Evaluation of anion chain length impact on aqueous two phase systems formed by carboxylate anion functionalized ionic liquids

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ABSTRACT

Aqueous biphasic systems (ABS) based on ionic liquids (ILs) are considered as promising separation and extraction media for replacing conventional extraction systems consisting of volatile organic solvents. In the present work, set of ILs consisting of tetrabutylammonium cation and carboxylate anions were synthesised and studied for their ability to form ABS in presence of strong salting-out agent K_3PO_4 at 298.15 K and atmospheric pressure. The influence of alkyl chain length of ILs' anions on the phase splitting ability has been systematically investigated. Experimentally determined binodal curve data has been fitted to Merchuk's equation and corresponding fitting parameters have also been determined. Further, selected ternary systems have been analysed for their extraction efficiencies for an amino acid, Tryptophan. Solvatochromic parameters of aqueous solutions of ILs have been determined to further scrutinize their influence on extraction efficiencies of studied ABS. The results indicated that phase behaviour and extraction efficiencies are governed by multiple factors prevailing at microscopic level like hydrophobicity, hydrogen bond accepting ability etc. The combination of suitable cation and anion entities of ILs, in turn, decides the dominant physical phenomenon and consequent phase behaviour and extraction aptitudes. In addition, this work addresses the effect of temperature on ABS formation and temperature dependence similar to that of ABS consisting of polymers and inorganic salts have been observed. This work gives insights into multifaceted effects of longer alkyl chains of IL's anion on phase behaviour and extraction aptitudes of IL based ABS.

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1. Introduction

Aqueous biphasic systems (ABS) have gained substantial amount of interest among both academia and research community as promising alternatives for classical organic solvents based solvent extraction systems like liquid-liquid extractions (LLE). The unique advantage of ABS over traditional organic separation systems is the existence of water in abundance in both phases. ABS consist of aqueous solutions of appropriate pairs of solutes that split into two co-existing phases under certain concentrations. Conventional ABS are either composed of two incompatible polymers for example like polyethylene glycol and dextran or polymers and inorganic salts as proposed by Albertsson [1]. In recent years, the range of combinations has extended beyond salt-salt to comprise other type of compounds like amino acids, proteins, sugars, surface active substances in combination with either polymers or salts also were reported to form ABS [2–5]. Out of variable

combinations, ABS formed by two salts have gained significant interest and are explored to greater extent in recent past and out of these two salts, one is generally of high charge density and consequently gets hydrated strongly in comparison to another salt. Salts consisting of ions with delocalized charges result in lower melting temperature and such salts fit into the category of Ionic Liquids (ILs). In general, ILs also known as molten salts were found to be fairly efficient in the formation of ABS [2,6].

ILs have kindled the interest of research community pertaining to various arenas including but not limited to chemistry, biotechnology, chemical engineering etc., The substantial interest created by ILs can be attributed to their interesting and engaging features like low volatility, higher solvation capacity for a wide range of compounds, wide liquid temperature range, possible structure modulations to suit desired applications and also to tune polarities and physicochemical properties [7–11]. Further, ILs are considered to have undisputed benefits in various fields like bioengineering, electrochemistry, analytical chemistry, surface and catalysis science etc. [12–14]. Thus improved features of ILs allow them to be better replacements for usual volatile, flammable and harmful molecular solvents used in traditional LLE.

ABS provides mild environment due to abundant quantities of water and consequent lower surface tension and biocompatibility of these systems [15]. Therefore they are most compatible for separation and extractions of biomolecules. The most significant and unique advantage with respect to IL based ABS is that ILs enable the customisation of ABS to suit specific separation and extraction by manipulating cation and anion combinations [16]. Thus, ILs coupled ABS open a wide horizon for generation of novel and improved systems for separation of metabolites of biological and industrial interest [16–19].

In recent years, a large amount of work has been devoted to ABS based on ILs in combination with inorganic salts [20–21] taking the lead from the reports by Rogers and co-workers [2]. The most studied classes of ILs includes imidazolium [22], pyridinium, piperidinium, quaternary ammonium and phosphonium ILs etc [16]. In combination with ILs, different types of salts ranging from inorganic salts [23,24] to organic salts [25,26] have also been explored. Nevertheless preliminary research focussed on the formulation of phase diagrams of ABS based on various classes of ILs and to study effects of multiple factors including structures of ILs, salt effect, temperature, pH etc, [16,27–30] eventually emphasis has shifted more towards designing suitable systems for extraction of value added compounds [17].

However, understanding various factors that govern phase splitting as well as extraction behaviour is of utmost importance for making a right choice of cations and anions. Various researchers have systematically investigated the influence of cation core and their alkyl side chain length on phase behaviour [16]. Few studies have also focussed on the effect of anions and their chain length [20,23] and have indeed concluded that IL anions with lower hydrogen bond basicity readily undergo phase splitting. A recent study based on ILs composed of choline cation and fatty acid anions [31] has reported excellent phase splitting ability and extraction efficiencies for long chain anion functionalized ILs due to their favourable hydrogen bond basicity values calculated based on Kamlet-Taft parameters [32–34]. Thus, it is crucial to study and develop a clear understanding of factors governing phase behaviour at microscopic level in order to account for observed behavioural trends.

In this context, the present work aims at providing useful insights into the mechanisms that control phase behaviour with particular emphasis on understanding the effect of anion chain length on the formation of ABS. To fulfil this objective, we have synthesised ILs based on Tetrabutylammonium [TBA] cation and carboxylate anions of variable chain length ranging from butanoate to decanoate and investigated the phase behaviour of their ternary systems in combination with strong salting out agent, K_3PO_4 and water at 298.15 K and atmospheric pressure. For comparison purpose, IL consisting of TBA cation and bromide anion has also been included in the current study. Further, these ternary systems have also been analysed for their extraction abilities for aminoacids, a class of most useful bioproducts, by considering Tryptophan as an example. Further, the influence of anion chain length on phase formation has been analysed with the support of additional insights provided by Kamlet-Taft parameters.

Liquid liquid extraction systems consisting of either both organic or organic and aqueous phases display strong dependence on temperature and therefore is an important parameter to be analysed. Further, the temperature induced phase transitions in IL containing systems have been exploited in separation of useful organic products, metals, catalysts [35] as well as for bioactive compounds like proteins [36]. In this context, number of studies related to the effect of temperature has amplified over years [37–39]. These studies indicated that most IL based ABS exhibit upper critical solution temperature (UCST) behaviour similar to polymer–polymer ABS and very few systems showed lower critical solution temperature (LCST) behaviour. However, considering the importance of temperature as one of the determining factor of phase formation and extraction capabilities, temperature variant studies remain insufficient and unfathomed for many classes of ILs. In current study, we attempted to understand the effect of temperature on studied ternary systems and their phase behaviour. We have determined phase diagrams at different temperatures and tried to correlate the experimentally observed behaviour to that observed in already reported systems in terms of UCST or LCST behaviour.

2. Experimental methods

2.1. Materials

For the synthesis of ILs used in present study, Tetrabutylammonium hydroxide (40%) aqueous solution and six carboxylic acids namely butanoic, pentanoic, hexanoic, heptanoic, octanoic and decanoic acid were used. Details of chemical suppliers, purity and CAS numbers are enlisted as Table 1. The salting out agent used for phase determination i.e. Tripotassium phosphate, K_3PO_4 (≥98%) and Tryptophan (≥98%) used in extraction experiments were supplied by Sigma Aldrich. For the preparation of all aqueous solutions, ultra-pure water treated by Milli Q3 purification system with resistivity of 18.2 MΩ.cm at 25 °C was used.

2.2. Synthesis and characterisation of ionic liquids

All studied ILs namely Tetrabutylammonium butanoate [TBA][But], Tetrabutylammonium pentanoate [TBA][Pent], Tetrabutylammonium hexanoate [TBA][Hex], Tetrabutylammonium heptanoate [TBA][Hept], Tetrabutylammonium octanoate [TBA][Oct] and Tetrabutylammonium decanoate [TBA][Dec] were synthesised via acid base neutralization method. The model synthesis method for tetra butyl ammonium butanoate is described here. For the synthesis of [TBA][But], stoichiometric quantities of butanoic acid and tetrabutylammonium hydroxide solution were taken. Butanoic acid was added dropwise to the aqueous solution of tetrabutylammonium hydroxide taken in round bottomed flask. The temperature was maintained below 278.15 K during the addition since the neutralisation reactions are exothermic in nature. The reaction mixture was then allowed to stir continuously for 24 h at room temperature in order to ensure the completion of the reaction. Later most of the water was removed at 333.15 K using rotary evaporator. The product was further vacuum dried for a minimum of 24 h and then the tetrabutylammonium butanoate was obtained as a viscous liquid. Other ILs including [TBA][Pent], [TBA][Hex], [TBA][Hept], [TBA][Oct] and [TBA][Dec] were synthesised using similar procedure. The general synthesis scheme is presented in scheme 1. Further, synthesised ILs were characterised by ^{1}H and ^{13}C NMR spectroscopic techniques and spectral data is presented below and corresponding spectra are given in Supplementary Information (Figs. S1–S12). The water content was measured using Karl-Fischer Titrator and are presented in Table 1 along with the percentage purity and method of purification for all ILs. Structures of all synthesised ILs are given in Fig. 1.

NMR data:

[TBA][But]   ^{1}H NMR data: 0.88 (3H, t), 0.96 (12H, t), 1.40 (8H, m), 1.60 (10H, m), 2.11 (2H, t), 3.30 (8H, t).
^{13}C NMR data: 13.70, 14.57, 19.73, 20.41, 24.02, 41.27, 58.67, 179.24

[TBA][Pent]   ^{1}H NMR data: 0.85 (3H, t), 0.96 (12H, t), 1.30 (2H, m), 1.40 (8H, m), 1.60 (10H, m), 2.13 (2H, t), 3.32 (8H, t).
^{13}C NMR data: 13.79, 14.25, 19.83, 22.68, 23.25, 24.14, 29.63, 39.31, 58.80, 179.56