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The use of ionic liquids for separation of binary hydrocarbons mixtures based on gamma infinity data measurements

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ABSTRACT

The effect of interactions between 64 organic solvents and water on the interfacial and bulk properties at infinite dilution of two ionic liquids (ILs) namely *N*-triethyl-*N*-octylammonium bis(fluorosulfonyl)imide, $[N_{2,2,2,8}]$[FSI] and 1-butyl-3-methylpyrrolidynium bis(fluorosulfonyl)imide, [BMPyr][FSI] were determined via measurement of activity coefficients γ_{13}^{∞} at infinite dilution using the gas-liquid chromatography technique. Measurements were undertaken at six temperatures, in 10 K intervals, in the range of (318.15 to 368.15) K. The solutes studied included both non-polar and polar compounds, as alkanes, alkenes, and alkynes, as well as aromatic hydrocarbons, alcohols, water, ethers, ketones, pyridine, thiophene, esters, acetonitrile and 1-nitropropane. The gas-liquid partition coefficients, K_L at infinite dilution, and the fundamental thermodynamic functions, partial molar excess Gibbs energy, enthalpy and entropy at infinite dilution were calculated from the experimental data measurements. The values of selectivity and capacity for four important in petrochemical technology separations, viz. hexane/hex-1-ene, hexane/benzene, cyclohexane/cyclohexene, and cyclohexane/benzene were calculated from γ_{13}^{∞} values and compared to literature data for ammonium ILs with different cations and anions and for ILs with $[BMPyr]^-$ cation and different anions. The results from the study indicate that $[N_{2,2,2,8}]$[FSI] reveals not satisfied selectivity values in comparison with [BMPyr][FSI] and literature values for all four of the separation cases studied.

1. Introduction

Ionic liquids (ILs) are important new salts with unusual properties, such as very low vapour pressure, high thermal stability, non-flammability, and high solvation properties. They have been widely studied in many disciplines of science, and have been proposed as potential replacement solvents for conventional organic solvents in separation processes [1–4]. Important new results were proposed for the separation of aromatic hydrocarbons from aliphatic hydrocarbons and desulphurization and denitrification of diesel oil and [4–7]. Among the many potential separation applications, one of the most relevant is the employment of ILs as extractants for separation of alkenes from alkanes such as hexane/hex-1-ene, or cyclohexane/cyclohexene [8–10].

The hydrophobic ILs consisting of bis(fluorosulfonyl)imide $[FSI]^-$ anion reveal good results as electrolytes for Li-ion-based electric storage devices [11]. They exhibit relatively low viscosity, high conductivity, wide electrochemical stability window and high chemical stability [11]. ILs composed of the $[FSI]^-$ anion and imidazolium-based, or pyrrolidinium-based cation have much lower viscosity than those ILs with bis{(trifluoromethyl)sulfonyl}imide, $[NTf_2]^-$ anions [12]. The physical and electrochemical properties of the mixture of $Na[NTf_2]$ with 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide, [PMPYR][FSI] have been determined to show that they have a potential for the sodium battery electrolyte [13]. The following ILs were proposed by us for the separation of 2-phenylethanol (PEA) from water phase after the biosynthesis: 1-hexyl-l-methylmorpholinium bis(fluorosulfonyl)imide, [HMMOR][FSI], *N*-octylisoquinolinium bis(fluorosulfonyl)imide, [OiQuin][FSI], 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide, [BMPYR][FSI] and *N*-triethyl-*N*-octylammonium bis(fluorosulfonyl)imide, $[N_{2228}]$[FSI] [14]. The selectivities of extraction of PEA from the fermentation broth were not satisfied [14]. The goal of this work is to continue our studies on separation processes using two bis(fluorosulfonyl)imide-based ILs in binary systems of hydrocarbons.

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Preliminary information about suitable entrainers for separation can be obtained from activity coefficients measurements at infinite dilution, γ_{13}^{∞} by the gas-liquid chromatography (GLC) technique. The information obtained is generally the first step in the engineering design process to determine the most suitable extraction and separation processes.

The present work is focused on two ILs, namely *N*-triethyl-*N*-octylammonium bis(fluorosulfonyl)imide, $[N_{2,2,2,8}]$[FSI] and 1-butyl-3-methylpyrrolidydinium bis(fluorosulfonyl)imide, [BMPyr][FSI]. In recent years ILs have been widely promoted as solvents for alkane/alkene separations [15,16]. Recently, γ_{13}^{∞} data were measured by us for 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA] and 1-allyl-3-methylimidazolium dicyanamide, [AMIM][DCA] [10,17]. These measurements revealed a very promising selectivity and capacity for the hexane/hex-1-ene, and cyclohexane/cyclohexene separation processes [10,17]. The bis{(trifluoromethyl)sulfonyl}imide, $[NTf_2]$-based ILs are appropriate alternatives for a polar molecular liquids and are widely proposed as new entrainers for many processes [18]. However, our many years experience have shown that $[NTf_2]$-based ILs exhibit much lower separation parameters in hydrocarbons mixtures than those with $[DCA]^-$, tricyanomethanide, $[TCM]^-$ and thiocyanate, $[SCN]^-$ anions [8,17]. As an example, 1-allyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, $[AMIM][NTf_2]$ has a selectivity ($S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty} = 1.94$) [19] and [AMIM][DCA] has a selectivity ($S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty} = 2.51$) [10] at $T = 328.15$ K in the hexane/hex-1-ene separation process. In this work we present an analysis of the selectivities and capacities for hexane/hex-1-ene, hexane/benzene, cyclohexane/cyclohexene and cyclohexane/benzene separation processes based on the measurements of γ_{13}^{∞} as well as the gas-liquid partition coefficients K_L and thermodynamic functions at infinite dilution for all measured solutes.

2. Materials and methods

2.1. Materials

The ILs were synthesized in our laboratory with purity >0.97 mass fraction [14]. The names, abbreviation of names, structures, molar masses, purification method, purity and water content are listed in Table 1. The procedures of synthesis, yield of reactions, Elemental Analysis, ^{1}H NMR, ^{13}C NMR diagrams, DSC diagrams and densities were reported earlier [14]. The different solutes, purchased from Aldrich or Fluka, had purities better than 0.97 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

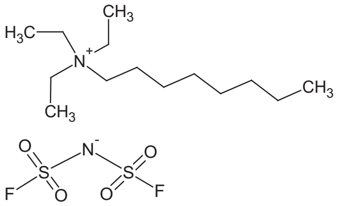
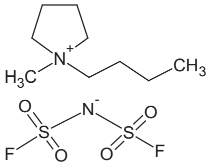
The water content of the solvents was analysed by the Karl-Fischer titration technique (method TitroLine KF). The sample of IL, or solvent was dissolved in methanol and titrated in steps of 0.0025 cm^3. The uncertainty on the water content was u (w.c.) = 10×10^{-6} for the 3 cm^3 sample of IL injected. The water content in ILs was 282×10^{-6} and 166×10^{-6} wt fraction for $[N_{2,2,2,8}]$[FSI] and [BMPyr][FSI], respectively.

2.3. Apparatus and experimental procedure

Experiments were performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using the TotalChrom Workstation software. Glass columns of length 1 m, with a 4 mm internal diameter were used. The solid support Chromosorb W/AW-DCMS 100/120 mesh was supplied by Sigma-Aldrich. Coating of the solid support material with the IL was performed by dispersing a certain portion of the IL in methanol, followed by evapouration of the solvent using a rotary evapourator. The masses of the stationary phase and of the solid support were weighed with a precision ±0.0001 g, achieving an uncertainty in the IL loading on the column in the order of 2×10^{-4}mmol. The solvent loading on the column for ILs was 45.0% mass percent (6.075×10^{-3} mol and 7.700×10^{-3} mol for $[N_{2,2,2,8}]$[FSI] and [BMPyr][FSI], respectively). In our work we always use the large loading of columns, which prevents possible residual adsorption of solutes onto the column packing. Prior to each experiment, the column was conditioned by blowing hot carrier gas through it at a high flow rate ($\sim$2.0 cm^3·s^{-1}) at temperature $T = 370$ K for about 8 h. The pressure drop ($P_i - P_o$) was varied between 60 kPa and 80 kPa depending on the flow rate of the carrier gas as for almost all measured by us ILs. The inlet pressure, P_i, was measured by a pressure gauge installed on the gas chromatograph with an uncertainty of ±0.1 kPa and the outlet pressure, P_o, was measured using an Agilent Precision Gas Flow Meter having an uncertainty of ±0.07 kPa. The mean column pressure, $\bar{p}$, inlet column pressure, P_i, outlet column pressure, P_o and standard state of solutes at given temperatures and st. state are listed in Tables 2S and 3S in the SM.

Table 1

Investigated ionic liquids: structure, name and abbreviation of name, molar mass, purification method and purity.

Structure	Name, abbreviation	M/(g·mol^{-1})	Purif.method	Mass fraction purity/water content (mass fraction)
	*N*-triethyl-*N*-octylammonium bis (fluorosulfonyl)imide, $[N_{2,2,2,8}]$[FSI] Synthesis [14]	394.54	Low pressure, 24 h, 320 K	0.975 282×10^{-6}
	1-Butyl-1-methylpyrrolidinium bis (fluorosulfonyl)imide, [BMPyr][FSI] Synthesis [14]	322.39	Low pressure, 24 h, 320 K	0.974 166×10^{-6}