



Synthesis and characterization of novel hexafluorophosphate salts with tropine-type cations



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ABSTRACT

In this study, a series of new ionic liquids (ILs) with tropine as cationic nucleus and hexafluorophosphate as anion were synthesized. As two types of functional groups, aliphatic chains and benzyl with different substituents have been linked on the tropine nucleus in order to modulate the physicochemical properties of the ILs. The whole family of ILs was comprehensively identified by FT-IR, NMR and MS. Furthermore, the thermal properties of these ILs were evaluated by different scanning calorimetry (DSC) together with their melting points and enthalpy of fusion. Then the polarities of these tropine-type ILs were investigated and discussed. Resultantly, it was proved that their polarity was comparable with that of short-chain alcohols. Moreover, the Hammett function values of these involved ILs were determined to describe their Brønsted acidities. Finally, molar conductivities (Λ) of the tropine-type ILs in dilute solutions at 298.15 K were determined. The data were correlated with the Arrhenius–Ostwald model to obtain limiting molar conductivities (Λ^∞) and association constants (K_A). The influences of the branch chain of ILs on the ion transfer and association were also discussed. It was found that the size of cation was the main factor influencing the ion transfer. And the weak ion association of tropine-type ILs in water was proved by K_A , which was less than $7 \text{ L} \cdot \text{mol}^{-1}$.

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1. Introduction

Ionic liquids have been described as molten salts with various cationic and anionic species. They are organic–inorganic multi-component materials whose physicochemical properties can be tailored by modifying the cations and anions [1]. Based on the promising designability and diversity of ILs, a large scale of ILs have been continuously developed including imidazolium, ephedrinium, pyrrolidinium, pyridinium, pyrazinium, piperidinium, quinolinium, isoquinolinium and morpholinium (as shown in Table 1 [2–28]). It is easy to find that some ILs originated from alkaloid skeleton with various nitrogenous heterocycles. As known to all, tropane alkaloid is an important representative of natural bioactive products, which exists extensively in many advanced plants and can act as anticholinergics (e.g. atropine, hyoscyamine, scopolamine) or stimulants (e.g. cocaine, hydroxytropacocaine) [29]. As the hydrolyzate of tropane alkaloids, tropine has been applied to synthesize atropine as a kind of pharmaceutical intermediate. Recently, one tropine-type IL and its X-ray powder diffraction information have been reported in our work [30]. However, to the best of our knowledge, further study of synthesis and characterization of more similar tropine-type ILs has not been reported. On the other side, the potential application as a solvent to extract target substances from their solution

was considered in the design of tropine-type ionic liquid. Hexafluorophosphate, as a hydrophobic anion, was very popularly applied in most extraction process for its advantage of easy recycling from an aqueous solution and strong intermolecular interaction. And the potential ability of six fluorine atoms to form hydrogen bond between ionic liquid and solute molecules would benefit the selectivity of separation.

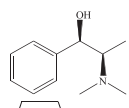




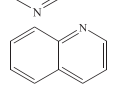
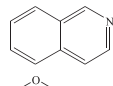

Polarity, as one of the most fundamental parameters for ILs, is of great importance for solvation and related applications of ILs, especially for polarity-sensitive reaction and separation process [31,32]. For example, Diels–Alder reaction processed in highly polar ILs could produce a much higher endo/exo ratio as compared with others [33]. It was also found that the polarity played a crucial role in the design of ILs as solvents for cellulose dissolution [34]. Moreover, the high polarity of a Brønsted acidic pyrrolidinium IL was considered to be an important factor for the oxidative desulfurization of diesel fuel in the presence of H_2O_2 [35]. To characterize the polarity of IL, the common approach was developed with the aid of some solvatochromic dyes, and among them the Reichardt's dye is the most widely used probe (see Fig. 1) [36]. Now, a lot of data on the polarity of ionic liquids have been reported with this kind of dye [37]. Some fundamental studies have demonstrated that common ILs could exhibit similar polarity as short chain alcohols, and the polarities of ILs were mainly dominated by the nature of their cations [38].

Acidity, as another important property for ILs, is also vital for their widespread applications especially in the field of catalysis [39,40]. It has been found that the acidity order of ILs was consistent with their

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Table 1
Ionic liquids based on similar alkaloid parent nucleus and their applications.

Cation	Anion	Application	Reference
Ephedrinium 	PF ₆ ⁻ , OTf ⁻ , (CF ₃ SO ₂) ₂ N ⁻	Catalyst	[2]
Pyrrole 	PF ₆ ⁻ , Tos ⁻ , Mes ⁻ , NTf ₂ ⁻ , TFSI ⁻	Electrolyte	[3–10]
Piperidine 	BF ₄ ⁻ , OTs ⁻ , TFSI ⁻	Catalyst Electrolyte	[11–17]
Pyrazine 	NTf ₂ ⁻ , BF ₄ ⁻	Catalyst	[18,19]
Pyridine 	NO ₃ ⁻ , BF ₄ ⁻ , Ac ⁻ , HSO ₄ ⁻ , PF ₆ ⁻ , Cl ⁻ , OH ⁻ , DCA ⁻ , NTf ₂ ⁻ , CF ₃ SO ₃ ⁻	Separation Catalyst Extraction	[20–22]
Quinoline 	Br ⁻ , Cl ⁻ , BF ₄ ⁻ , PF ₆ ⁻ , DOS ⁻	Separation Catalyst Antimicrobial	[23–25]
Isoquinoline 	(CF ₃ SO ₂) ₂ N ⁻ , NTf ₂ ⁻ , PF ₆ ⁻ , Br ⁻ , BF ₄ ⁻ , DOS ⁻ , BETA ⁻	Extraction	[26,27]
Morpholine 	TFSI ⁻	Electrolyte	[28]

activity order in some acid-catalyzed reactions [41]. For example, the SO₃H-functionalized 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate with strong acidity exhibited an excellent catalytic activity and selectivity in the esterification of salicylic acid with isoamyl alcohol [42]. A strong Brønsted acidity of ionic liquids could contribute to the catalytic reaction of methylal with trioxane for the preparation of polyoxymethylene dimethyl ethers [43]. In addition, four novel Brønsted acidic ionic liquids were applied in Fisher esterification for the synthesis of aromatic esters under solvent-free micro-wave irradiation conditions [44]. Until now, many methods have been utilized to measure the acidity of IL. Among these methods, the most well-known

one is the Hammett method in which a range of closely related UV–vis probes are used to describe the Hammett acidity (H_0). It has been successfully applied for imidazolium, pyridinium and benzothiazolium ILs [40,41,45].

Additionally, the ion–ion and IL–solvent interactions can play a great influence on potential applications of ILs. To provide important insights of ion–ion, IL–solvent and solvent–solvent interactions in the IL–solvent mixture, the ion association constant (K_A) together with the limiting molar conductivity (Λ^∞) was well established. Currently, conductivity study of IL in solvents was always applied to reveal K_A and Λ^∞ . Through conductivity studies, a great amount of researches on the ion association and transfer have been reported. It has been revealed that the stability of the ion pair was significantly dependent on the substituent groups in the cation and the type of the anion [46]. Also the weak association of IL in water, with the low constant below 20 L·mol⁻¹, has been found compared with the other non-aqueous solvents [47].

Based on the above research status, a homologous series of N-alkytropine salts containing alkyl substituents from propyl to hexyl and aromatic substituents have been prepared with the hexafluorophosphate anion in this work for the first time (as shown in Fig. 2). This family of ILs has been fully characterized by FT-IR, ¹H NMR, ¹³C NMR and MS. The thermal properties of ILs have also been evaluated by different scanning calorimetry (DSC). The influence of the branched chain in cation on the melting points and the enthalpy of fusion have been explored. Moreover, the polarity of each IL has been studied by Reichardt's dye and UV–vis diffuse reflection spectroscopy. The influence of branched chain on the polarities of these ILs has been discussed. Additionally, the Hammett acidity function has been used to determine the acidity of the tropine-type ILs. Furthermore, the conductivities of ILs in water at 298.15 K have been measured. From the experimental data, K_A and Λ^∞ have been determined to reveal the ion association and transfer, respectively. Finally, the influence of the structure of ILs on their dissolving behavior in water has also been discussed. This work is expected to expand the kinds and properties of tropine-type ILs as well as to provide fundamental information for their further research and application.

2. Experimental

2.1. Reagents and materials

Tropine was purchased from Aladdin Industrial Co. Ltd (Shanghai, China). *N*-propyl bromide, *n*-butyl bromide, *n*-amyl bromide, *n*-hexyl bromide, benzyl chloride, *m*-methoxybenzyl chloride, *p*-nitrobenzyl chloride, *p*-nitroaniline and the other solvents were purchased from Kelong Chemical Co. Ltd (Chengdu, China). 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino) phenolate was purchased from Santa Cruz Biotechnology Corporation (Delaware, USA). All reagents and solvents were of pure analytical grade and were used without further purification, if not stated otherwise. Deionized water was obtained by the UPR-I-5T water purification system from Ulupure Technology Co. Ltd (Chengdu, China).

2.2. Synthesis and characterization

2.2.1. Spectroscopy measurement

All the spectral measurements were carried out at room temperature. IR spectra were measured on a Perkin Elmer Fourier transform infrared spectrometer (Waltham, USA) in potassium bromide discs, which were scanned from 400 to 4000 cm⁻¹ with 4 cm⁻¹ resolution. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz nuclear magnetic resonance spectrometer (Fällanden, Switzerland) equipped with a 5 mm probe with all shifts referred to internal tetramethylsilane (TMS). Besides *N*-(*p*-nitrobenzyl)-tropine hexafluorophosphate dissolved in deuterated dimethyl sulfoxide, other samples (each 15 mg) were dissolved by deuterated methanol in the sample

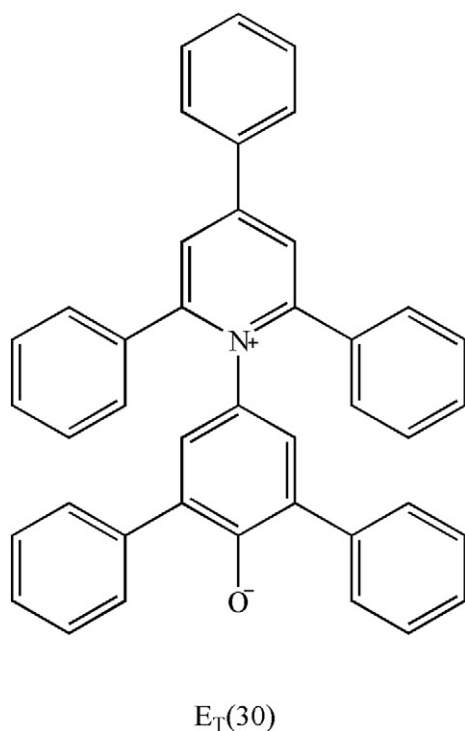


Fig. 1. Chemical structure of polarity probe Reichardt's dye.

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