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Effect of the number, position and length of alkyl chains on the physical properties of polysubstituted pyridinium ionic liquids

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ABSTRACT

The knowledge of the physical properties of ionic liquids is of high importance in order to evaluate their potential applicability for a given purpose. In the last few years, ionic liquids have been proposed as promising solvents for extractive desulfurization of fuels. Among them, recent studies have shown that ionic liquids derived from pyridinium affords excellent S-compounds removal capacity. In this work, the thermal analysis of five ionic liquids derived from pyridinium cation polysubstituted with different alkyl chains was carried out by Differencial Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). Furthermore, the density, speed of sound, refractive index and dynamic viscosity for all the pure ionic liquids were also measured from $T = (298.15 \text{ to } 343.15)$ K. The effect of the number of cation alkyl chains, their length, and their position on the pyridinium ring, on the ionic liquid physical properties is also analyzed and discussed.

1. Introduction

Nowadays, the emission of sulfur and nitrogen oxides to the atmosphere is one of the main environmental issues worldwide and the origin of acid rain. The main source of emissions of these compounds to the atmosphere is the combustion of fossil fuels containing sulfur compounds [1]. Moreover, the presence of sulfuric oxides in exhaust fumes compromises the efficiency of the catalytic converters employed in cars for reducing contaminating emissions. For all these reasons, current legislation has set very strict limits to the content of sulfur compounds in diesel and gasoline [2,3], and the obtaining of ultra-low sulfur-containing fuels has become one of the main challenges for refinery industries.

The use of ionic liquids (ILs) as environmentally benign alternative solvents has been extensively studied and reviewed in the last few years [4]. ILs present a series of characteristics, as thermal and chemical stability, wide liquid range, non-flammability, ability to dissolve a wide range 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 of high importance under the 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 of fuels, which has been recently reviewed [5].

Studies of Holbrey and co-workers [6] have shown that the extractive ability of ILs is mainly affected by the cation type, and vary following the sequence dimethylpyridinium > methylpyridinium > pyridinium ≈ imidazolium ≈ pyrrolidinium. More recently, it has been shown that the tetraalkylsubstituted pyridinium ILs 1-ethyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl)imide $[^{1}\text{E}^{3}\text{M}^{5}\text{M}^{2}\text{PPy}][\text{NTf}_2]$ and 1-butyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethanesulfonyl)imide $[^{1}\text{B}^{3}\text{M}^{5}\text{M}^{2}\text{PPy}][\text{NTf}_2]$ present high values of selectivity and solute distribution ratio when used as solvents for extraction of thiophene from heptane [7].

The knowledge of the physical properties of an IL is very important to evaluate its capacity for a particular application. Taking into account the interest of polysubstituted pyridinium based ILs as extractants for fuels, thermal decomposition temperature, density, speed of sound, refractive index, and viscosities of a series of five ILs derived from pyridinium cation substituted with different alkyl chains are reported in this work. The influence of the number of cation alkyl chains, their length, and their position on the pyridinium ring, on the ionic liquid physical properties is also analysed and discussed.

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To our knowledge only the thermal analysis and viscosity values for one of the ILs studied in this work, 2-ethyl-1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide, [$^2E^1H^3M^5MPy$][NTf_2], were previously published [8].

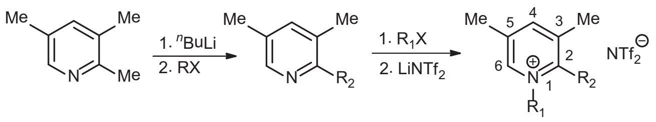
2. Experimental

2.1. Chemicals

Acetonitrile (Sigma–Aldrich, ACS reagent, ⩾99.5%), bis(trifluoromethane)sulfonylimide lithium salt (Fluka, ⩾99%), 1-bromobutane (Sigma–Aldrich, 99%), bromoethane (Sigma–Aldrich, 98%), 1-bromohexane (Aldrich, 98%), diethyl ether (Merck, GR, ⩽0.03% H_2O), 1-iodohexane (Acros organics, 98+%, stabilized) and iodomethane (Acros organics, 99%, stabilized) were procured from the commercial supplier and used without any pre-treatment, except diethyl ether, which was dried before its use.

2.2. Synthesis

The ILs were synthesized from 2,3,5-trimethylpyridine according to a procedure previously reported [7]. Their structures are shown in scheme 1. Full names, abbreviations, purity and water content of the studied ILs are described in table 1. Selective metalation of 2,3,5-tetramethylpyridine allowed the introduction of different alkyl groups in pyridine position 2 to afford 2-alkyl-3,5-dimethylpyridines with high yields. The pyridinium halides were then prepared by a quaternization reaction of the corresponding 2-alkyl-3,5-methylpyridines by treatment with an alkyl halide. [NTf_2] anion was subsequently introduced by a metathesis reaction with bis(trifluoromethane)sulfonylimide lithium salt to afford ILs **1**–**5**. The ILs were washed several times with 30 mL of distilled water until no Br^- was indicated by the solution of $AgNO_3$/HNO_3. Their structures were determined by ^1H, ^{13}C, ^{19}F NMR spectroscopy and HR–MS (see Supporting Information) and confirmed by comparison with previously described data [7]. All ILs were dried by heating at (373.15 to 383.15 K) and stirring under high vacuum ($2 \cdot 10^{-1}$ Pa) for 48 h before use. Their purity was estimated by ^1H NMR (400 MHz) showing to be no less than 99%.



1, R_1= Et, R_2= Pe
2, R_1= Bu, R_2= Pe
3, R_1= He, R_2= Me
4, R_1= He, R_2= Et
5, R_1= He, R_2= Pe

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

2.3. Apparatus and procedure

2.3.1. Thermal analysis

2.3.1.1. Phase transition temperatures. Measurement of phase transition temperatures were performed using a Mettler-Toledo differential scanning calorimeter (DSC), model DSC827^e and the data were evaluated using the Mettler-Toledo STAR^e software version 10.0. The instrument was calibrated for temperature and heat flow with zinc and indium reference sample provided by Mettler-Toledo. The accuracy of this apparatus was ±0.3 K and $\pm 1\ J \cdot g^{-1}$ in temperature and heat flow, respectively. A known mass of sample (1.5 to 4 mg) was placed in an aluminum pan of 40 μL with a pinhole at the top hermetically sealed. The sample pan and blank (an empty pan) were placed on separated raised platforms within the furnace and they were exposed to a flowing N_2 atmosphere. The samples were further dried at 393 K during 120 min in order to eliminate water or organic solvents. The *in situ* drying in the DSC was repeated until the phase transition temperatures remained constant. After this step, the sample was cooled from 393 K to 243 K at 10 K/min, followed by a heating step from 243 K to 423 K at 10 K/min. This test was developed under N_2 atmosphere. Thermal stability of ILs was determined with a heating ramp from 288 K to 773 K at rate of 10 K/min.

2.3.1.2. Decomposition temperature. Evaluation of decomposition temperature was measured with a thermogravimetric equipment (TGA) from TA instrument, Q600 model. The data were evaluated using the TA instrument software version 8.01. The instrument was calibrated for temperature and mass loss (%) with calcium oxalate as reference sample provided by TA instrument. The balance sensibility was 0.1 μg and the temperature accuracy ±0.5 K. A known mass of sample (5 to 10 mg) was placed into a platinum pan and heated from room temperature (298 K) to 773 K at a rate of 10 °C/min with a N_2 flow of 100 mL/min. Reproducibility was verified by running three replicates for each IL.

Decomposition temperature (T_{decom}) is defined as the intersection between the tangents of baseline weight and temperature curve where the decomposition take place.

As it was previously mentioned, thermal stability was also evaluated by DSC. Both techniques (TGA and DSC) working under N_2 atmosphere are complementary, and therefore it is possible to distinguish between different thermal transitions as phase transitions or evaporation phenomena of volatile compounds. ILs were evaluated with a Mettler Toledo 27HP model, control software and calibration procedure was the same as described for DSC827^e.

2.3.2. Physical properties

2.3.2.1. Density and speed of sound. Densities and speeds of sound were measured using an Anton Paar DSA-5000 M digital vibrating-tube densimeter with an accuracy of $5 \cdot 10^{-6}$ and $0.5\ m \cdot s^{-1}$, respectively. This apparatus is equipped with a density cell and a speed of sound cell thus combining the proven Anton Paar oscillating U-tube method with a highly accurate measurement of speed of sound. Both cells are temperature-controlled by a built-in Peltier thermostat that keeps the samples at working temperature with an accuracy of ±0.01 K. Uncertainties of measurements were esti-

TABLE 1
Full names, abbreviations, purity and water content of the studied ILs.

IL	Name	Abbreviation	Purity, mass fraction	Water content, mass fraction
1	1-ethyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethylsulfonyl)imide	[$^1E^3M^5M^2PPy$][NTf_2]	⩾0.99	$5.54 \cdot 10^{-4}$
2	1-butyl-3,5-dimethyl-2-pentylpyridinium bis(trifluoromethylsulfonyl)imide	[$^1B^3M^5M^2PPy$][NTf_2]	⩾0.99	$9.98 \cdot 10^{-4}$
3	1-hexyl-2,3,5-trimethylpyridinium bis(trifluoromethylsulfonyl)imide	[$^1H^2M^3M^5MPy$][NTf_2]	⩾0.99	$6.31 \cdot 10^{-4}$
4	2-ethyl-1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide	[$^2E^1H^3M^5MPy$][NTf_2]	⩾0.99	$4.61 \cdot 10^{-4}$
5	1-hexyl-3,5-dimethyl-2-pentylpyridinium bis(trifluorometylsulfonyl)imide	[$^1H^3M^5M^2PPy$][NTf_2]	⩾0.99	$1.03 \cdot 10^{-3}$