



Phase equilibrium investigation with ionic liquids and selectivity in separation of 2-phenylethanol from water



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ABSTRACT

This work presents some important issues and topics related to possible extraction of 2-phenylethanol (PEA) from aqueous phase “*in situ*” during the biosynthesis with ionic liquids (ILs). It consists of a series of experimental phase equilibrium measurements in binary and ternary systems. Three ILs as extraction media are proposed for the extraction process based on phase equilibria in ternary systems {IL (1) + PEA (2) + water (3)} at temperature $T = 308.15$ K and ambient pressure. The systems are composed of the following ILs: 1-hexyl-1-methylmorpholinium bis((trifluoromethyl)sulfonyl)imide, [HMMOR][NTf₂], 1-allyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [AMIM][NTf₂], and diethylmethylsulfonium bis((trifluoromethyl)sulfonyl)imide, [S₂₂₁][NTf₂]. A differential scanning calorimetry (DSC) was used to determine the thermal properties of the ILs. The synthesis of new [HMMOR][NTf₂] IL and its thermal and physicochemical properties as density, viscosity, surface tension were presented. The volume expansivity, as well as the surface thermodynamic functions, such as surface entropy and enthalpy have been derived from the temperature dependence of the surface tension values, as well as the critical temperature, parachor and speed of sound for all ILs were presented. The correlation of the liquidus curves in binary systems and tie-lines in ternary systems was undertaken with the NRTL equation. These results of solubility can be used to design future alternative technological processes of the extraction of PEA from fermentation broth.

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1. Introduction

Ionic liquids (ILs) are organic salts with low melting points, low vapour pressure, good stability and high solvation properties [1,2]. ILs exist in the liquid phase in a wide range of temperature, which enable their use in many chemistry and biochemistry reactions [3,4]. ILs may be used as solvents, as co-solvents in the aqueous phase, or as biphasic systems [5]. They also have a broad spectrum of separation applications [6–10]. This generation of solvents provides not only an environment for fragrance materials solubility, but also a highly efficient extraction medium for biocatalytic reactions [11–13]. During the last decade we worked in our Faculty on chemical synthesis of 2-phenylethanol (PEA) [14,15]. However, according to new directives of European Parliament, the fragrance materials must be determined from natural sources or from biosynthesis [16]. This work proposes to study a particular type of biosynthesis of PEA with fast extraction of PEA “*in situ*” with ILs. PEA is an important commercial flavour compound with a

rose-like aroma [17–19,11]. PEA is included in the production of food, soft drinks, candy, ice cream, pudding, chewing gum and cookies. The natural PEA is usually produced by *Saccharomyces cerevisiae* yeast in water phase [17–19,11]. There are several examples in literature of using ILs as extraction solvents in the biosynthesis for extraction of PEA “*in situ*” from aqueous phase [11–13,20]. The ionic liquids used in such a process have to be biocompatible with the yeast [13], reveal non-miscibility with water and large or complete miscibility with PEA at low temperatures. The critical aspect in biosynthesis is that some ILs are toxic to the yeast and may be in the industrial waste processing and enter the aquatic ecosystems. In this paper we continue our investigations concerned on applications of organic solvents [21] and of ILs in PEA extraction [22–27].

Recently, we measured the possibility of using hydrophobic ILs as 1-octylisoquinolinium bis((trifluoromethyl)sulfonyl)imide, [OiQuin][NTf₂] [22], 1-hexylquinolinium bis((trifluoromethyl)sulfonyl)imide, [HQuin][NTf₂], 1-hexylisoquinolinium bis((trifluoromethyl)sulfonyl)imide, [HiQuin][NTf₂] [23], and piperidinium-based ILs [23]. The 1-hexyl-3-methylpyridinium triflate, [HM³Py][CF₃SO₃], and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [EMIM][FAP] have shown complete miscibility with

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PEA [24]. Also the pyrrolidinium-based, imidazolium-based and phosphonium-based ILs were tested recently by us for this extraction [25]. The complete miscibility with PEA was observed for 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [BMPYR][FAP], 1-butyl-1-methylpyrrolidinium dicyanoamid, [BMPYR][DCA], 1-butyl-1-methylimidazolium tricyanomethanide, [BMIM][TCM] [25]. Additionally, the possible use of Deep Eutectic Systems, (DES) in PEA production was presented [25]. 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 for extraction was {choline chloride + malonic acid (1:1)} [25]. Optimistic results were obtained also with: 1-hexyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide, [C₆C₁PYR][NTf₂], 1-hexyl-1,4-diazabicyclooctanium bis((trifluoromethyl)sulfonyl)imide, [C₆DBCO][NTf₂], 1-(2-methoxyethyl)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [COC₂C₁IM][NTf₂], and 1-(2-methoxyethyl)-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide, [COC₂C₁PYR][NTf₂] [26].

Recently, we studied also ternary phase equilibria of chosen ammonium-based ILs with PEA and water {IL (1) + PEA (2) + water (3)} with the aim of determining the best solvent which may be used in biotechnological production of PEA [27]. The following ILs were tested: *N*-butyl-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₁₁₄][NTf₂], (2-hydroxyethyl)-*N*-trimethylammonium bis((trifluoromethyl)sulfonyl)imide, [N_{1112OH}][NTf₂], *N*-*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis((trifluoromethyl)sulfonyl)imide, [N_{2212OCH₃}][NTf₂], *N*-methyl-*N*-triethylammonium bis((trifluoromethyl)sulfonyl)imide, [N₁₈₈₈][NTf₂], and *N*-triethyl-*N*-octylammonium bis((trifluoromethyl)sulfonyl)imide, [N₂₂₂₈][NTf₂]. The best selectivities of extraction with ammonium based ILs were obtained with [N₂₂₂₈][NTf₂] or [N₁₈₈₈][NTf₂]. Unfortunately, some ILs, including ammonium-based are reported to have toxic effects towards yeasts, bacteria and fungi [16,28].

Thus, this study aimed at (a) synthesis of 1-hexyl-methylmorpholinium bis((trifluoromethyl)sulfonyl)imide, [HMMOR][NTf₂] and described the thermal and physico-chemical properties of [HMMOR][NTf₂]; (b) analyzing and discussing the phase equilibria in binary systems (IL + PEA), (PEA + water) and (IL + water); (c) investigating ternary liquid-liquid phase equilibrium of {IL (1) + PEA (2) + water (3)} including three ILs: 1-hexyl-1-methylmorpholinium bis((trifluoromethyl)sulfonyl)imide, [HMMOR][NTf₂], 1-allyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [AMIM][NTf₂], and diethylmethylsulfonium bis((trifluoromethyl)sulfonyl)imide, [S₂₂₁][NTf₂] at temperature *T* = 308.15 K and ambient pressure. The *N*-alkyl-*N*-methylmorpholinium ILs differing in the alkyl chain length attached to the *N*-methylmorpholinium cation are popular in electrochemical measurements. The physicochemical characteristics of these largely unexplored ILs are very rare. The fluorescence behaviour of coumarin-153 (C153), or two dipolar solutes, 4-aminophthalimide (AP) and 6-propionyl-2-dimethylaminonaphthalene, and a nonpolar solute, anthracene has been studied in four morpholinium-based bis((trifluoromethyl)sulfonyl)imides including [HMMOR][NTf₂] as a function of the excitation wavelength and temperature and was recently presented in literature [29,30].

2. Experimental

2.1. Synthesis of [HMMOR][NTf₂]

The precursor organic salt 1-hexyl-1-methylmorpholinium bromide, [HMMOR][Br] has been prepared according to the synthesis procedure described earlier for [C₅C₁Pip][Br] [31]. For the synthesis

a 250 cm³ flask, equipped with a magnetic stirrer and condenser was used. To a solution of 13.91 g (0.1375 mol) of 1-methylmorpholine (Sigma Aldrich, Reagent Plus[®], ≥99%) in 100 cm³ of acetonitrile (P.O.Ch., HPLC grade) 24.97 g (0.1513 mol, 1.1 equivalents) of 1-bromohexane (Sigma Aldrich, Reagent Plus[®], ≥98%) was added. The mixture was stirred at 353 K for 24 h and afterwards the ethyl acetate was added to the mixture and the solution was allowed to cool down and the product crystallized. The product was filtered and washed with ethyl acetate. Crystals were dried in vacuum at 353 K for 24 h yielding 34.77 g (95.5%).

¹H NMR δ_H (400 MHz, CDCl₃): 0.763 (3H, t, *J*_{HH} = 7.2 Hz); 1.144 (6H, m); 1.598 (2H, m); 2.910 (3H, s); 3.142 (2H, m); 3.283 (4H, m); 3.721 (4H, t, *J*_{HH} = 4.4 Hz).

¹³C NMR δ_C (100 MHz, D₂O): 13.624, 21.345, 22.955, 25.601, 30.826, 46.409, 59.827, 60.444, 66.560.

The ionic liquid 1-hexyl-1-methylmorpholinium bis((trifluoromethyl)sulfonyl)imide, [HMMOR][NTf₂] has been prepared according to the well known procedure, used by us earlier for synthesis of *N*-octylisoquinolinium bis((trifluoromethyl)sulfonyl)imide [32].

[HMMOR][NTf₂]: for the synthesis a 250 mL flask, equipped with magnetic stirrer and condenser was used. To a solution of 34.77 g (0.1306 mol) of 1-hexyl-1-methylmorpholinium bromide (synthesized), in 100 ml water, 27.74 g (0.1445 mol, 1.1 equivalents) of lithium bis((trifluoromethyl)sulfonyl)imide (Sigma Aldrich, Reagent Plus[®], ≥99%) was added. Solution became lighter in color and second heavier phase was formed. The mixture was stirred for 24 h, afterwards phases were separated. The heavier phase was diluted with 50 ml dichloromethane and extracted with distilled water till aqueous phase gave negative response on addition of AgNO₃. Dichloromethane was removed in vacuum, and the product was dried under vacuum at 353.15 K for 12 h. Yield: 53.07 g (87.1%).

¹H NMR δ_H (400 MHz, CDCl₃): 0.821 (3H, t, *J*_{HH} = 7.2 Hz); 1.267 (6H, m); 1.673 (2H, m); 3.060 (3H, s); 3.275 (2H, m); 3.343 (4H, m); 3.876 (4H, t, *J*_{HH} = 4.4 Hz), (see Fig. 1S in the SM).

¹³C NMR δ_C (100 MHz, CDCl₃): 13.416, 21.103, 21.978, 25.333, 30.676, 46.151, 59.690, 60.225, 66.230, 119.545 (*q*, *J*_{CF} = 319.4 Hz), (see Fig. 2S in the SM).

The NMR -spectra are shown in Figs. 1S and 2S in the SM.

2.2. Materials

Two ILs studied in this work, the [AMIM][NTf₂] and [S₂₂₁][NTf₂] were purchased from IoLiTec. The structure, names, abbreviation of names, CAS numbers, molar masses, purification method and purity are listed in Table 1. PEA was obtained from Merck (purity 99 wt.%). Doubly distilled and degassed water was used in the solubility measurements. The samples of ILs were dried for 24 h to 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 (4 × 10⁻⁸ cm) (Union Carbide). The sources and mass fraction purities of materials used are specified in Table 1S in the Supplementary Material (SM). The densities for all substances were measured at *T* = 298.15 K or other temperatures as specified, and pressure *p* = 101 kPa.

2.3. Water content

The water content was analysed 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 ±10 × 10⁻⁶ for the 3 cm³ IL sample injected. The water content in ILs were: (320, 234, 361, and 330)10⁻⁶ for [HMMOR][NTf₂], [AMIM][NTf₂], [S₂₂₁][NTf₂] and PEA, respectively.

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