



Feasibility of phosphonium-based ionic liquids as solvents for extractive desulfurization of liquid fuels



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ABSTRACT

Binary solid–liquid equilibria for phosphonium based ionic liquids with dibenzothiophene (DBT) were measured within the temperature range of 303.15–353.15 K. The influence of temperature and ionic liquid structure on solubility of dibenzothiophene is presented. The solubility of DBT in all tested ionic liquids increased with temperature and as high as 52.93 wt% DBT in solution was obtained at 353.15 K. At this temperature, the solubility of DBT in ILs based on the trihexyl(tetradecyl)phosphonium cation depends on the anion of the IL. This dependency was found to be in the order; $\text{Cl}^- > \text{Br}^- \approx \text{N}(\text{CN})_2^- > [\text{NTf}_2]^- > \text{bis}(2,4,4\text{-trimethylpentyl})\text{phosphinate}$. The experimental solubility data was satisfactorily correlated using NRTL thermodynamic model. Finally, more than 99% (DBT) and 96% (thiophene) sulfur removal were achieved after 4th and 5th extraction stages respectively using the triisobutyl (methyl) phosphonium tosylate ionic liquid under mild operating conditions.

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1. Introduction

Sulfur and its compounds have both direct and indirect effects on our environment. Sulfur in its oxidized form (SO_x) causes acid rain and poses great health hazard in its reduced form (H_2S). Sulfur also poisons highly efficient exhaust emission control systems in diesel engines designed to significantly reduce other pollutants such as NO_x and particulate matters (PM) [1]. Governments have therefore imposed strict legislations on maximum sulfur content allowable in liquid fuel forcing it down to 10 and 15 ppm in EU and US respectively [2]. This in turn has forced refiners to seek for alternative desulfurization techniques. This is not because the current desulfurization technique (hydrodesulfurization, HDS) cannot do the job but it does so at the expense of about 3 times more catalyst requirement, 311.15 K increase in temperature and 50–100% increase in hydrogen partial pressure (hydrogen consumption) [3–5] among others. The consequence of this is not only financial loss, but also loss in quality of liquid fuel as it is accompanied by significant loss of octane number [6].

Due to the inefficiency of HDS when it comes to the removal of refractory sulfur compounds, adsorption [7], oxidation [8],

biodesulfurization [9] and extraction [10] have all been studied to investigate their potential as efficient desulfurization techniques. Extractive desulfurization (EDS) is a promising technique because it uses mild operating conditions, which translates to lower energy consumption, elimination of hydrogen consumption while avoiding special equipment requirements [11].

Many organic solvents are available for EDS. This includes *N,N'*-dimethylformamide (DMF), acetonitrile (ACN), dimethyl sulfoxide (DMSO), pyrrolidones and even methanol [4,8]. But the major setback of these solvents are their poor environmental performance and extraction efficiency [4]. Due to their non-volatility, non-flammability, high thermal stability and ease of handling [10], ionic liquids (IL) have received great deal of attention by researchers. Imidazolium [12], pyridinium [13] and thiazolium [14] based ILs, which are Lewis acidic, Bronsted acidic or neutral, have been investigated as potential solvents for EDS. The feasibility of these ILs have also been studied through phase equilibria and modeled using non-random two-liquid (NRTL) models. Particularly, imidazolium and pyridinium based ILs have been investigated using a binary (IL + thiophene/aliphatic hydrocarbon) [15,16] and ternary (IL + thiophene + HC (Aliphatic or Aromatic)) [17,18] systems.

Despite the promises ILs present as solvents for EDS, challenges still exist. These include low capacity and affinity for aromatic S-compounds, regenerability and high cost among others. It has been shown that the structure of the IL plays an important role in

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its extraction ability. Large cation with large alkyl chain groups have better extraction ability while pyridinium based IL have better extraction ability than imidazolium based IL [17–19]. This therefore indicates that out of about 10^6 possible ILs, only a certain combination of cation and anion can produce an IL with high sulfuric compounds affinity. This serves as an incentive for further investigation into feasibility of other types of ILs for EDS.

Relatively unexplored group of ILs in EDS are the phosphonium and quaternary ammonium based ILs. These ILs however, possess higher thermal and chemical stability than their imidazolium and pyridinium counterparts in addition to their unique behavior and solvating properties [20]. Phosphonium based ILs were reported to possess, in general, higher thermal stability and electronic polarizabilities than their ammonium based analogues [20,21]. Phosphonium-based ILs have been used as a reaction medium in Suzuki cross-coupling reaction [22], a phase transfer catalyst [23] and as a solvent for extraction of heavy metals from aqueous solutions [24]. These set of ILs are moisture-stable and commercially available. However, the performances of most these ILs on extraction of dibenzothiophene (DBT) have not been studied in the literature.

One way of studying the efficiency of a particular solvent toward desulfurization is through optimization of thermodynamic models describing phase equilibria. Therefore, the selection of an appropriate algorithm for the optimization of these models is crucial. Differential evolution (DE) is a stochastic population based algorithm which works on real variables [25]. In DE two different arrays are maintained and the newly found better solutions take part in mutation and crossover in next generation. Against DE, modified

differential evolution (MDE) maintains only one array of population members and is updated as and when a better solution is found. The survival of the fittest principle is used in both DE and MDE. The newly found better solutions can take part in mutation and crossover operation in the current generation itself. It has been found in the previous studies that an updating the single array continuously enhances the convergence speed leading to less function evaluations as compared to DE. MDE also offers advantages of one array consuming less memory and an improvement on CPU time. By wisely/appropriately choosing the key parameters of MDE (such as NP, CR and F) the problem of premature convergence can be avoided to a large extent. Thus such an improvement in an algorithm can be advantageous in many real world problems where the evaluation of a candidate solution is a computationally expensive operation and consequently finding the global optimum or a good sub-optimal solution with the original differential evolution algorithm is too time consuming, or even impossible within the time available [26,27]. This has been found to be very true in examples such as optimization in the field of non-linear chemical processes, process synthesis and design problems, continuous polymer reactor, electrical power systems, etc. [27–30]. Similarly multi-objective optimization strategies of differential algorithms are also successfully applied on selected real world optimization problems such as MOO of LDPE tubular reactor, wiped film PET reactor, styrene reactor (both adiabatic and pseudo-isothermal reactor), industrial naphtha cracker, etc. [31–35]. These single objective and MOO strategies of DE algorithms are in general found to outperform some other existing evolutionary strategies of MOO.

Table 1
Names, structure and important physical properties (at 298.15 K) of the investigated ILs.

Commercial and chemical names	Chemical structure	Purity ^c (wt %)	Viscosity ^a (mPa s)	Density ^a (g/cm ³)	Surface tension ^b (mN m ⁻¹)	Solubility in water ^c
CYPHOS IL101 Trihexyl(tetradecyl)phosphonium chloride CAS No.: 258864-54-9		>95	2729.1	0.8899	29.57	N
CYPHOS IL 102 Trihexyl(tetradecyl)phosphonium bromide CAS No.: 654057-97-3		>96	2988.4	0.9552	28.62	N
CYPHOS IL 104 Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate CAS No.: 465527-59-7		>95	1401.7	0.8853	26.66	N
CYPHOS IL 105 Tetradecyl(trihexyl)phosphonium dicyanamide CAS No.: 701921-71-3		>95	438.57	0.8990	30.69	N
CYPHOS IL 106 Triisobutyl(methyl)phosphonium tosylate CAS No.: 344774-05-6		98	Not available	1.0700*	36.43	Y
CYPHOS IL 109 Trihexyl(tetradecyl)phosphonium bis(triflamide) CAS No.: 460092-03-9		>97	336.74	1.0661	28.64	N

R₁: hexyl, R₂: tetradecyl for all except cyphos IL 106 where R₁: *iso*-butyl, R₂, R₃: methyl.

^a Data obtained from Neves et al. [45].

^b Data obtained from experiment. Relative uncertainty ($u_r(\text{surface tension})$) = 0.012.

^c Data were obtained from Cytec website.

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