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## Synthesis and Physiochemical Properties of Supramolecular Phosphonium-based Symmetrical Dicationic Ionic Liquids

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**Abstract:** In the present study, a novel phosphonium-based Dicationic Ionic Liquids (DCILs) were synthesized and characterized using <sup>1</sup>H NMR and elemental analysis. Physiochemical properties such as density and viscosity are measured and reported for a temperature range of 293.15 to 353.15 K while the refractive index was measured in the range of 293.15 to 333.15 K. The start and decomposition temperatures are determined at heating rate 10°C min<sup>-1</sup>. The influence of the spacer alkyl chain on these properties is discussed. The results show that the new DCILs possess lower density higher thermal stability and higher viscosity compare to monocationic ionic liquids.

**Key words:** Dicationic liquids, density, viscosity, refractive index

### INTRODUCTION

Ionic Liquids (ILs) are a common name given to the organic salts where the molecules composed of ions and having melting points below 100°C and negligible vapor pressure (Earle and Seddon, 2000). ILs composed exclusively of organic cations and inorganic or organic anions, they vary in size and can be either hydrophilic or hydrophobic (Canongia *et al.*, 2005; Freire *et al.*, 2007). The unique combination of the inherent physical and chemical properties namely, low melting points, high thermal stability, liquidity over a wide temperature range, negligible vapor pressures, low inflammability, highly solvating capacity for both polar and non polar compounds, high electrical conductivity (Freire *et al.*, 2007; Chiappe and Pieraccini, 2004), easy recycling, make these compounds attracting a considerable attention in many fields. The unique properties, tunability beside the enormous number of these compounds make them receiving increasing and continuing attention in many important areas of researches and commercial applications such as: absorption media for gas separations, solvents for reactions, heat transfer fluids, separating agent in extractive distillation, for processing biomass, as the working fluid in a variety of electrochemical applications (batteries, capacitors, solar cells, etc.) (Vila *et al.*, 2006), as lubricants (Chengfeng *et al.*, 2001) and in biocatalysts (Zhong *et al.*, 2007) with great advantages.

Dicationic Ionic Liquids (DCILs) are a relatively new class of molecules containing two head groups linked by a rigid or flexible spacer (Ding *et al.*, 2007). DCILs have special properties and potential applications in many areas. In fact, it appears that an advantage of DCILs over mono cationic ILs is that they provide more opportunities to fine-tune their physical and chemical properties. To facilitate molecular design of DCILs, fundamental understanding of the alkyl groups and spacer lengths effects on the properties are to be essential. Although DCILs with different spacer lengths have been synthesized, correlation of alkyl groups and spacer lengths of DCILs with fixed cationic and anionic species still needs to be explored (Wang *et al.*, 2006; Liu *et al.*, 2006). The cation and its structure can certainly influence the physical and chemical properties such as viscosity, density, refractive index and thermal stability as well as interaction with dissolved molecules (Anderson *et al.*, 2005).

Compared with the popular imidazolium-based ILs, phosphonium ILs are known to possess some rather interesting and often advantageous properties such as; lower density, lack of an acidic proton and high thermal stability. These have obvious advantages when employing an IL solvent in liquid-liquid extraction and in organic syntheses (Anderson *et al.*, 2005; Breitbach and Armstrong, 2008).

Much work has been carried out on the physiochemical properties of trihexylphosphonium-based DCILs and the effect of the spacer length unit linking the two cations on the physiochemical properties (Ding *et al.*, 2007). However, synthesis and physiochemical properties of trioctylphosphonium-based symmetrical DCILs and the effect of the length of alkyl chain and the spacer length on the thermophysical properties has not been studied.

In this study, new phosphonium-based symmetrical DCILs with different length of the alkyl chains linking the two cations were synthesized. The <sup>1</sup>H-NMR and elemental analysis were used to verify the structures of these compounds. Physiochemical properties such as density, viscosity and refractive index were measured have been measured at T = 293.15 to 353.15 K whereas, start and decomposition temperatures were measured at heating rate 10°C min<sup>-1</sup>.

### MATERIALS AND METHODS

The source and grades of the chemicals used for the synthesis of the present DCILs are: trioctylphosphine (Aldrich 90%), 1,6-dichlorohexane (Aldrich 98%), 1,10-dichlorohexane (Aldrich 99%) and acetone (Sigma-Aldrich 99.9%).

1,6-bis(trioctylphosphonium) hexane chloride was synthesized into a three-necked round bottom flask equipped with a heating oil bath, a nitrogen inlet adapter, magnetic stirrer and a reflux condenser. The flask is flushed with dry nitrogen then trioctylphosphine (0.042 mol, 18.7 mL) and 1,6-dichlorohexane (0.02 mol, 3.3 mL) were added. The system was heated to 120°C and stirred for 24 h under nitrogen atmosphere then placed under vacuum at 100 °C to remove any volatile components. The product was then cooled to room temperature and washed with acetone. The remaining solvent was removed at 80°C under vacuum and then dried in a vacuum oven for 48 h to afford the clear viscous gel product 1,6-bis(trioctylphosphonium)hexane chloride [P<sub>888</sub>C<sub>6</sub>P<sub>888</sub>]Cl<sub>2</sub>. 1,10-bis (trioctylphosphonium) decane chloride [P<sub>888</sub>C<sub>10</sub>P<sub>888</sub>]Cl<sub>2</sub> was synthesised in a similar manner as [P<sub>888</sub>C<sub>6</sub>P<sub>888</sub>]Cl<sub>2</sub> except, 1,10-dichlorodecane (0.02 mol, 4.2 mL) was used instead of 1,6-dichlorohexane (0.02 mol, 3.3 mL).

**Characterisation:** <sup>1</sup>H NMR spectra (taken in CDCl<sub>3</sub> solvent and recorded on a Bruker Avance 300 spectrometer) and CHNS-932 (LECO instruments) elemental analyzer were used to characterise the synthesised ILs.

Dried samples kept in desiccators were directly used for each measurement and reproducibility of the results

was confirmed by performing at least three experiments for each sample.

Coulometric Karl Fischer titrator, DL 39 (Mettler Toledo) with Hydranal coulomat AG reagent (Riedel-de Haen) was used to determine the water content of the synthesized ILs. The measurement for each IL was made in triplicate and the values are reported in Table 1.

The start and decomposition temperatures of the synthesised ILs were determined using Perkin-Elmer, Pyris V-3.81. The samples were placed in aluminum pans under a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. The measured start temperature (T<sub>s</sub>) and decomposition temperature (T<sub>d</sub>) are presented in Table 1.

A Stabinger viscometer (Anton-Paar model SVM3000) with temperature controlled to within ±0.01°C, 0.35% and ±5×10<sup>-4</sup> g cm<sup>-3</sup> repeatability for viscosity and density respectively was used to measure density and viscosity of the synthesized ILs at a temperature range 293.15 to 353.15 K.

The refractive index measurements of various ILs were carried out at a temperature range (298.15 to 333.15) K using ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of ±4×10<sup>-5</sup>.

### RESULTS AND DISCUSSION

The present phosphonium-based symmetrical DCILs were synthesised by the procedure, as shown in Fig. 1. The structures of the synthesised ILs were confirmed using <sup>1</sup>H NMR and elemental analysis (CHNS). The <sup>1</sup>H NMR and elemental analysis results are as follows:

1,6-bis(trioctylphosphonium)hexane chloride [P<sub>888</sub>C<sub>6</sub>P<sub>888</sub>]Cl<sub>2</sub>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.79 (18H, t, CH<sub>3</sub>CH<sub>2</sub>); 1.21 (12H, m, CH<sub>3</sub>CH<sub>2</sub>); 1.35-1.55 (16H, br, CH<sub>2</sub>CH<sub>2</sub>P); 2.1-2.25 (52H, br, CH<sub>2</sub>); 2.30-2.42 (16H, br CH<sub>2</sub>CH<sub>2</sub>P). Elemental analysis: % found (% calculated) C, 72.21 (72.34); H, 12.75 (12.84).

1,10-bis(trioctylphosphonium)decane chloride [P<sub>888</sub>C<sub>10</sub>P<sub>888</sub>]Cl<sub>2</sub>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.74 (18H, t, CH<sub>3</sub>CH<sub>2</sub>); 1.15 (12H, m, CH<sub>3</sub>CH<sub>2</sub>); 1.30-1.60 (16H, br, CH<sub>2</sub>CH<sub>2</sub>P); 2.0-2.08 (60H, br, CH<sub>2</sub>); 2.25-2.40 (16H, br CH<sub>2</sub>CH<sub>2</sub>P). Elemental analysis: % found (% calculated) C, 73.01 (73.12); H, 12.85 (12.93).

The water content values of the phosphonium-based symmetrical DCILs synthesized are presented in Table 1.

Table 1: Water content, start and decomposition temperatures for [P<sub>888</sub>C<sub>6</sub>P<sub>888</sub>]Cl<sub>2</sub> and [P<sub>888</sub>C<sub>10</sub>P<sub>888</sub>]Cl<sub>2</sub>

DCIL	Water content (ppm)	T <sub>s</sub>	T <sub>d</sub>
		-----°C-----	
[P <sub>888</sub> C <sub>6</sub> P <sub>888</sub> ]Cl <sub>2</sub>	530	378	395
[P <sub>888</sub> C <sub>10</sub> P <sub>888</sub> ]Cl <sub>2</sub>	553	354	381

The water content of this series of ILs is relatively high compared to the phosphonium monocationic ILs reported by Tarig *et al.* (2009), where the water content of trihexyltetradecylphosphonium trifluoromethanesulfonate  $[P_{6,6,6,14}][OTf]$ , trihexyltetradecylphosphonium acetate  $[P_{6,6,6,14}][OAc]$  and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide  $[P_{6,6,6,14}][NTf_2]$ , was in the range of 20-150 ppm, due to the high ability of the chloride anion to attract water.

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The start temperatures for weight loss ( $T_s$ ) and decomposition temperatures ( $T_d$ ) of present ILs are reported in Table 1. Decomposition temperatures of this series of ILs are affected slightly by the alkyl chain length between the two cation; the decomposition temperature decreases as the alkyl chain increases as reported by Anderson *et al.* (2005) for DCILs. The measured decomposition temperatures values of the present ionic liquids are comparable to other DCILs reported by Yu *et al.* (2007).

In Fig. 2, the densities of the phosphonium-based symmetrical DCILs were decrease with increasing temperature and also with increasing length of the hydrocarbon linkage chain; density of  $[P_{8,8,8}C_6P_{8,8,8}]2Cl$  is greater than that of  $[P_{8,8,8}C_{10}P_{8,8,8}]2Cl$ . The decrease in density with increasing spacer alkyl chain length has been reported for a large series of DCILs (Yu *et al.*, 2007). The density of the present DCILs is lower compared to the phosphonium-based monocationic ILs, the density of  $[P_{2,2,2,8}][NTf_2]$  and  $[P_{2,2,2,12}][NTf_2]$  are 1.26, 1.21 and 1.61  $g\ cm^{-3}$ , respectively which results from the increases of free volume due to the long alkyl chain.

Experimental results of the viscosities for the synthesized DCILs are shown in Fig. 3. Viscosities decrease with increasing temperature for each of the DCILs. The viscosity values of the present DCILs are much higher comparable to phosphonium-based monocationic ILs; the viscosities of  $[P_{6,6,6,14}][NTf_2]$ ,  $[P_{2,2,2,5}][NTf_2]$  and  $[P_{2,2,2,12}][NTf_2]$  is 450, 88 and 180 mPa.s respectively [15]. The viscosity values increases as the spacer alkyl chain length increase and the result is in agreement with that observed by Tokuda *et al.* (2005).

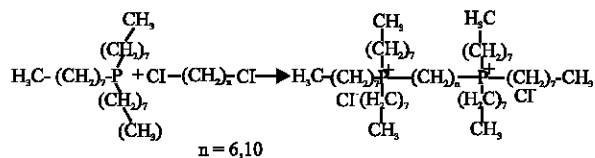


Fig. 1: Synthesis of 1,6-bis (trioctylphosphonium) hexane chloride  $[P_{8,8,8}C_6P_{8,8,8}]Cl_2$  and 1,10-bis (trioctylphosphonium) decaon chloride  $[P_{8,8,8}C_{10}P_{8,8,8}]Cl_2$

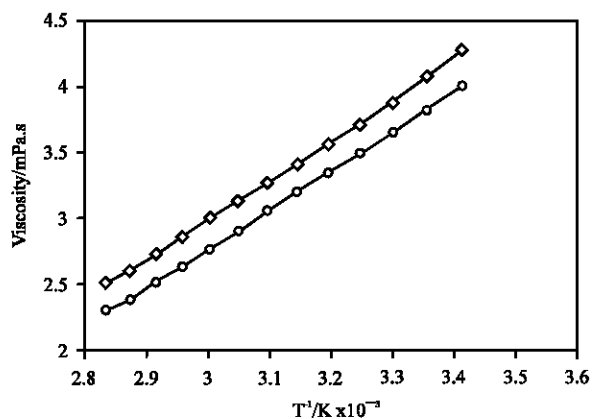


Fig. 2: Temperature-dependent densities of  $[P_{8,8,8}C_n P_{8,8,8}]Cl_2$ .  $\diamond$ ,  $[P_{8,8,8}C_6 P_{8,8,8}]Cl_2$ ;  $\circ$ ,  $[P_{8,8,8}C_{10} P_{8,8,8}]Cl_2$

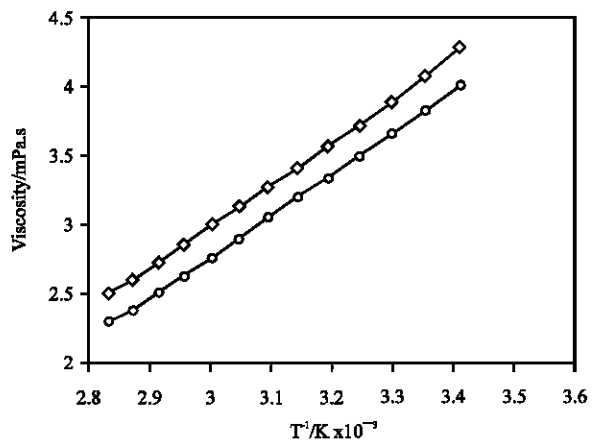


Fig. 3: Log  $\eta$  against  $T^{-1}$  for  $[P_{8,8,8}C_n P_{8,8,8}]Cl_2$  as a function of temperature.  $\diamond$ ,  $[P_{8,8,8}C_6 P_{8,8,8}]Cl_2$ ;  $\circ$ ,  $[P_{8,8,8}C_{10} P_{8,8,8}]Cl_2$

The high viscosity of the DCILs was attributed to an increase in van der Waals forces, hydrogen bonding between cationic protons and anionic halides the symmetry of the cations and anions (Huddleston *et al.*, 2001).

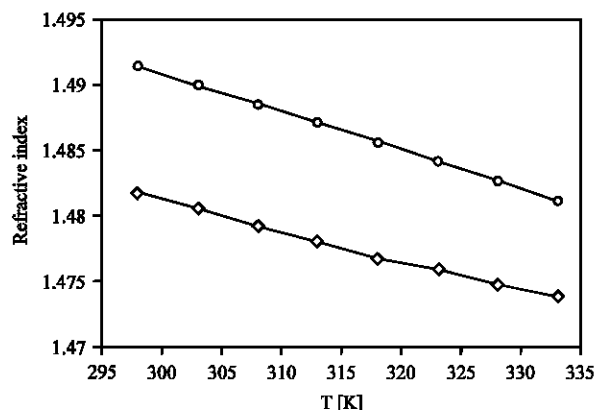


Fig. 4: Refractive index of  $[P_{888}C_nP_{888}]Cl_2$  as a function of temperature.  $\diamond$ ,  $[P_{888}C_6P_{888}]Cl_2$ ;  $\circ$ ,  $[P_{888}C_{10}P_{888}]Cl_2$

The refractive index is related to the excess molar refraction which is used in the least squares energy relationships (LSERs) as a predictor of solute distribution (Yu *et al.*, 2007). The refractive indices of the present DCILs in the temperature range from 298.15 to 333.15 K for the present DCILs are represented in Fig. 4 and in agreement with other phosphonium ILs, the refractive index of  $[P_{6,6,6,14}][OTf]$  and  $[P_{6,6,6,14}][NTf_2]$  is 1.4585 and 1.4587 as reported by Tarig *et al.* (2009). As expected, the refractive index values decrease almost linearly with increasing temperature and also decrease with increasing the spacer alkyl chain length.

### CONCLUSION

A series of novel dicationic symmetrical ILs based on trioctyl phosphonium were synthesized. The thermal stability was improved dramatically compared with their pure counterparts with single cation. The density, viscosity and refractive index values decrease with increasing temperature. Also, density and refractive index decreases as the spacer alkyl chain length increases while viscosity increase. The present DCILs have low density, high thermal stability, high viscosity and low refractive index as compare to the phosphonium-based monocationic ILs and phosphonium ILs incorporating short alkyl chain.

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