



Gamma infinity data for the separation of water-butan-1-ol mixtures using ionic liquids



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ABSTRACT

Bio-butanol is produced from biomass by fermentation and must be separated from the aqueous phase. Ionic liquids (ILs) are a novel attractive solvents, which can be used for removing butan-1-ol from the aqueous fermentation broth. The thermal properties, obtained with DSC and the densities of IL octyltriethylammonium bis((trifluoromethyl)sulfonyl)imide, [N_{8,2,2,2}][NTf₂] as a function of temperature have been measured over a temperature range (289.15–385.15) K. The activity coefficients at infinite dilution, γ_{13}^{∞} , for 63 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, tetrahydrofuran, ethers, and ketones in the [N_{8,2,2,2}][NTf₂] were determined by gas-liquid chromatography at six temperatures from 318.15 K to 368.15 K. The gas-liquid partition coefficients, K_L were calculated for all solutes. The partial molar excess Gibbs energies $\Delta G_1^{E,\infty}$, enthalpies $\Delta H_1^{E,\infty}$, and entropies $\Delta S_1^{E,\infty}$ at infinite dilution were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The selectivity and capacity for water/butan-1-ol separation problem were calculated from γ_{13}^{∞} data and were compared to literature values for bis((trifluoromethyl)sulfonyl)imide-based ILs with different cations, and with all available data for ILs.

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1. Introduction

Researchers have been focusing their interest in biomass based fuels, which currently is the only alternative for sustainable development in a context of both economical and environmental postulates. Bio-fuels like alcohols are produced from biomass by fermentation, and distillation. This method is commonly used to separate an alcohol from the fermentation broth [1,2]. While ethanol has received the most attention as a fuel additive; butanol is proposed as a better direct fuel alternative [3,4]. A great number of industrial separation processes are concerned with liquid mixtures containing isomers of butan-1-ol (butan-1-ol, butan-2-ol, *tert*-butan-1-ol) and water. All isomers contain about the same energy and can be used in blending of gasoline and in combustion. However, distillation is a high energy consumption process [1,5], and distillative recovery of butan-1-ol from fermentation broth is not economical (higher boiling temperature than that of ethanol). The alternative recovery methods have been considered including liquid-liquid equilibrium using ionic liquids (ILs) [3,5–11],

stripping, pervaporation, or liquid membranes with ILs [12]. The later methods are proposed also without using ILs [13–17]. None of these methods has been economically proved yet.

The requirements of a suitable IL for the separation of butan-1-ol and water are the high, or complete miscibility of butan-1-ol with the IL and non-miscibility, or low solubility of water in the IL. This is usually achieved by choosing the hydrophobic IL, which interacts strongly with the hydroxyl group of an alcohol *via* the hydrogen bonding and not with water. Butan-1-ol is popular organic solvent, and is an important substance with a wide range of industrial uses as surface coating, superb-sorbents, fibers, plastics, resins, hard-surface cleaners, electronics, paints, as in fragrance material and in pharmaceuticals [12]. The physicochemical parameters of butan-1-ol, as low vapor pressure, higher than that of water boiling temperature, low solubility in water makes it a medium, which could be potentially used as an additive to gasoline without concerning about evaporation and subsequent related complications. The next-generation bio-fuels will probably include bio-butan-1-ol, or the mixtures of bio-butan-1-ol and ethanol.

The extraction of alcohols from water was proposed by now with the following ILs: 1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [HMIM][NTf₂] [3,18], 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆] and 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF₆] [6],

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1-(6-hydroxyhexyl)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [OHHMIM][NTf₂] [7,8], 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate, [HMIM][eFAP] [7,8], 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [BMIM][NTf₂] [3,19], 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate, [EOHMIM][BF₄] and 1-hydroxyethyl-2,3-dimethylimidazolium tetrafluoroborate, [EOHMMIM][BF₄] [11], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] [20], 1-hexyl-3-methylimidazolium tetracyanoborate, [HMIM][TCB] [10], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] [10] and trihexyltetradecylphosphonium tetracyanoborate, [P_{14,6,6,6}][TCB] [10]. The ternary liquid–liquid equilibrium (LLE) data for most of these ILs exhibit high selectivity for butan-1-ol only at low concentration of butan-1-ol in the initial aqueous phase. The selectivity of separation in LLE is lower than 100. Only for [DMIM][TCB] [10] and [HMIM][eFAP] [7,8], the selectivity was higher than 100 and for [P_{14,6,6,6}][TCB] the maximum selectivity was 903 [10]. The phosphonium based ILs were found as well to be the best reported yet for water–ethanol separation [9]. The production of bio-butanol using [DMIM][TCB] was recover by MERCK as both, low energy process and co-extraction with acetone from water and fast mixing–settling process.

The values of the selectivity of separation in water/butan-1-ol system at $T = 308.15$ K coming from the analysis of activity coefficients at infinite dilution (γ_{13}^{∞}) are quite low and on the same range for few measured tetracyanoborate-based ILs. The values of water/butan-1-ol selectivity were as follow: for 1-ethyl-3-methylimidazolium tetracyanoborate, [EMIM][TCB] $S_{ij}^{\infty} = \gamma_{13}^{\infty} / \gamma_{13}^{\infty} = 1.21$ [21], for 1-butyl-1-methylpyrrolidinium tetracyanoborate, [BMPYR][TCB] $S_{12}^{\infty} = 0.86$ [22], for [HMIM][TCB] $S_{12}^{\infty} = 0.69$ [23] and for [DMIM][TCB] $S_{12}^{\infty} = 0.46$ [24].

In this work we report the γ_{13}^{∞} for 63 solutes, including diverse *n*-alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, thiophene, tetrahydrofuran (THF), ethers, acetone, and other ketones, in the IL [N_{8,2,2,2}][NTf₂]. Values of γ_{13}^{∞} were determined by gas–liquid chromatography at 10 K intervals from 318.15 K to 368.15 K. This work also provides an opportunity to make comparisons with previously-published results found in the literature for ILs.

2. Experimental

2.1. Materials

The ionic liquid [N_{8,2,2,2}][NTf₂] (CAS. No. 210230-48-1, purity 0.995 mass fraction) was purchased from IoLiTec. The name, abbreviation of name, structure, molar mass, and glass transition parameters are listed in Table 1. The different solutes, purchased from Aldrich or Fluka, had purities better than 0.99 mass fraction and were used without further purification due to the fact that the GLC technique separates any impurities on the column. The specification and purity is shown in Table 1S in the Supplementary Material (SM).

2.2. Water content

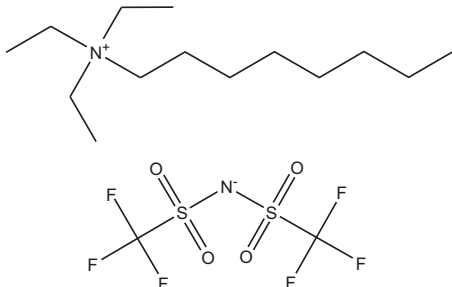
The water content was analyzed by the Karl-Fischer titration technique (method TitroLine KF). The sample of IL, or solvent was dissolved in methanol and titrated with steps of 0.0025 cm³. The uncertainty on the water content was $u(\text{w.c.}) = 10$ ppm for the 3 cm³ injected IL. The water content in IL was 970 ppm.

2.3. Differential scanning calorimetry, DSC

The basic thermal characteristics of ILs, i.e. temperature of glass transition and heat capacity at glass transition temperature (T_g , $C_{p(g)}$)

Table 1

The name, abbreviation, structure, glass transition temperature, T_g and change of heat capacity at the glass transition temperature, $\Delta C_{p(g)}$ of investigated ionic liquid at pressure $p = 0.1$ MPa.^a

Name, abbreviation	Octyltriethylammonium Bis(trifluoromethylsulfonyl)imide, [N _{8,2,2,2}][NTf ₂]
Structure	
M/g mol ⁻¹	494.56
T_g /K	192.3
$\Delta C_{p(g)}$ / J mol ⁻¹ K ⁻¹	146.4

^a Standard uncertainties u are as follows; $u(T_g) = 0.1$ K; $u(\Delta C_{p(g)}) = 5$ J mol⁻¹ K⁻¹, $u(p) = 1$ kPa.

Table 2

Density, ρ as a function of temperature, T for ionic liquid [N_{8,2,2,2}][NTf₂] at pressure $p = 0.1$ MPa.^a

T /K	ρ /g cm ⁻³	ρ /g cm ⁻³ .lit
298.15	1.24771	1.2512 ^c , 1.25 ^d , 1.25339 ^e , 1.28 ^f , 1.25 ^g
303.15	1.24319	1.24560 ^b , 1.2472 ^c
308.15	1.23911	1.2429 ^c
313.15	1.23502	
318.15	1.23088	
323.15	1.22655	
328.15	1.22231	
333.15	1.21768	
338.15	1.21298	
343.15	1.20811	
348.15	1.20411	
353.15	1.19977	
358.15	1.19546	
363.15	1.19138	1.19581 ^b , 1.2002 ^c
368.15	1.18637	1.1960 ^c

^a Standard uncertainties u are $u(T) = 0.01$ K, $u(\rho) = 10^{-5}$ g cm⁻³, $u(p) = 1$ kPa.

^b Ref. [25].

^c Ref. [26].

^d Ref. [27] at $T = 293.15$ K.

^e Ref. [28] at $T = 293.15$ K.

^f Ref. [29].

^g Ref. [30] at $T = 293$ K.

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 (DSC 1 STAR^e System firmy Mettler Toledo with Liquid Nitrogen Cooling System) was calibrated with a 0.999999 mol fraction purity indium sample. The repeatability of the glass transition temperature value was ± 0.1 K. The uncertainty of the glass transition temperature was $u(T_g) = 0.1$ K and that of the heat capacity at glass transition $u(C_{p(g)}) = 5$ J mol⁻¹ K⁻¹. The DSC diagram of the IL is shown as Fig. 1S in the SM.

2.4. Density measurements

The density of IL was measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria), thermostated over a temperature range (289.15–385.15) K. Two integrated Pt 100 platinum thermometers provided good precision in temperature control internally ($T \pm 0.01$ K). Densimeter includes an automatic correction

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