosphonium chloride	[P _{4,4,4,4}]Cl	96.8
Tetrabutylphosphonium bromide	[P _{4,4,4,4}]Br	95.2
Tributyl(methyl)phosphoniummethylsulfate	[P _{4,4,4,1}][CH ₃ SO ₄]	98.6
Triisobutyl(methyl)phosphoniumtosylate	[P _(4,4,4,1)][Tos]	99
1-Butyl-3-methylimidazolium chloride	[C ₄ mim]Cl	99
1-Butyl-3-methylpyridinium chloride	[C ₄ mpy]Cl	98

2. Experimental section

2.1. Materials

In this work, thirteen distinct ILs were investigated in terms of their capacity for ABS formation in conjugation with three salts. Their full name, acronym and purities are presented in table 1, being their respective ionic structures depicted in figure 1.

Phosphonium- and cholinium ILs were purchased from Cytec and Fluka, respectively and the ammonium-based ILs were acquired at Sigma–Aldrich. The [C₄mim]Cl and [C₄mpy]Cl were from

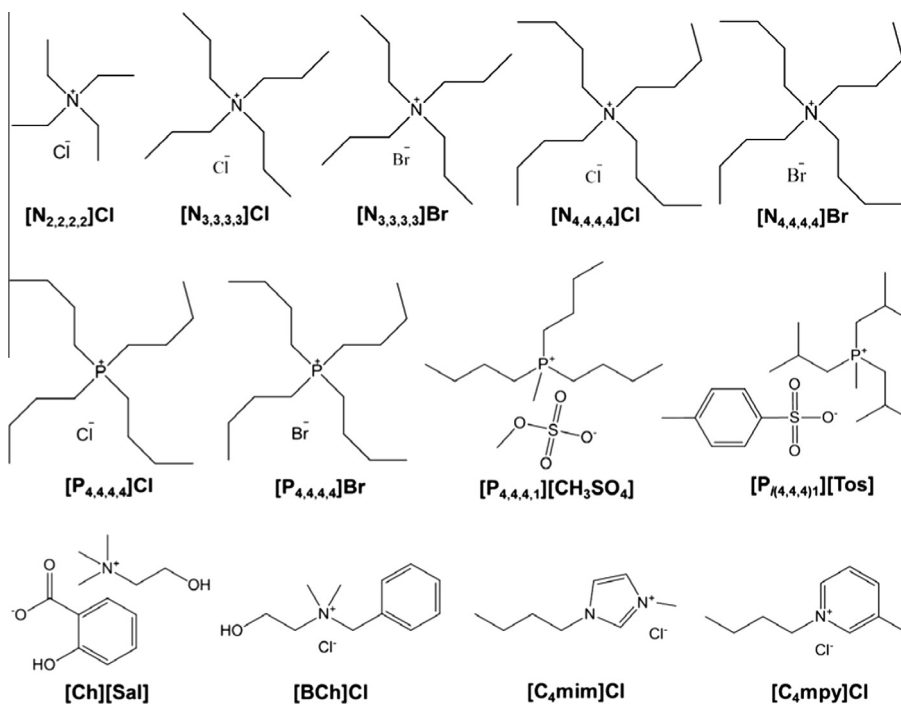


FIGURE 1. Chemical structure of the ILs studied.

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