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Phenyl/alkyl-substituted-3,5-dimethylpyrazolium ionic liquids

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ABSTRACT

The synthesis and characterization of a series of new phenyl/alkyl-substituted-3,5-dimethylpyrazolium ionic liquids ([Phpz^R][X] R = C_nH_{2n+1} n: 1,2,3,4,5,6,7 [X] = $CH_3SO_3^-$, BF_4^-, PF_6^-) are described. Their melting points, thermal stabilities, electrochemical windows, and solubility properties in common solvents were investigated. They were found to exhibit very good electrochemical and thermal stabilities. The results indicate that these ionic liquids have a high thermal stability up to 374 °C and a large electrochemical window of 4.63 V. The thermophysical properties such as density, viscosity and refractive index were also measured as a function of temperature for the ionic liquids which are in liquid state at room temperature.

1. Introduction

Ionic liquids (ILs) composed of cations and anions have a unique combination of properties such as low vapor pressure, non-flammability and high thermal stability as well as a wide liquid range and wide electrochemical window [1–5]. Furthermore, the physical and chemical properties of ILs can be adjusted or tuned by controlling the nature of cations and anions [6–9]. Numerous ILs based on imidazolium, pyridinium, and quarternary ammonium cations with a variety of anions such as PF_6^-, BF_4^-, $(CF_3SO_3)_2N^-$, and $CF_3SO_3^-$ have been successively synthesized and are widely utilized in organic synthesis, catalysis, and the preparation of nanostructured materials [10–15].

Researches involving pyrazolium-based ILs are quite rare in contrast with imidazolium-based ILs. This is probably due to the lower nucleophilicity of the imine nitrogen atoms of pyrazoles compared to those of imidazoles. From a structural viewpoint, the presence of two directly bounded nitrogen atoms could not be neglected being able to modify charge distribution and probably some of the physicochemical properties of the resulting salts.

Some 1,2-dialkylpyrazolium ILs have been investigated as electrolytes [16–19], catalysts for organic synthesis [20] and antibacterial cationic surfactants [21]. These salts, though structurally analogous to imidazolium-based ILs, are generally characterized by a relatively low viscosity and a high conductivity with relevant electrochemical properties [22]. Recently, ionic liquid crystals based on pyrazolium salts have been described [23].

Currently, attempts have been focused on the design and synthesis of ionic liquids based on aryl/alkyl-substituted ILs which constitute a new generation of ionic liquids termed TAAILs (Tunable Aryl Alkyl Ionic Liquids). This new concept has been applied for the synthesis of imidazole and 1,2,4-triazole-based tunable aryl/alkyl ILs with different chain lengths [24,25].

In this context, we decided to extend this new concept to aryl/alkyl-substituted-3,5-dimethylpyrazolium salts. We kept the aryl part constant (phenyl) and studied the influence of different alkyl chains (C_1–C_7) and anions ($CH_3SO_3^-$, BF_4^-, and PF_6^-) on the properties of the pyrazolium salts.

2. Results and discussion

2.1. Synthesis and characterization

As shown in Fig. 1, the synthesis of phenyl/alkyl-substituted-3,5-dimethylpyrazolium ILs starts with the preparation of 3,5-dimethyl-1-phenyl-1H-pyrazole (1). Compound 1 was synthesized by an improved procedure from phenylhydrazinium hydrochloride and acetylacetone under MW irradiation since using conventional heating methods [26] is time consuming. Subsequent quarternization by alkyl methanesulfonates of different alkyl chain lengths in acetonitrile at 80 °C under MW irradiation for a period of 30 to 120 min led to phenyl/alkyl-substituted-3,5-dimethylpyrazolium methanesulfonates (2a–2g). The yields of the methanesulfonate alkylation reactions were typically 75–91%. One advantage of the methanesulfonate ionic liquids is that the methanesulfonate anion is base stable, and very easy to exchange for other anions. Thus, the BF_4^- and PF_6^- salts (compounds 3a–3g and 4a–4g) were simply

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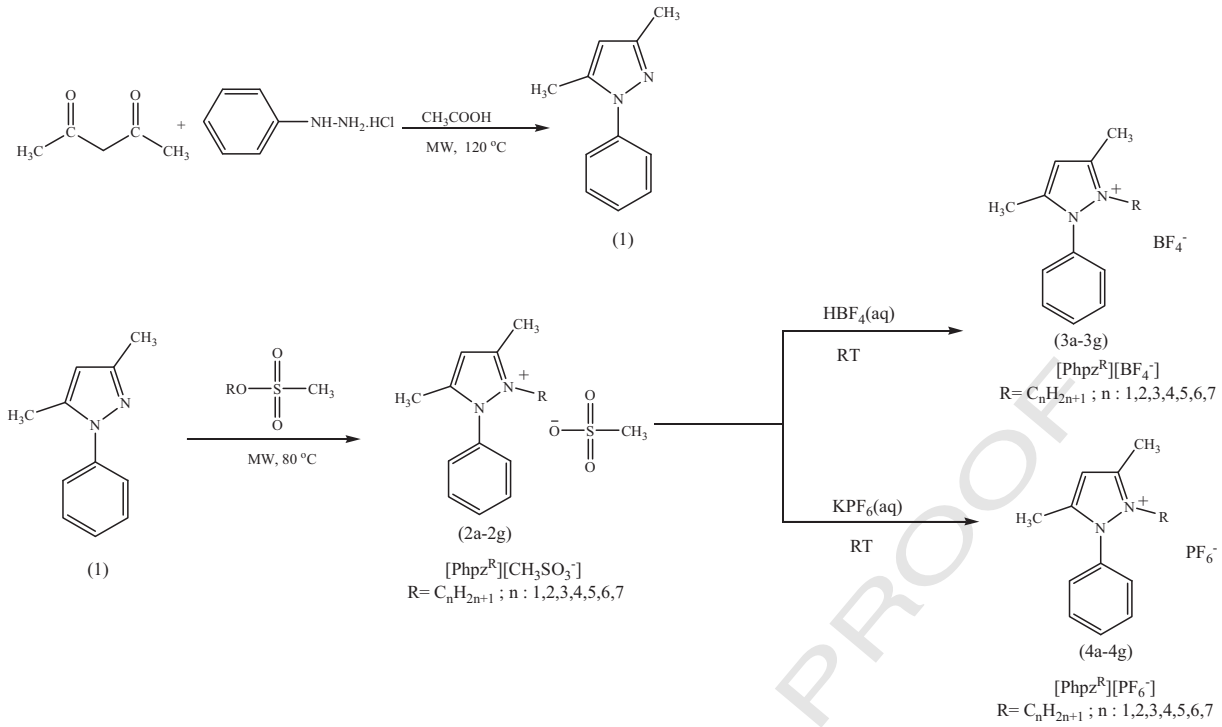

Fig. 1. Synthesis of the ionic liquids described in this work.

prepared by anion exchange reactions of corresponding methanesulfonate salts (2a–2g) with HBF_4 and KPF_6 in aqueous solution at room temperature with yields of 75–88% and 80–90%, respectively.

All of the pyrazolium salts were characterized by IR, ^1H NMR, ^{13}C NMR, TOF MS and elemental analysis. In addition, ^{19}F NMR spectra were recorded for the salts 3a–3g and 4a–4g. All the characterization data were consistent with the expected structures and compositions. The IR spectra of all the pyrazolium salts show the characteristic bands of the pyrazolium moiety as well as those of the corresponding counterions, where appropriate. In particular, the ν(C═N) and ν(C═C) absorption bands from the pyrazolium cation appear at ca. 1595–1560 cm^{-1}. In addition, characteristic bands of the BF_4^-, PF_6^- and $CH_3SO_3^-$ salts were observed at ca. 1030, 825 and 1198 cm^{-1}, respectively.

2.2. Thermal properties

The thermal behavior of the phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts was investigated with differential scanning calorimetry (DSC) (Table 1). Some of the pyrazolium salts (2b, 3a, 3b, 4a and 4c) have melting points above 100 °C and do not fulfill the IL criteria. Generally, increasing the alkyl chain length causing less efficient packing in the solid resulted in a lower melting point and starting with a chain length of more than three carbon atoms, all pyrazolium salts fulfill the IL criteria. It is also noteworthy that the melting points of phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts are lower in comparison with dialkylpyrazolium salts having the same counterion [27].

Two effects were taken into account to discuss thermal behaviour of the compounds; the effect of the alkyl chain length and the effect of the counterion. When studying the alkyl chain length, some features have been determined. It is noticeable that most of the methanesulfonate salts are in liquid state at room temperature and increasing the substituent length initially increases the melting point with a major trend towards glass formation. As seen in Fig. 2, the BF_4^- salts show almost a linear dependency of the melting point on the alkyl chain length from one to four carbon atoms. Initial lengthening of the substitution leads to reduction of melting points through destabilization of coulombic

Table 1
Thermal properties of the phenyl/alkyl-substituted-3,5-dimethylpyrazolium ILs.

Entry	Salts	T_m[a] (°C)	T_g[b] (°C)	T_d[c] (°C)	Entry	Salts	T_m[a] (°C)	T_g[b] (°C)	T_d[c] (°C)
1	2a	–	−53.3	282.1	12	3e	–	−47.4	344.4
2	2b	122.5	–	274.9	13	3f	–	−46.6	342.7
3	2c	92.5	–	274.7	14	3g	56.3	–	343.2
4	2d	–	−45.7	291.0	15	4a	125.1	–	373.9
5	2e	–	−54.7	272.2	16	4b	95.1	–	371.2
6	2f	–	−56.4	274.9	17	4c	102.2	–	320.9
7	2g	–	−49.0	260.2	18	4d	60.8	–	347.3
8	3a	145.2	–	361.0	19	4e	61.5	–	353.5
9	3b	113.0	–	366.7	20	4f	38.9	–	356.5
10	3c	80.0	–	345.5	21	4g	43.0	–	341.1
11	3d	67.6	–	348.4					

[a] T_m — melting point.
[b] T_g — glass transition temperature.
[c] T_d — decomposition temperature.

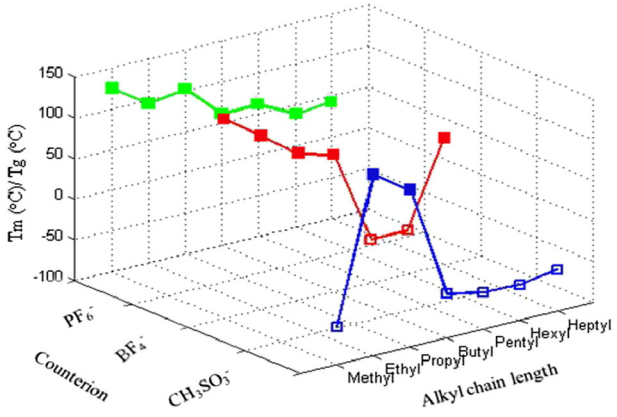

Fig. 2. Dependence of the melting points (closed square) or glass transitions (open square) of phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts on the alkyl chain length with the counterions; BF_4^-, PF_6^- and $CH_3SO_3^-$.

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