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Effect of the cation and anion of the ionic liquid on desulfurization of model fuels

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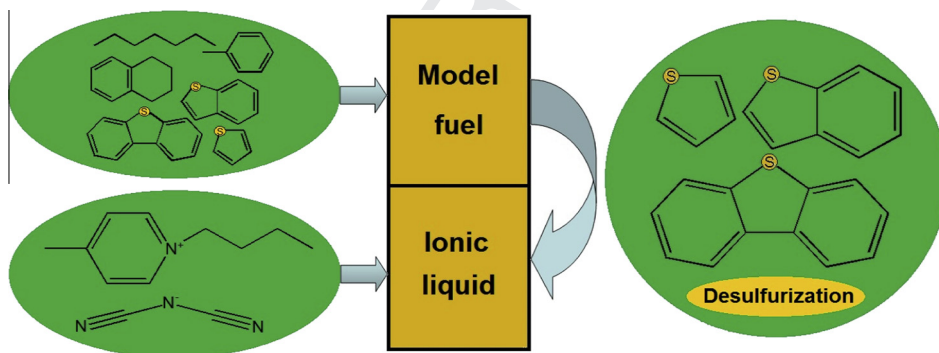
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HIGHLIGHTS

- Extraction of sulfur compounds and aromatic compounds from model fuel is carried out.
- The ternary liquid–liquid equilibrium with 21 ILs was measured.
- The selectivity and solute distribution ratio were calculated.
- Extraction was proposed with: [bmPY][DCA], [bmPYR][DCA] and [bmMOR][TCM].
- About 74% of sulfur compounds were removed from fuel with [bmPY][DCA].

GRAPHICAL ABSTRACT



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ABSTRACT

Ionic liquids (ILs) are known as a new solvents with high extraction capacity for aromatic sulfur and aromatic compounds from gasoline and diesel in comparison to the conventional solvents. In this work the desulfurization ability of 21 ionic liquids in the extraction of sulfur organic compounds from hydrocarbons, which were used as a model of gasoline and diesel oils by solvent extraction, has been developed. With this aim, ternary liquid–liquid phase equilibrium data (LLE) has been obtained for mixtures of {IL + model fuel (thiophene, benzothiophene, dibenzothiophene, toluene, tetralin) + heptane} at $T = 298.15$ K and ambient pressure. The ILs studied: pyridinium-, pyrrolidinium-, morpholinium-, imidazolium-, piperidinium-, phosphonium-, and ammonium-based with different anions as dicyanoamide, [DCA], tetracyanoborate, [TCB], tricyanomethanide, [TCM], bis((trifluoromethyl)sulfonyl)imide, [NTf₂], trifluorotris(perfluoroethyl)-phosphate, [FAP], trifluoroacetate, [TFA], and trifluoromethanesulfonate, [CF₃SO₃]. The suitability of ILs used as solvents for extractive desulfurization has been evaluated in terms of solute distribution coefficient and selectivity. Few of proposed ILs, as 1-butyl-4-methylpyridinium dicyanamide, [bmPY][DCA], 1-butyl-1-methylpyrrolidinium dicyanamide, [bmPYR][DCA], and *N*-butyl-*N*-methylmorpholinium tricyanomethanide, [bmMOR][TCM] show high selectivities (>200) and high distribution coefficients (>1.2) for extraction of sulfur compounds. The experimental results obtained in this work are evaluated in view of the results reported in literature [1,2]. It is shown that the ionic liquids investigated in this work are able to extract sulfur in preference to toluene and tetralin. Moreover, the distribution coefficients for [bmPYR][TCM], [bmIM][TCM] and [bmPYR][TCB] ILs are the best for the extraction of thiophene, the [bmPY][DCA], [bmPYR][TCB], [bmPYR][TCM] and [bmIM][TCM] ILs have the best distribution

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coefficients for benzothiophene; the [bmPY][DCA], [bmPYR][TCM] and [P_{6,6,6,14}][TCM] ILs have the best distribution coefficients for dibenzothiophene.

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1. Introduction

Ionic liquids (ILs) are proposed as entrainers for new alternative technologies to the classical hydrodesulfurization process, or for the deep-desulfurization of low level aromatic-sulfur compounds [1–10]. The challenge of petroleum industry is to diminish the typical aromatic-sulfur compounds that are found in fuels as thiophene, benzothiophene, methyl dibenzothiophenes, 4,6-dibenzothiophenethiols, thioethers and disulfides [11]. For the application of ILs in refinery processing, the possibility of the entrainer has to be investigated on model fuel, representing the real feed mixtures.

Deep desulfurization of diesel fuel has become an important industry subject due to the new legislative regulations to reduce sulfur content in the USA and Europe [12,13]. The emission of sulfur from petrol and diesel oils, which is linked to acid rain phenomena, plays a crucial role in pollution problems of cities in Europe and USA. Due to this situation, the European Union approved a new Directive stating that the content of total sulfur in European gasoline and diesel fuels from 2010 onwards must be at a maximum concentration level of 10 ppm [13]. Nowadays, the hydrodesulfurization (HDS) processes which is employed by refineries to remove organic sulfur from fuels for several decades needs high temperature and pressure, larger reactor volumes, and more active catalysts [14]. Faced with continuing fuel quality challenges, the scientific fundamental research have begun to pay close attention to extraction of sulfur and nitrogen compounds with ionic liquids (ILs), which have the potential for alternative and future complementary technology for deep desulfurization [15–23]. In order to solve this problem, the ternary liquid–liquid equilibrium (LLE) desulfurization with ILs [15–23] and activity coefficients at infinite dilution have been proposed as the first information of selectivity [24–31].

Undoubtedly, the future of the desulfurization process will be proposed with ILs together with the oxidative process [2,3]. It may be industrially favorable process because of low temperature, low use of energy and low cost. Many of reductive desulfurization with ILs and different substances is also proposed [7]. However, new proposals include adsorption process on Ni-loaded carbon [32] or iron supported on activated carbon [33], or using new biotechnological process of utilization of sulfur-organic compounds with a strain of *Achromobacter* sp, isolated from a contaminated petroleum-oil soil sample [34]. The adsorption ability of polymer-supported ILs with different lengths of alkyl chain linkers was shown to remove aromatic sulfides from model gasoline on a level of $\geq 30\%$ [35].

Piperidinium-based ILs [23], pyrrolidinium-based ILs with different anions [20], and 1-alkylcyanopyridinium-based ILs [22] have been recently studied in our laboratory in ternary LLE {IL + thiophene, or benzothiophene + heptane} with promising results. However, the best selectivities for extraction of thiophene and benzothiophene were obtained with 1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM] IL [21]. High selectivities for the extraction of sulfur compounds from hydrocarbons with high solute distribution ratios were obtained with dicyanoamide-based ILs, [DCA][−] [1], and tricyanomethanide-based ILs, [TCM][−] [1,20,21].

Attractive extraction parameters were presented as well as for 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [EMIM][NTf₂], [16], 1-ethyl-3-methylimidazolium acetate, [EMIM][OAc] [17], 1-ethyl-3-methylimidazolium thiocyanate,

[EMIM][SCN], [15] and 1,3-dimethylimidazolium methylphosphonate [DMIM][MP] [15].

The careful analysis of the values of activity coefficients at infinite dilution for the selectivity of separation of thiophene from hexane using pyrrolidinium-based IL ($n = 3–10$) [24,25] and piperidinium-based ILs ($n = 3–6$) [26,27] with different alkane chains and the popular bis((trifluoromethyl)sulfonyl)imide, [NTf₂][−] anion revealed better results in the piperidinium-based ILs.

This work is a continuation of our studies on the extraction abilities of chosen ILs from model fuel based on our previous fundamental thermodynamic measurements on activity coefficients at infinite dilution, solubility measurements in binary systems and ternary LLE measurements. Model fuel represents the petrochemical streams which contain, in addition to mono- and poly-aromatic components, heterocyclic components comprising sulfur compounds. The use of ILs as extraction solvents provides to the co-extraction of aromatic hydrocarbons and sulfur-aromatic compounds in one separation step, which is expected from the technological point of view [1]. This is also beneficial in terms of investment and operational costs [36].

The ionic liquids investigated in this work are chosen based on the literature and our own results on the thermodynamic measurements of activity coefficients at infinite dilution [24–31], binary and ternary LLE data [15–23] and extraction results from model fuels [1,2].

In this work we report experimental ternary LLE data for twenty one ILs in the systems {IL + model fuel + heptane} at temperature $T = 298.15$ K and ambient pressure. The total sulfur removal will be investigated in comparison to toluene and tetralin, representatives for gasoline and diesel fuels. Therefore, the model feed has been proposed consisting of the three sulfur-aromatic compounds (thiophene, benzothiophene and dibenzothiophene), toluene, tetralin, and heptane. From the experimental data the extraction selectivity of different sulfur and organic compounds and the solute distribution coefficients were determined and are discussed.

2. Experimental

2.1. Chemicals and materials

The ILs used in this work were purchased from IoLiTec, Merck and Fluka and the solvents from Sigma Aldrich or POCH (the origins of the chemicals, supplier, mass fraction purity, CAS numbers of solvents are listed in Table 1a and those of ILs in Table 1b. The

Table 1a
Names, supplier and purity of the original materials used in this study.

Compound	Supplier	Mass fraction purity	CAS number
Acetone	POCH S.A. ^a	0.999	67-64-1
Benzothiophene	Sigma Aldrich	0.980	95-15-8
Butan-1-ol	Sigma Aldrich	0.998	71-36-3
Dibenzothiophene	Sigma Aldrich	0.980	132-65-0
Heptane	Sigma Aldrich	0.995	142-85-5
Pentylbenzene	Sigma Aldrich	0.990	538-68-1
Propan-1-ol	Sigma Aldrich	0.998	71-23-8
1,2,3,4-Tetrahydronaphthalene (Tetralin)	Sigma Aldrich	0.990	119-64-2
Thiophene	Sigma Aldrich	0.990	110-02-1
Toluene	POCH S.A. ^a	0.998	108-88-3

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