



Separation of 2-phenylethanol (PEA) from water using ionic liquids



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ABSTRACT

This work presents some important issues and topics related to chemical thermodynamics of ionic liquids (ILs). It consist of a series of experimental measurements in binary and ternary phase equilibrium systems connected with possible extraction of 2-phenylethanol (PEA) from aqueous phase “*in situ*” during the bioproduction. New experimental (solid + liquid) phase equilibrium (SLE) data for two binary systems {IL (1) + PEA (2)} and few (liquid + liquid) phase equilibrium (LLE) in binary systems {IL (1) + H₂O (2)}, as well as LLE in five ternary systems of {IL (1) + PEA (2) + water (3)} at temperature $T = 308.15$ K and ambient pressure are reported. The systems are composed of the ILs: *N*-butyl-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₁₁₄][NTf₂], (2-hydroxyethyl)-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N_{11120H}][NTf₂], *N*-*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis((trifluoromethyl)sulfonyl)imide, [N_{22120CH3}][NTf₂], *N*-methyl-*N*-triethylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₈₈₈][NTf₂], and *N*-triethyl-*N*-octylammonium bis((trifluoromethyl)sulfonyl)imide, [N₂₂₂₈][NTf₂], with PEA or water. The miscibility of some of these ILs with water was known from the literature. A differential scanning calorimetry (DSC) was used to determine the melting point and the enthalpy of melting, solid-solid phase transition temperature and enthalpy, as well as glass transition of the ILs. The [N₁₁₁₄][NTf₂] and [N_{11120H}][NTf₂] showed complete miscibility in the liquid phase in a binary system with PEA at temperatures higher than the solubility curve. The latest ILs as [N_{22120CH3}][NTf₂], [N₁₈₈₈][NTf₂], and [N₂₂₂₈][NTf₂] showed complete miscibility with PEA at temperature $T = 308.15$ K. The solubility of the ILs in PEA decreases in the order [N₁₁₁₄][NTf₂] > [N_{11120H}][NTf₂]. All systems revealed immiscibility gap with water (literature and our data). The solubility of water in the ILs increases in the order [N₁₈₈₈][NTf₂] < [N₂₂₂₈][NTf₂] < [N_{22120CH3}][NTf₂] < [N₁₁₁₄][NTf₂] < [N_{11120H}][NTf₂]. The average selectivity of the extraction of PEA from water increases in the following order: [N_{11120H}][NTf₂] ($S_{av} = 130$) < [N₁₁₁₄][NTf₂] ($S_{av} = 294$) < [N_{22120CH3}][NTf₂] ($S_{av} = 319$) < [N₂₂₂₈][NTf₂] ($S_{av} = 711$) < [N₁₈₈₈][NTf₂] ($S_{av} = 806$). The correlation of the solubility curves in binary systems, and tie-lines in ternary systems was undertaken with the NRTL excess Gibbs energy equation. The model correlates the solubility of the ternary systems with an acceptable average root mean square deviation ($\sigma_x = 0.0039$). Our results of ternary LLE may be used to design future alternative technological processes of the extraction of PEA from the fermentation broth with [N₁₈₈₈][NTf₂] or [N₂₂₂₈][NTf₂].

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1. Introduction

Ionic liquids (ILs) are well known new generation solvents, which have attracted great interest as the high-tech reaction media of the future with distinct properties, such as high thermal stability,

negligible vapour pressure and high solvation properties [1–3]. The physical properties, polarity, hydrophobicity and transport properties mostly depend on the type of cation/anion, the alkyl chain length and polar substituent on the cation/anion [4]. ILs may be used as solvents, as co-solvents in the aqueous phase, or as biphasic system together with other organic solvents [5–7].

Nowadays, the biotechnological production of fragrance materials has become increasingly attractive [8]. 2-Phenylethanol (PEA) is an important commercial flavour compound with a rose-like

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aroma [9–13]. It is used as an ingredient in the production of food, soft drinks, candy, ice cream, pudding, chewing gum and cookies. Because of difficult purification problem after chemical synthesis, natural PEA is usually used due to consumer preference [9–13]. PEA is usually produced by *Saccharomyces cerevisiae* yeast in water phase. According to literature studies, there are several examples of using ILs in the biocatalytic reactions for the continuous (liquid + liquid) extraction of PEA [12–15]. The ILs used in such a process have to be biocompatible with the yeast [14].

Meanwhile, an increasing number of investigations have concerned applications of ILs in PEA production [15–17]. Unfortunately, some ILs are reported to have toxic effects towards yeasts, bacteria and fungi [8,18,19]. Recently, our research group has tested new organic solvents with possible use for PEA extraction and biosynthesis [20]. Nevertheless, we measured the phase equilibrium in binary and ternary systems of hydrophobic ILs as 1-octylisoquinolinium bis((trifluoromethyl)sulfonyl)imide, [OiQuin][NTf₂] [16], 1-hexylquinolinium bis((trifluoromethyl)sulfonyl)imide, [HQuin][NTf₂], 1-hexylisoquinolinium bis((trifluoromethyl)sulfonyl)imide, [HiQuin][NTf₂] [17], and piperidinium-based ILs [17] with PEA and water. The 1-hexyl-3-methylpyridinium triflate, [HM³Py][CF₃SO₃], and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [EMIM][FAP] have shown complete miscibility with PEA [21]. The pyrrolidinium-based, imidazolium-based and phosphonium-based ILs were tested recently for this reaction [22]. The complete miscibility of PEA was observed with [BMPYR][FAP], [BMIM][TCM] and [BMPYR][TCM] [22]. Additionally, the possible use of Deep Eutectic Systems, (DES) in PEA production was presented by us earlier [22]. The chosen DES were: {choline chloride + resorcinol (1:4), or phenylacetic acid (1:1), or phenylacetic acid (1:2), or oxalic acid (1:1), or malonic acid (1:1)} and {acetylcholine chloride + 1,10-decanediol}. The best solvent was {choline chloride + malonic acid (1:1)} [22].

Ammonium-based ILs are known as a hydrophobic, air and moisture stable, not expensive and multifunctional organic salts [23–27]. Specific ammonium-based ILs were found to have practical value as antibacterial, anti-fungal agents and huge potential application for wood preservation [24] and antielectrostatic agents [25]. Ammonium-based ILs are the most popular cationic surfactants, biocides, germicides, adhesion promoters in asphalt, corrosion inhibitors and many others [26]. The possible use in the extraction processes as pure solvents, or DESs have been also proposed, especially in the process of the desulfurization of fuels [28–31]. DES composed of quaternary ammonium salts were used for separation of phenols from model oils [32]. The use of DES with ammonium-based ILs was inspired by many innovative works, where the very good results were obtained as catalysts [33,34]. Ammonium ILs with special herbicidal anions are proposed as a promising herbicide efficacy [35]. The most popular, choline chloride is the (2-hydroxyethyl)-*N*-trimethylammonium chloride, [N_{11120H}][Cl] salt. It is crucial for several biological functions [36]. Ammonium-based ILs play an important role in the living process beginning at vitamins (vitamin B complex and Thiamine) to enzymes, which participate in the carbohydrate and choline metabolism. Physicochemical properties and the interaction of several choline chloride derivatives with alcohols, water, ethers and many others were presented in the open literature [37–46]. Recently, we have published the density, and dynamic viscosity, for binary solutions containing ionic liquids (ILs) and alkanediols: {[N₁₁₁₄][NTf₂] + 1,2-propanediol, 1,2-butanediol, 2,3-butanediol} and {[N_{1120H}][NTf₂] + 1,2-propanediol, 1,3-propanediol, 1,5-pentanediol} at wide temperature and composition range [47]. Additionally, we have measured the excess enthalpies of [N₁₁₁₄][NTf₂] with 1,2-propanediol, or 1,2-butanediol, or 2,3-butanediol at *T* = 298.15 K [47].

Choline-based ILs are known as less toxic and more biodegradable alternatives to popular imidazolium-, or pyridinium-based ILs [48,49]. The phase equilibrium in binary, or ternary mixtures including choline-based ILs have been presented for few systems [28,29,38,40–42]. In this work we continue the phase equilibrium measurements in binary and ternary systems for ammonium-based ILs with PEA and water to find the possible extractive properties for the ammonium entrainers in the bio-production of PEA.

Thus the goal of this work is to continue our studies on phase equilibria of chosen ammonium-based ILs with PEA and water in binary mixtures and (liquid + liquid) phase equilibria (LLE) in ternary mixtures {IL (1) + PEA (2) + water (3)} with the aim of determining the best solvent which may be used in biotechnological production of PEA. In this work, the following ILs are proposed: *N*-butyl-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₁₁₄][NTf₂], (2-hydroxyethyl)-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N_{1120H}][NTf₂], *N*-*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis((trifluoromethyl)sulfonyl)imide, [N_{22120CH3}][NTf₂], *N*-methyl-*N*-trioctylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₈₈₈][NTf₂], and *N*-triethyl-*N*-octylammonium bis((trifluoromethyl)sulfonyl)imide, [N₂₂₂₈][NTf₂]. The structure type of cation and anion is the key factor to physicochemical properties of ILs and their interaction with polar solvents.

2. Experimental

2.1. Materials

All ILs studied in this work were purchased from IoLiTec. The names, abbreviation of names, molar masses, structure, and solubility in PEA and water are listed in Table 1 [42,50,51]. PEA was obtained from Merck. The origins of the chemicals, CAS numbers, purity, water content, and densities are listed in Table S1 in the Supplementary Data (SD). Doubly distilled and degassed water was used in the solubility measurements. The samples of ILs were dried for 24 h–48 h at 370 K under reduced pressure with mixing to remove volatile impurities and trace water. PEA was stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The densities for all substances were measured at *T* = 298.15 K or other temperatures as specified, and pressure *p* = 101.3 kPa. The experimental method for the (solid + liquid) phase equilibrium, SLE, LLE and densities measurements and uncertainties are described in previous studies [17,47].

2.2. Water content

The water content was analyzed using the Karl-Fischer titration technique (method TitroLine KF). The sample of IL, or solvent was dissolved in methanol and titrated in steps of 0.0025 cm³. The uncertainty in the water content is $\pm 10 \cdot 10^{-6}$ for the 3 cm³ IL sample injected. The water content in ILs and solvents used is presented in Table S1 in the SD.

2.3. Differential scanning calorimetry, DSC

The basic thermal characteristics of ILs, i.e. temperature of fusion (*T*_{fus}), enthalpy of fusion ($\Delta_{fus}H$), temperature of phase transition (*T*_{tr}), enthalpy of phase transition ($\Delta_{tr}H$) and parameters of the glass transition were measured using a differential scanning microcalorimetry technique (DSC). The applied scan rate was 5 K min⁻¹, with power and recorder sensitivities of 16 mJ s⁻¹ and 5 mV, respectively. The apparatus (Thermal Analysis Q200, USA with Liquid Nitrogen Cooling System) was calibrated with a

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