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Aqueous biphasic system formation using 1-alkyl-3-ethylimidazolium bromide ionic liquids as new extractants

Aleksandra Dimitrijević [a], Nebojša Zec [b], Nikola Zdolšek [a], Sanja Dožić [b], Aleksandar Tot [b], Slobodan Gadžurić [b], Milan Vraneš [b], Tatjana Trtić-Petrović [a,*]

[a] Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
[b] Faculty of Sciences, University of Novi Sad, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

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ABSTRACT

In this work three 1-alkyl-3-ethylimidazolium bromide ionic liquids (alkyl = ethyl, hexyl and octyl) were synthesized applying both, conventional and microwave assisted synthetic paths. The phase diagrams for aqueous solutions of 1-alkyl-3-ethylimidazolium bromide ionic liquids as novel extractants combined with phosphate-based salts are reported and discussed in terms of aqueous biphasic system (ABS) formation. Merchuk equation was applied in order to correlate the experimental binodal data. The liquid–liquid equilibrium data (tie-line compositions and tie-line length) were also experimentally determined by a gravimetric method. The influence of the alkyl chain length on ABS formation ability was investigated. It was found that ability to form ABS increases with the increase of the alkyl chain length on the imidazolium cation. Also, it was found that ionic liquids with ethyl group in the N-3 position better form ABS compared to those with methyl substituent. This was discussed in terms of increasing ionic liquid hydrophobicity and poor affinity for water. In order to better understand the impact of the alkyl side chain of the imidazolium ion and the efficiency of ABS formation, computer simulations were performed using investigated ionic liquids with the ethyl group in the position N-3 of the cation and different alkyl substituents in the position N-1. Also, extraction of selected organic dyes was performed to demonstrate application of studied ionic liquids as novel extractants.

Introduction

It is well known that ionic liquids are widely used as alternative solvents for toxic volatile organic compounds due to their low toxicity, biodegradability, non-corrosivity, negligible vapor pressure and high thermal stability [1]. Also, their tunable physical and chemical properties make the applications possible in many sustainable industrial and technological processes, as well in analytical separation techniques [2–8]. Liquid–liquid extraction based on the ionic liquids and water structuring salts as aqueous biphasic systems have been successfully used to separate various environmentally important substances from water [9–15]. Thus, liquid–liquid equilibrium data at different temperatures and compositions are essential for the optimization of extraction process ABS using water-soluble hydrophilic ionic liquids as extracting solvent, inducing formation of aqueous biphasic systems with suitable kosmotropic agents [16–18]. These extraction media with the right proportions of ionic liquid and kosmotropic salt can be used as an alternative to conventional liquid–liquid or liquid–solid type systems. In our previous work [19], a structure maker ionic liquid 1-butyl-3-ethylimidazolium bromide, [beim][Br], was investigated among various commercially available ILs as a potential media for LLE in the presence of the commonly used phosphate inorganic salts. Such bromide based ILs are in the most cases liquids at room temperature which is not always observed in the case of the chloride based ILs. It was found that newly studied [beim][Br] with the ethyl group in the position N-3 of the imidazolium cation forms ABS better than corresponding ILs with

Abbreviations: ABS, aqueouss biphasic system; DFT, density functional theory; IL, ionic liquid; LLE, liquid–liquid equilibrium; MD, molecular dynamic; NMR, nuclear magnetic resonance; RDF, radial distribution function.

* Corresponding author. Tel.: +381 11 644 7700.
E-mail addresses: daleksandra@vinca.rs (A. Dimitrijević), nebojsa.zec@dh.uns.ac.rs (N. Zec), zdolsek@vinca.rs (N. Zdolšek), sanja.dozic@dh.uns.ac.rs (S. Dožić), aleksandar.tot@dh.uns.ac.rs (A. Tot), slobodan.gadzuric@dh.uns.ac.rs (S. Gadžurić), milan.vranes@dh.uns.ac.rs (M. Vraneš), ttrtic@vinca.rs (T. Trtić-Petrović).

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methyl group. Also, the bromide based ionic liquids comparing to corresponding chloride based ILs can be prepared easily applying one-step synthesis. Obtained ionic liquids with bromide anion show weaker ion-dipole interactions less structuring the water and thus enabling better ABS formation and cation influence investigation. In the same time, the solubility of many substances (such as organic pollutants, dyes, metal salts) in bromide based ionic liquids is high, allowing application of these liquids in the separation techniques as novel extractants. It is also worth to say that ILs with increasing number of methyl groups in the N-3 position of the imidazolium ion are showing low viscosity making the applications in an industrial scale cheaper and easy-to-handling [20].

In order to better assess advantages of increasing N-3 alkyl chain length of imidazolium cation, in this work LLE was studied using newly synthesized bromide based ionic liquids as a potential extractants: 1,3-diethylimidazolium bromide, [eeim][Br], 1-hexyl-3-ethylimidazolium bromide, [heim][Br] and 1-octyl-3-ethylimidazolium bromide, [oeim][Br]. All investigated ionic liquids are synthesized applying classical synthetic path, but also microwave assisted reaction approach respecting the main principles of green chemistry – energy consumption as well as reaction time reduction. The effect of the alkyl chain length in 1-alkyl-3-ethylimidazolium bromide on ABS formation was examined applying both, experimental techniques and molecular dynamic simulations.

Experimental

Materials and methods

The inorganic salt, K_3PO_4, reactants for IL synthesis and ethyl acetate were analytical grade reagents purchased from Sigma–Aldrich (St. Louis, MO, USA). Congo red and rhodamine B were supplied from Acros Organics (New Jersey, USA). All solutions were prepared with Milli-Q water (Millipore Corporation, Bedford, MA, USA).

Nuclear magnetic resonance (NMR) data were recorded in $CDCl_3$ at 298.15 K on a Bruker 300 DRX spectrometer (Coventry, UK) and the solvent peak was used as reference. Infrared spectra were recorded as neat samples from (4000–500) cm^{-1} on a Thermo-Nicolet Nexus 670 spectrometer fitted with a Universal ATR Sampling Accessory.

The vibrating tube Rudolph Research Analytical DDM 2911 densimeter with the repeatability of 0.00001 g cm^{-3} was used for density measurements. The instrument was thermostated within ±0.01 K and viscosity was automatically corrected. An average value of at least three measurements with the reproducibility within 0.01% at temperatures from 298.15 to 313.15 K is presented in this work. Standard uncertainty of determining the density is less than 7.6×10^{-4} g cm^{-3}.

Synthesis of 1-alkyl-3-ethylimidazolium bromide ionic liquids

Chemical names and structures of the synthesized ionic liquids are given in Table 1.

The equimolar amounts of 1-ethylimidazole and 1-bromoalkane were mixed and stirred under nitrogen atmosphere for 72 h at low temperature. While stirring, the mixture was cooled using the ice. Obtained product was purified by liquid–liquid extraction using ethyl acetate. In order to remove ethyl acetate from the samples, the ionic liquids were heated for 45 min at 343.15 K under the vacuum. When achieving a constant mass, the ionic liquid was additionally dried under the vacuum for the next 72 h. After drying, water content in the ILs was determined by the Karl Fischer titration.

The same ILs were obtained using a single mode microwave reactor (Discover BenchMate, purchased from CEM Corporation) by irradiation at 240 W and heating at 353.15 K of the 1-ethylimidazole and 1-bromoalkane mixture in a quartz vessel for 7 min. Time of the irradiation and reaction temperature were increased for 2 min and 10° for every additional methyl group in the alkyl chain. The process was monitored by NMR spectroscopy. After completion of the reaction the pale yellow mixtures were purified by liquid–liquid extraction using ethyl acetate. The lower (1-alkyl-3-ethylimidazolium bromide) phase was collected, the solvent removed under the vacuum and the ionic liquid dried for the next 72 h.

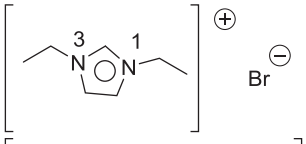
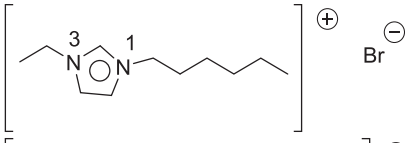
For the structure confirmation of the synthesized ILs, the IR and NMR spectra were recorded and presented as Figs. S1 and S2 together with their assignations in the Supplementary file of this manuscript. The provenance and purity of the applied ILs are given in Table 2. There was no difference in purity between ionic liquid synthesized in these two approaches – classical and microwave assisted.

Also, experimental density is measured for all investigated ionic liquids at several temperatures: 298.15; 303.15; 308.15 and 313.15 K and at atmospheric pressure (p = 0.1 MPa). These values are tabulated in Table 3.

Phase diagrams and tie-lines

The binodal curves of the ternary phase diagrams {water + inorganic salt + IL} were determined applying the cloud point

Table 1
Chemical structures and the names of the investigated ILs.

Chemical name	Structure of IL
1,3-diethylimidazolium bromide	
1-hexyl-3-ethylimidazolium bromide	
1-octyl-3-ethylimidazolium bromide