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Physicochemical properties of piperidinium, ammonium, pyrrolidinium and morpholinium cations based ionic liquids paired with bis(trifluoromethylsulfonyl)imide anion

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ABSTRACT

This study aims to investigate the temperature dependence of the physicochemical properties of five cations paired with bis(trifluoromethylsulfonyl)imide anion, namely 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide, 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, N-methoxyethyl-N-methylmorpholinium bis(trifluoromethylsulfonyl) imide, N-ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide and ethyl-dimethyl-propylammonium bis(trifluoromethylsulfonyl)imide. The density, viscosity, conductivity and surface tension of the resulting ionic liquids (ILs) have been determined within the temperature range (298.15–353.15) K. It has been found that all ILs exhibited Arrhenius behavior for conductivity and viscosity while the surface tension and density followed a linear trend. A satisfactory agreement was obtained between our experimental densities and those predicted by the group contribution model. This study is essential in the application of these ILs for process design and will reinforce the development of new correlations and other predictive methods in particular when the physicochemical properties are scarce, like in the case of morpholinium-based ILs.

1. Introduction

Ionic liquids have been the subject of great interest in recent years due to their many attractive properties. ILs are salts which melt at 100 °C or below [1,2], usually composed of an organic cation combined with an organic or inorganic anion [3–6]. ILs have many desirable characteristics such as low volatility and thermal stability [3]. Furthermore, ILs are highly tunable and can be designed with a specific task in mind, hence termed 'designer solvents' that is sometimes used to describe them [7]. For this reason, ILs have been explored for a wide range of applications including catalysis [8,9], electrochemistry [10,11], fuel cells [12] and separation processes [13].

The high electrostatic interactions between the ions of ILs give their physicochemical properties which distinguish them from conventional organic solvents [14]. These properties, such as density and viscosity, can be easily tuned or tailored by variation of cation and anion [15–17]. The determination and understanding of these fundamental physical and transport properties is indispensable for process design [18]. Furthermore, the collection of a large data bank for physicochemical properties of various ILs is essential, not only for product process design but also for the development of predictive methods and the structure of ILs [19].

Bis(trifluoromethylsulfonyl)imide [TFSI] is one of the most commonly used anions in ILs, as a result of the favorable properties of the resulting ILs. [TFSI] based ILs commonly are a liquid above 0 °C and exhibit low viscosity, which makes them favorable as

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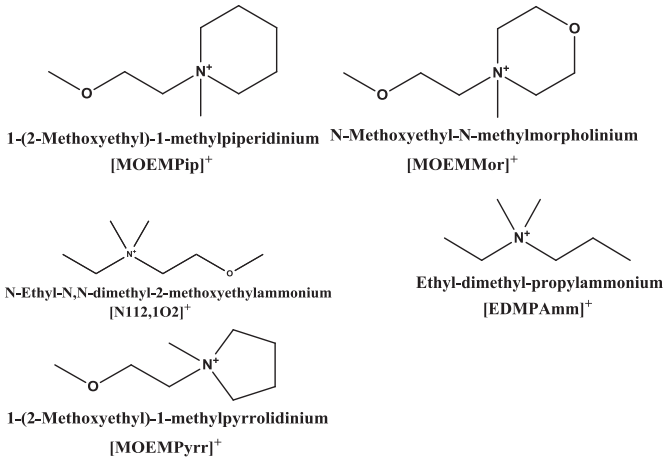
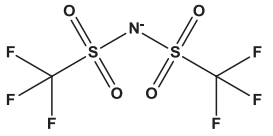
solvents [20]. In addition, ILs with hexafluorophosphate and tetrafluoroborate anions have been found to be disadvantageous for industrial applications due to their possible decomposition to toxic hydrofluoric acid [15].

Most studies on physical properties at various temperatures have focused on imidazolium cations [18,21,22], and other families of cations have been less extensively studied. In particular reports on the physicochemical properties of morpholinium based ILs are scarce [23,24]. This is despite the low cost of morpholinium cation sources [23]. Furthermore, morpholinium based ILs have been the subject of much interest due to their structural properties particularly for ionic liquid crystals [25]. They have also received attention for electrochemical applications and as heat stabilizers, catalysts and antioxidants [24]. In addition, morpholinium based cations have been reported to have high stability for superoxide ion ($O_2^{\bullet -}$) which makes them desirable as media for $O_2^{\bullet -}$ generation [26].

In this work, we have investigated the physicochemical properties of five ILs, namely 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [MOEMPip][TFSI], 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [MOEMPyrr][TFSI], N-methoxyethyl-N-methylmorpholinium bis(trifluoromethylsulfonyl)imide [MOEMMor][TFSI], N-ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide [N112,1O2][TFSI] and ethyl-dimethyl-propylammonium bis(trifluoromethylsulfonyl) imide [EDMPAmm] [TFSI] in the temperature range of 25–80 °C (298.15–353.15 K) at atmospheric pressure. The essential physicochemical properties of density, conductivity, viscosity and surface tension have been obtained as a function of temperature.



Scheme 1. Structure of cations of studied ILs.



Scheme 2. Structure of anion of studied ILs.

2. Methods and materials

2.1. Chemicals

In this study, synthesis grade ILs provided by Merck (Germany) were used. These ILs are summarized in Table 1 with the abbreviation adopted in this work. The ILs were dried overnight in a vacuum oven at 50 °C and the purity of these ILs was checked by ^{1}H NMR analysis. The spectra results are provided as supplementary material in Fig. S1 which confirms that no impurities were detected. Moreover, FT-IR characterization was used to identify the functional groups of three ILs among those used in this work. Fig. S2 shows the FT-IR spectra and Table S1 lists the functional groups identified. The water content in each IL was determined by Karl Fischer titration and is also listed in Table 1. Schemes 1 and 2 show the structure of cations and anion used respectively.

2.2. Technical methodology

In this study, all physical properties were measured in temperature range of 25–80 °C. Fresh samples were analyzed to avoid air moisture and contaminants which may have an impact on the physical properties of ILs. Density was determined using Mettler Toledo DM40 density meter. The density meter was calibrated using four Mettler Toledo liquid standard reference substances of water, dodecane, 2,4-dichlorotoluene and 1- bromonaphthalene.

Conductivity was measured using Trans instruments BC3020 conductivity meter, calibrated using standard conductivity solutions. The standard conductivity solutions used were Eutech Instruments standard potassium chloride solution of 84 μS at 25 °C, 1413 μS at 25 °C and 500 μS at 25 °C. Temperature variation was achieved using a water circulator (Protech 631D).

The viscosities of the ILs were measured with Brookfield R/S plus rheometer. The rheometer was calibrated to zero point before each set of experiments. Temperature was controlled by a water

Table 1
ILs studied in this work.

IL	Abbreviation	Molecular weight	Formula	Purity[a] (%)	Halides[a] (%)	Water (ppm) (KF)
1-(2-Methoxyethyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	[MOEMPip][TFSI]	452.44	$C_{12}H_{22}F_6N_2O_5S_2$	≥98.0	≤0.1	176
N-Methoxyethyl-N-methylmorpholinium bis(trifluoromethylsulfonyl)imide	[MOEMMor][TFSI]	440.38	$C_{10}H_{18}F_6N_2O_6S_2$	≥98.0	≤0.1	232
1-(2-Methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide	[MOEMPyrr][TFSI]	424.38	$C_{10}H_{18}F_6N_2O_5S_2$	≥98.0	≤0.1	190
N-Ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide	[N112,1O2][TFSI]	412.37	$C_9H_{18}F_6N_2O_5S_2$	≥98.0	≤0.1	318
Ethyl-dimethyl-propylammonium bis(trifluoromethylsulfonyl)imide	[EDMPAmm][TFSI]	396.37	$C_9H_{18}F_6N_2O_4S_2$	≥98.0	≤0.1	243

[a] Merck MSDS.