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# High selective water/butan-1-ol separation on investigation of limiting activity coefficients with $[P_{8,8,8,8}][NTf_2]$ ionic liquid

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ABSTRACT

The limiting activity coefficients ($\gamma_{13}^{\infty}$) for 65 solutes, including polar and non-polar solutes as alkanes, alkenes and alkynes as well as aromatic hydrocarbons, alcohols, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, esters and water in the tetraoctylphosphonium bis{(trifluomethyl)sulfonyl}imide ionic liquid (IL), $[P_{8,8,8,8}][NTf_2]$ were determined by gas-liquid chromatography at six temperatures in range of (318.15–368.15) K. The synthesis and DSC data are presented for this IL. Density, $\rho$ and viscosity, $\eta$ as a function of temperature, $T$ in a range of (298.15–398.15) K for $[P_{8,8,8,8}][NTf_2]$ were measured at pressure $p$ = 101 kPa. The gas-liquid partition coefficients, $K_L$ at infinite dilution and the thermodynamic functions, the limiting partial molar excess Gibbs energy, enthalpy and entropy were calculated. The values of selectivity and capacity for water/butan-1-ol separation problem were calculated from $\gamma_{13}^{\infty}$ and compared to literature values for phosphonium-based or other selected ionic liquids for the same separation problem. The Abraham solvation parameter model was also presented for all solutes. On the basis of the results, the intermolecular interactions of the chosen IL and solutes were discussed. The data presented here show that $[P_{8,8,8,8}][NTf_2]$ reveals very large selectivity for the water/butan-1-ol separation.

## 1. Introduction

The production of bio-fuels like alcohols from biomass by fermentation of sugars, starch, cellulose, beetroot and others using yeast or bacteria has been one of the most popular scientific problems of the last decade. After bioprocessing, distillation is the most commonly used method to separate an alcohol from the fermentation broth [1,2]. It is however a high energy consumption process [1,3]. While ethanol has received a lot of attention as the most popular fuel of the first generation, butan-1-ol is currently thought of as the most promising fuel of the second generation [4,5]. The recovery of butan-1-ol *in situ* from fermentation broth has gained considerable attention. Several techniques have been investigated for this process such as stripping, adsorption, liquid–liquid extraction, pervaporation and membrane solvent extraction [6]. Among these methods, which show low selectivities, the liquid–liquid extraction and pervaporation have advantages over the others. The liquid–liquid extraction can be performed with high selectivity. It is possible to carry out the separation inside the fermenter. The extract (solvent + butan-1-ol) is collected at the fermenter outlet. However, the pervaporation process can only be used when the separation process is carried out outside the fermenter [7]. Ionic liquids (ILs) composed entirely of ions are liquid at room temperature, have negligible vapor pressure, non-flammability, and tunable physiochemical properties [8–10]. ILs have recently gained much attention as alternatives “designer solvents” for organic solvents in many processes [8–10].

The requirements of a suitable IL for the extraction of butan-1-ol from aqueous phase are the high, or complete miscibility of butan-1-ol with the IL and non-miscibility, or low miscibility of water with the IL. The liquid–liquid extraction for the recovery of butan-1-ol from aqueous solution was performed by imidazolium based ILs with alkyl chains of varying length in cation in combination with the anions, tetrafluoroborate, $[BF_4]-$, trifluoromethanesulfonate, $[TfO]^-$, hexafluorophosphate $[PF_6]^-$, and bis{(trifluoromethyl)

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sulfonyl}imide, $[NTf_2]^-$ in order to understand the effect of ILs extracting properties [11]. Many ILs have now been proposed for the extraction of alcohols from water. Very optimistic results were obtained in ternary liquid-liquid equilibrium (LLE) measurements with 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB], 4-decyl-4-methylmorpholinium tetracyanoborate, [DMMOR][TCB], 1-decyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [DMIM][$NTf_2$] and decyl-4-methylmorpholinium bis{(trifluoromethyl)sulfonyl}imide, [DMMOR][$NTf_2$] [12]. The average selectivity in mass fraction for [DMIM][$NTf_2$] was ($S_{23,av} = 93.5$) at $T = 308.15$ K [12]. In this process not only the $[NTf_2]^-$-based ILs were used. The following ILs are described in the literature: 1-hexyl-3-methylimidazolium bis{(trifluomethyl)sulfonyl}imide, [HMIM][$NTf_2$] [4,13], 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][$PF_6$] and 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][$PF_6$] [9], 1-(6-hydroxyhexyl)-3-methylimidazolium bis{(trifluomethyl)sulfonyl}imide, [OHHMIM][$NTf_2$] [10], 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate, [HMIM][eFAP] [10], 1-butyl-3-methylimidazolium bis{(trifluomethyl)sulfonyl}imide, [BMIM][$NTf_2$] [4,14], 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate, [EOHMIM][$BF_4$] and 1-hydroxyethyl-2,3-dimethylimidazolium tetrafluoroborate, [EOHMMIM][$BF_4$] [15], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] [16], 1-hexyl-3-methylimidazolium tetracyanoborate, [HMIM][TCB] [17], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] and trihexyltetradecylphosphonium tetracyanoborate, [$P_{14,6,6,6}$][TCB] [17]. Recently, the bis{(trifluoromethyl)sulfonyl}imide-based ILs have been studied in ternary LLE systems: octyltriethylammonium bis{(trifluoromethyl)sulfonyl}imide, [$N_{8,2,2,2}$][$NTf_2$], methyltrioctylammonium bis{(trifluoromethyl)sulfonyl}imide, [$N_{8,8,8,1}$][$NTf_2$], 1-dodecyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [DoDMIM][$NTf_2$] and 1-hexyloxymethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [$C_6H_{13}OCH_2MIM$][$NTf_2$] [18]. Quite large recovery selectivity was observed for [DMIM][TCB] [17], and for [$P_{14,6,6,6}$][TCB] [17]. The production of bio-butan-1-ol using [DMIM][TCB] was proposed by MERCK. It was described as a low energy, fast mixing-settling process with co-extraction with acetone from water.

Initial information about selectivity of a solvent could be obtained from the analysis of activity coefficients at infinite dilution ($\gamma_{13}^{\infty}$). For example the values of selectivity ($S_{12}^{\infty} = \gamma_1^{\infty}/\gamma_2^{\infty}$) for water (1)/butan-1-ol (2) separation at $T = 328.15$ K with ILs were as follows: for 1-butyl-1-methylpyrrolidynium tetracyanoborate, [BMPYR][TCB] $S_{12}^{\infty} = 1{,}12$ [19], for [DoDMIM][$NTf_2$] ($S_{12}^{\infty} = 2.76$) [20], for [$N_{8,2,2,2}$][$NTf_2$] ($S_{12}^{\infty} = 2.36$ at $T = 338.15$ K) [21], for 1-octylisoquinolinium bis{(trifluoromethyl)sulfonyl}imide, [OiQuin][$NTf_2$] ($S_{12}^{\infty} = 2.22$) [22], for 1,3-dihexyloxyimidazolium bis{(trifluoromethyl)sulfonyl}imide, [$(C_6OC)_2IM$][[$NTf_2$] ($S_{12}^{\infty} = 2.67$) [23].

Analysis of the results obtained from LLE measurements in ternary systems and in the limiting activity coefficients measurements shows that the selectivity of recovery of butan-1-ol from aqueous solution was larger by using ILs with longer alkyl chains ($C_4$-$C_{12}$) in cation, and/or in anion. Recently, in our study we focused on ILs with long alkane-chain in cation or/and anion such as [DoDMIM][$NTf_2$] [20] or [OiQuin][$NTf_2$] [22], or tributyltetradecylphosphonium dodecylbenzenesulfonate, [$P_{14,4,4,4}$][DBS] [24].

In this work we report the $\gamma_{13}^{\infty}$ for 65 solutes, including polar and non-polar solutes and water, in the IL tetraoctylphosphonium bis{(trifluomethyl)sulfonyl}imide, [$P_{8,8,8,8}$][$NTf_2$]. Limiting activity coefficients were determined by gas-liquid chromatography at six temperatures in range of (318.15–368.15) K. The DSC data, density and viscosity were measured for this new IL. We reported also gas-liquid partition coefficients $K_L$ for the set of 65 selected organic solutes (hydrocarbons, alcohols, water, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, and esters) in the [$P_{8,8,8,8}$][$NTf_2$] as a function of temperature. The obtained thermodynamic properties were analyzed to show the intermolecular interactions between solutes and the IL. The comparison with previously-published phosphonium-based and many others ILs, which are attractive to this separation process was made. The Abraham solvation parameter model was also presented for all solutes.

## 2. Material and methods

### 2.1. *Materials*

The ionic liquid, tetraoctylphosphonium bis{(trifluoromethyl)sulfonyl}imide [$P_{8,8,8,8}$][$NTf_2$] used in this work was synthesized in our laboratory and is presented in Table 1.

#### 2.1.1. *Tetraoctylphosphonium bis{(trifluoromethyl)sulfonyl}imide*

To a 37.21 g of tetraoctylphosphonium bromide (0.0660 mol, Io-Li-Tec >95%, as received) 20.29 g of lithium bis{(trifluoromethyl)sulfonyl}imide (0.0707 mol, 7% excess, Sigma-Aldrich 98%, used as received) in 100 $cm^3$ of water was added. The mixture was diluted with 200 $cm^3$ of dichloromethane (P.O.Ch.) and it was stirred in the room temperature for 24 h. Afterwards, phases were separated and organic phase was extracted with $10 \times 50$ $cm^3$ of water to remove residual LiBr and $LiNTf_2$. The solvent was removed by rotary evaporation and the product was further dried in vacuum at $T = 348$ K for 24 h. The product was obtained as colorless liquid 48.43 g. Yield 96%.

$^1$H NMR: $\delta_H$(500 MHz; $CDCl_3$): 0.83 (12 H, t, $^3J_{H,H} = 6.85$ Hz), 1.23 (32 H, m), 1.43 (16 H, m), 2.05 (8 H, m).

$^{13}$C NMR: $\delta_C$(100 MHz; $CDCl_3$): 13.84, 18.40, 18.78, 21.40, 22.44, 28.59, 28.77, 30.34, 30.45, 31.53, 119.88 (q, $^1J_{C,F} = 323$ Hz).

The NMR of [$P_{8,8,8,8}$][$NTf_2$], $^1$H NMR and $^{13}$C NMR are presented in Fig. 1S in the Supplementary Material (SM).

The solutes, purchased from Aldrich and Fluka, were used without further purification because the GLC technique separates any impurities on the column. The list of materials, the sources and purities are presented in Table 1S in the SM.

The water content of IL was analyzed by the Karl-Fischer titration technique (Metrohm, 716 DMS Titrino) before preparing the column. The sample of 1 $cm^3$ of the IL was dissolved in methanol (Merck) and titrated with portions of 0.0025 $cm^3$. The mass fraction of water in a sample was less than $460 \times 10^{-6}$ with an uncertainty of $u(\text{w.c.}) = 8 \times 10^{-6}$.

### 2.2. *Differential scanning calorimetry, DSC*

The basic thermal characteristics of IL, i.e. temperature of fusion ($T_{fus}$) and glass transition ($T_g$), enthalpy of fusion ($\Delta_{fus}H$) as well as heat capacity at glass transition temperature ($C_{p(g)}$) 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 by 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 fusion and glass temperature was $u(T_{fus}, T_g) = 0.1$ K and that of the fusion enthalpy $u(\Delta_{fus}H) = \pm 10$ J $mol^{-1}$. Heat capacity at glass transition $u(C_{p(g)}) = 10$ J $mol^{-1}$ $K^{-1}$. The DSC diagram of the IL is shown as Fig. 2S in the SM and the data are presented in Table 1.