



Ternary (liquid + liquid) equilibria of {bis(trifluoromethylsulfonyl)-amide based ionic liquids + butan-1-ol + water}



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ABSTRACT

Ternary (liquid + liquid) phase equilibria for 3 systems containing bis(trifluoromethylsulfonyl)-amide ionic liquids (1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, {1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide} + butan-1-ol + water} have been determined at $T = 298.15$ K. The selectivity and solute distribution ratio were calculated for investigated systems and compared with literature data for other systems containing ionic liquids. In each system total solubility of butan-1-ol and low solubility of water in the ionic liquid is observed. The experimental results have been correlated using NRTL model. The influence of the structure of ionic liquid on phase equilibria, selectivity and solute distribution ratio is shortly discussed.

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1. Introduction

The interest in renewable energy sources is still growing. One of them is butan-1-ol, which is used inter alia as an additive to gasoline. Butan-1-ol (called as biobutanol) is produced by the anaerobic conversion of raw materials such as sugarcane, wheat, corn, straw as well as cellulose-containing materials (for example wood waste) by *Clostridium acetobutylicum* bacteria. This method is called ABE fermentation (acetone + butanol + ethanol), because the products of the process are acetone, butan-1-ol and ethanol with a product ratio of 3:6:1. The main disadvantage of this process is low yield of butan-1-ol ($10 \text{ g} \cdot \text{dm}^{-3}$ of butan-1-ol in fermentation broth), therefore the separation of this compound is troublesome [1,2]. In addition, the boiling point of butanol is higher than water which causes that conventional methods of separation such as distillation are energy intensive and uneconomical. Moreover butanol and water form an azeotrope. Therefore ethanol is often used as a bio-fuels component. However butanol has advantages over ethanol, inter alia has a higher calorific value, better mixes with fuel and less with water, is less volatile. Because of mentioned problems and many advantages of butan-1-ol it is necessary to investigate new, economic and environmentally friendly methods for separation of this alcohol. One of them is solvent extraction using ionic

liquids (ILs). In very briefly, ionic liquids are salts liquid at room temperature or their melting point is lower than 100°C . They have some important properties for extractants such as: wide temperature range of a liquid state; high thermal stability; and extremely low vapour pressure [3–5]. For environmental reasons the last mentioned property is especially important in extraction processes. To design or modify any process involving an ionic liquid as extractant in (liquid + liquid) extraction the measurements of ternary (liquid + liquid) equilibria (LLE) is needed as well as calculations of selectivity and solute distribution ratio. In this work the ternary (liquid + liquid) equilibria diagrams for 3 systems containing 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, {1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide} ionic liquids + butan-1-ol + water} have been determined at $T = 298.15$ K. The selectivity and solute distribution ratio were calculated for investigated systems and compared with literature data for other systems containing ionic liquids.

2. Experimental

2.1. Chemicals

The list of chemicals (including ILs abbreviations) used in this work with information about source and purity is presented in table 1. Structures of investigated ILs and basic physicochemical

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TABLE 1
Description of chemicals.

Chemical name ^a	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method	Water content/10 ⁻⁶
Bis(trifluoromethylsulfonyl)azanide; 1-butyl-1-methylpiperidin-1-ium (1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide) [bmPIP][NTf ₂]	IoLiTec	≥0.990	Vacuum heating			<250 ^c
Bis(trifluoromethylsulfonyl)azanide; 1-(2-methoxyethyl)-1-methylpiperidin-1-ium (1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide) [COC ₂ mPIP][NTf ₂]	Merck	≥0.995	Vacuum heating			<180 ^c
Bis(trifluoromethylsulfonyl)azanide; 1-(2-methoxyethyl)-1-methylpyrrolidin-1-ium (1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide) [COC ₂ mPYR][NTf ₂]	Merck	≥0.995	Vacuum heating			<160 ^c
Butan-1-ol	Aldrich	≥0.998		0.9995	GC ^b	nd ^d
Oxidane (water)	Own source		Distillation, filtration	≥0.999	Density	
Propan-2-one (acetone)	Fluka	≥0.999		0.9997	GC ^b	nd ^d
Propan-1-ol	Sigma-Aldrich	≥0.998		0.9987	GC ^b	nd ^d

^a Names in parentheses are common names used in text.^b (Gas + liquid) chromatography.^c Karl-Fisher titration.^d nd – not detectable, (gas + liquid) chromatography, TCD detector.

properties like density and viscosity as a function of temperature, decomposition temperature can be found in the previous works [6–9]. To remove any volatile chemicals and water from the ionic liquids they were purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at a temperature of about 363 K for approximately 5 h. Due to the high purity of the rest of chemicals (confirmed by GC analysis) they were used without further purification.

2.2. Apparatus and procedure

The experimental LLE tie-lines were determined by preparation of immiscible mixtures of the three compounds of the ternary system studied. Mixtures were placed into a jacketed glass cell with a volume of 10 cm³, together with a coated magnetic stirring bar, and closed to avoid losses of substances by evaporation. The jackets were connected to a thermostat bath (LAUDA Alpha) to maintain a constant temperature of 298.15 ± 0.02 K in the vessels. The mixtures were stirred using the magnetic stirrer for minimum 1 h and then allowed to settle for a minimum of 24 h to guarantee that the equilibrium state was completely reached. After phase separation, approximately 0.1 to 0.3 cm³ samples from both phases in equilibrium were taken using glass syringes with stainless steel needles, without disturbance of the interface. The samples were weighed. Acetone (about 0.5 cm³) was added to the samples to avoid phase splitting and to maintain a homogeneous mixture. Propan-1-ol with a known mass was used as internal standard for the GC analysis. Since ionic liquids have a very low vapour pressure, they cannot be analysed by GC, therefore, only the masses of butan-1-ol and water were analysed in the samples. For a ternary mixture, only two components need to be analysed, therefore the mass of ionic liquid was calculated by difference.

The composition was analysed by gas chromatography. The PerkinElmer Clarus 580 GC equipped with TCD detector was used. The data were collected and processed using TotalChrom Workstation software. The parameters of analysis were as follow: two columns connected in series – the first one: PerkinElmer Elite-5 (5% diphenyl-95% dimethyl polysiloxane), 30 m length, 0.53 mm inter-

nal diameter, 5 μm film thickness, and the second one: PerkinElmer Elite-WAX (Polyethylene Glycol), 30 m length, 0.53 mm internal diameter, 5 μm film thickness; column oven temperature: 70 °C; injector temperature: 200 °C; detector temperature: 200 °C; split ratio: 2:1; carrier gas: helium; analysis time: 12 min. To avoid of column contamination the ionic liquid was collected in the injector liner (filled with quartz glass) and in the pre-column. All samples were injected three times, and the average value was calculated. The uncertainty of the mole fraction did not exceed ± 0.002 . Results are presented in the [table 2](#).

3. Modelling

The experimental values were correlated with the NRTL model describing the excess Gibbs energy [10]. The NRTL non-random parameter α was set to a value of $\alpha = 0.3$. The values of the model parameters and the corresponding standard deviations are given in [table 3](#). The results of the correlation are presented in [figures 1–3](#).

4. Results and discussion

[Table 2](#) shows the compositions of the experimental tie lines for the ternary systems investigated at $T = 298.15$ K. Graphical representation of the results in the form of LLE phase diagrams is presented in [figures 1–3](#). The presence of polar methoxy group in the cation causes better solubility of water in [COC₂mPIP][NTf₂] and [COC₂mPYR][NTf₂] ILs than in [bmPIP][NTf₂] one. Additionally the miscibility gap is lower for system containing pyrrolidinium ionic liquid than that for piperidinium one due to less aliphatic character. The comparison of binodal curves is presented in [figure 1S](#). Similar shapes of binodal curves were previously observed for similar systems in work of Domańska [11].

Comparison of binary LLE data for systems (IL + water) with the literature results are presented in [figure 2S](#) [12,13]. The results are not consistent, and the differences are about 0.1 of mole fraction. These differences can be explained by the fact that the results were obtained using two different methods, static method in this work,

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