# Extractive denitrogenation of model oils with tetraalkyl substituted pyridinium based ionic liquids

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## A B S T R A C T

The emission of sulfur and nitrogen oxides to the atmosphere caused by the presence of heterocyclic sulfur and nitrogen compounds present in fuel oils, is one of the main environmental issues worldwide and the major contributor for acid rain and global warming. In this work, the ability of two tetraalkyl substituted pyridinium-based ionic liquids as solvents for the denitrogenation of model fuels by liquid extraction was tested. For that purpose, the liquid–liquid equilibrium data for {heptane + pyrrole, pyridine + ionic liquid} ternary mixtures were experimentally determined at $T = 298$ K and at atmospheric pressure. The selected designed and synthesized ionic liquids were derived from the 1-butyl-3, 5-dimethyl-2-pentylpyridinium [$^1$B$^3$M$^5$M$^2$PPy] cation, incorporating dicyanamide [N(CN)$_2$] and bis (trifluoromethylsulfonyl) imide [NTf$_2$] anions. The extraction power of these ionic liquids was evaluated in terms of selectivity and solute distribution ratio, which showed that heterocyclic nitrogen compounds are better extracted by the ionic liquid derived from dicyanamide anion than by that based on bis (trifluoromethylsulfonyl) imide. In any case, the obtained results using these ILs are very promising and they greatly improve the results achieved so far using other ILs.

The new ionic liquid [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] was synthetized for the first time in this work and its physical properties (density, speed of sound, refractive index, viscosity) were measured at atmospheric pressure from $T = (298.15$ to $343.15)$ K. The decomposition temperature, thermal expansion coefficient, isentropic compressibility, and molar refraction for the pure ionic liquid were also calculated.

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## 1. Introduction

Nowadays, the emission of sulfur oxides and nitrogen oxides to the atmosphere is one of the main environmental issues worldwide and the major contributor for acid rain and global warming [1]. The causes of these undesirable emissions are heterocyclic sulfur and nitrogen compounds present in fossil fuels. Nitrogen oxides (NO$_x$) are a group of highly reactive gasses produced by cars, trucks and buses, power plants, and off-road equipment, during the combustion process of fossil fuels. Besides contributing to the formation of ground-level ozone, and fine particle pollution, NO$_x$ is linked with a number of adverse effects on the respiratory system. For all these reasons, current legislation has set very strict limits to the content of nitrogen compounds in diesel and gasoline [2,3].

Nitrogen compounds are present in fuels in the form of amines, nitriles and heterocyclic aromatic compounds, as pyrrole or pyridine [4,5]. The conventional method used in the oil industry to remove these contaminants in fuel oils is the process of hydrodenitrogenation (HDN), consisting in a reduction reaction at high pressure and temperature (300–450 °C) of the N components in the presence of hydrogen using catalysts to produce NH$_3$ [6,7]. This process is extremely expensive, and although aliphatic N compounds are reduced, it is inefficient in the reduction of aromatic compounds. In addition, the catalysts are easily deactivated by the small amounts of aromatic N compounds present in the fuel, which are preferably adsorbed on the surfaces of the catalyst [8]. For all these reasons, the development of new approaches to reduce the N content in fuel oils is needed.

Different non-conventional alternatives to remove these contaminants in fuel oils have been studied [9]. One of them is the use of ionic liquids (ILs), which are a class of solvents that have attracted considerable attention in the last few years [10,11]. ILs often exhibit a series of unique properties, such as thermal and chemical stability, wide liquid range, non-flammability, ability to dissolve a wide range

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of materials, compatibility with oxidant and reducing agents and negligible vapor pressure, that make their use advantageous over the use of volatile organic solvents. The absence of vapor pressure in ILs is very important from an environmental point of view, as ILs do not produce air pollution and can be easily recovered.

One of the most promising industrial applications of ILs is their use in the extractive desulfurization and denitrogenation of fuels by liquid–liquid extraction [12–16]. Previous studies have revealed that the ILs extractive desulfurization capacity clearly depend on the cation class, following the sequence tetraalkylpyridinium > trialkylpyridinium > dimethylpyridinium > methylpyridinium > pyridinium ≈ imidazolium ≈ pyrrolidinium, with much less significant variation with the anion type [17,18]. Thus, in a previous work, we have found that the tetraalkyl substituted pyridinium ILs 1-ethyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl) imide [$^1$E$^3$M$^5$M$^2$PPy][NTf$_2$] and 1-butyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl) imide [$^1$B$^3$M$^5$M$^2$PPy][NTf$_2$] present high values of selectivity and solute distribution ratio when used as solvent for extraction of thiophene from heptane [18]. It was also found that an increase of the N-alkyl chain length leads to lower selectivity values and that substitution in position 2 of the cationic ring affords a greater extractive ability. On the other hand, these tetraalkyl substituted pyridinium ILs have shown high thermal stability with onset decomposition temperatures over 630 K and no weight loss after heating at 473 K for 10 h [19].

Taking into account that the extraction efficiency of imidazolium and pyridinium ILs is higher for N-containing heteroaromatics than for those S-containing [20], and our good previous results when using tetra alkyl substituted pyridinium ILs for thiophene extraction [18], the present work on denitrogenation was started by applying one of these ILs for the extraction of heterocyclic N-compounds from heptane. For that purpose, experimental liquid–liquid equilibrium (LLE) data for the ternary mixtures {heptane + pyrrole + [$^1$B$^3$M$^5$M$^2$PPy][NTf$_2$]} were measured at T = 298 K and atmospheric pressure. On the other hand, in view of the good results reported by Hansmeier et al. [20] and Asumana et al. [21], when using ILs derived from dicyanamide anion [N(CN)$_2$] for extractive denitrogenation, the new IL 1-butyl-3,5-dimethyl-2-pentylpyridinium dicyanamide, [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$], was also synthesized and the phase behavior of the ternary mixtures {heptane + pyrrole, or pyridine + [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] was experimentally determined at the same conditions. The physical properties (density, speed of sound, refractive index and viscosity), as well as the decomposition temperature of the new [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] were also determined.

## 2. Material and methods

### 2.1. Chemicals

Heptane (Fluka, ≥99.5%), pyrrole (Acros Organics, 99%) and pyridine (Acros Organics, 99%) were used as received, without

further purification. The following reagents 2,3,5-trimethylpiridine (Aldrich, 99%), 1-bromobutane (Sigma–Aldrich, 99%), n-butyllithium (Sigma–Aldrich, 2.5 M in hexane) and sodium dicyanamide (Acros Organics, 97%), required for synthesis, were procured from the commercial supplier and used without any pretreatment. The solvents acetonitrile and tetrahydrofuran (Sigma–Aldrich, ACS reagent, ≥99.5%) were dried before its use.

### 2.2. Synthesis

The ILs were synthesized from 2,3,5-trimethylpyridine according to a procedure previously developed in our laboratory (Scheme 1) [18]. The introduction of a pentyl group in position 2 of the pyridine ring of the starting material was carried out by selective metalation using n-BuLi as base, and later alkylation with 1-bromobutane. 1-butyl-3,5-dimethyl-2-pentylpyridinium bromide, [$^1$B$^3$M$^5$M$^2$PPy][Br], was then prepared by treatment of 2-pentyl-3,5-dimethylpyridine with an excess of 1-bromobutane and purified by column chromatography over Al$_2$O$_3$ (neutral, activity II–III) using gradient elution (from CH$_2$Cl$_2$ to CH$_2$Cl$_2$/CH$_3$OH 9:1). Finally, the [NTf$_2$] and [N(CN)$_2$] anions were introduced by metathesis reactions carried out by treatment with lithium bis(trifluoromethane) sulfonylimide and sodium dicyanamide, respectively, to afford the desired ILs [$^1$B$^3$M$^5$M$^2$PPy][NTf$_2$] (I) and [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] (II). Their full names, abbreviations, purity and water content are described in Table 1. Their structures were determined by $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy as well as MS spectrometry. The structure of [$^1$B$^3$M$^5$M$^2$PPy][NTf$_2$] (I) was also confirmed by comparison of its spectroscopic data with those previously described [18]. [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] (II) was synthesized in this work for the first time. Both ILs were dried by heating at (373.15 to 383.15 K) and stirring under high vacuum (2 × 10$^{-1}$ Pa) for 48 h before use. Their purity was estimated by $^1$H NMR (400 MHz) showing to be no less than 99%.

The $^1$H, $^{13}$C and $^{19}$F NMR spectra of the purified products were recorded in CDCl$_3$ on a Bruker ARX at 400.1621, 100.6314 and 376.5266 MHz, respectively, with chemical shifts given in parts per million and coupling constants (J) in hertz. ESI mass spectra were recorded on a micrOTOF Focus spectrometer and on an apex-Qe spectrometer.

### 2.2.1. Preparation of 1-butyl-3,5-dimethyl-2-pentylpyridinium dicyanamide [$^1$B$^3$M$^5$M$^2$PPy][N(CN)$_2$] (II)

[$^1$B$^3$M$^5$M$^2$PPy][Br] (11.5 g, 0.036 mol) was dissolved in water (25 mL) and sodium dicyanamide (3.2 g, 0.040 mol) was added. The mixture was stirred for 12 h at 323.15 K. After cooling at r. t., dichloromethane (50 mL) was added to the reaction mixture. The upper aqueous phase was decanted and the lower dichloromethane layer was washed with deionized water (3 × 10 mL). The organic layer was then dried over anhydrous Na$_2$SO$_4$, filtered and kept at 253 K for 12 h. The organic solution was then filtered through column chromatography over neutral Al$_2$O$_3$ (5 g per 1 g of
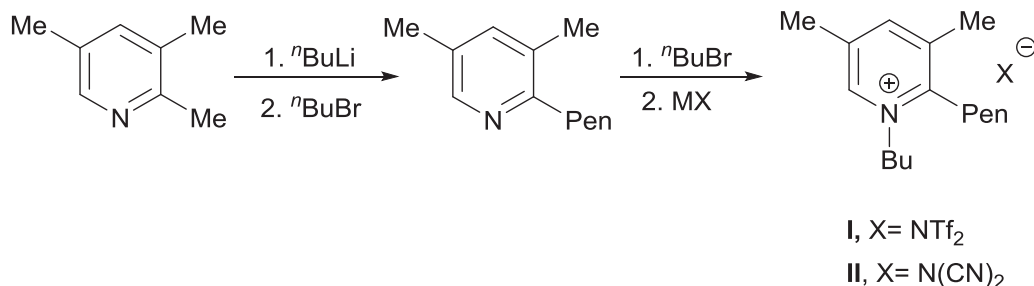


**Scheme 1.** Synthetic procedure and structures of the polyalkylpyridinium ILs studied in this work.