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Synthesis and Thermophysical Properties of Trioctyl Phosphonium - Based Mono and Dicationic Room Temperature Ionic Liquids Incorporating Dioctylsulfosuccinate Anion

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ABSTRACT

A new series of monocationic (MILs) and symmetrical dicationic (DILs) trioctyphosphonium-based room temperature ionic liquids (RTILs) incorporating dioctylsulfosuccinate(DOSS)anionnamely,trioctyltetradecylphosphoniumdioctylsulfosuccinate;$[P_{8,8,8,14}]$DOSS,1,10-bis (trioctylphosphonium) decane diocty lsulfosuccinate; $[P_{8,8,8}\,C_{10}\,P_{8,8,8}]$DOSS,1,6-bis(trioctylphosphonium)hexane dioctylsulfosuccinate; $[P_{8,8,8}\,C_6\,P_{8,8,8}]$DOSS have been prepared. The present ionic liquids (ILs) are characterised using NMR and elemental analysis and their physical properties such as density, viscosity and refractive index have been performed at a broad range of temperature (293.15 to 353.15) K and at atmospheric pressure. The present MILs possesses lower densities and higher viscosities comparable to the MILs with short alkyl chain while DILs possesses higher viscosities comparable to the MILs. The higher viscosity of the present ILs is due to the increased Van der Waals interactions resulting from the long alkyl chains of the cation and anion along with the large volume of the docusate anion which results in low ion mobility due to the electrostatic interaction between the cation and anion. The coefficient of thermal expansion, crystal energy and molar refraction were calculated from the experimental values of density and refractive index. These ILs show a weak temperature dependency on the thermal expansion coefficient and low crystal energy.

INTRODUCTION

Ionic liquids (ILs) are salts that have melting points below 100 °C and room temperature ionic liquids (RTILs) are those salts that exist as liquids at ambient temperatures. ILs are a class of solvents consisting only of ions, which makes them very different from conventional molecular solvents (Earle et al.2000). ILs often possess properties such as high thermal stabilities, negligible vapor pressures, tunable viscosities, hydrophobic or hydrophilic natures, nonflamability, highly solvating capacity for both polar and non polar compounds and high electrical conductivity (Freire et al. 2007). These reasons, along with the fact that ILs can undergo multiple solvation interactions have placed them at the forefront of many research programs. Recently, interest in ionic liquids (ILs) has extended to many areas of chemistry and thier uses have spanned a wide range of applications (Breitbach et al. 2008). They have been used as alternative solvents for many synthetic and catalytic reactions and as solvents for liquid extractions. ILs also can be used as surfactants, as stable, high temperature gas–liquid chromatographic (GLC) stationary phases, as absorption media for gas separations, as lubricants, heat transfer fluids, for processing biomass, as the working fluid in a variety of electrochemical applications(batteries, capacitors, solar cells, etc.), and in biocatalysts with great advantages (Zhong et al. 2007). Also, since there are a wide range of cation and anion combinations to choose from, chemists are able to select or “fine tune” these solvents for a variety of specific uses (Lopes et al. 2005).Phosphonium-based ILs are known to posses some interesting and valuable properties compared to the ILs that have nitrogen based cations, however the amount of research that has been conducted on phosphonium-based ILs is comparatively minimal. This may be due to the small number of commercially available phosphines compared to amines. Phosphonium ILs are more thermally stable and less dense than many nitrogen-based IL (some of them are less dense than water), also phosphonium cations lack an acidic proton which can lead to carbene formation. These properties has obvious advantages when using phosphonium ILs as GLC stationary phase, in liquids-liquid extraction and as solvent in organic synthesis (Breitbach et al. 2008).

Even though, many researchers have synthesized and studied the physiochemical properties of many tetraalkylphosphonium based ILs and reported the effect of the alkyl length on the thermophysical properties (Ziyada et al. 2010), but synthesis and thermophysical characterization of trioctyltetradecylphosphonium dioctylsulfosuccinate;$[P_{8,8,8,14}]$DOSS1,10bis(trioctylphosphonium)decanedioctylsulfosuccinate;$[P_{8,8,8}C_{10}P_{8,8,8}]$DOSS,and1,6-bis(trioctylphosphonium) hexane dioctylsulfosuccinate; $[P_{8,8,8}\ C_6\ P_{8,8,8}]$DOSS and the effect of the length of alkyl chains on the thermophysical properties has not been conducted.

In this paper, $[P_{8,8,8,14}]$DOSS, $[P_{8,8,8}\ C_{10}\ P_{8,8,8}]$DOSS and $[P_{8,8,8}\ C_6\ P_{8,8,8}]$DOSS ionic liquids were synthesized by reacting trioctylphosphine with 1-chlorotetradecane, 1,10-dichlrordecane and 1,6-dichlorohexane respectively, then the products were reacted with sodium dioctylsulfosuccinate (Figure 1).Thermophysical properties such as density, viscosity and refractive index were measured whereas coefficient of thermal expansion, crystal energy and molar refraction were calculated.

Synthesis of Ionic Liquids

Materials

The source and grades of the chemicals used for the synthesis of the ionic liquids in this study are: trioctylphosphine (Aldrich 90%), 1-chlorotetradecane (Aldrich 98%),ethylacetate, anhydrous (Sigma-Aldrich 99.8), acetone (Sigma-Aldrich 99.9%). sodium dioctylsulfosuccinate (Aldrich 98%) and anhydrous diethylether (Sigma-Aldrich 99%),1,6-dichlorohexane (Aldrich 98%), 1,10-dichlorodecane (Aldrich 99 %).

[$P_{8,8,814}$]DOSS Synthesis of trioctyltetradecylphosphonium dioctylsulfosuccinate

Trioctyltetradecylphosphonium docusate [$P_{8,8,814}$]DOSS was synthesized from trioctyltetradecylphosphonium chloride [$P_{8,8,814}$]Cl which was synthesized in a three-necked round bottom flask immersed in an oil bath with N_2 flow. The flask is connected to a reflux condenser. The flask is flushed with dry nitrogen before trioctylphosphine (0.04 mol, 17.8ml) and1-chlorotetradecane (0.042 mol, 11.4 ml) were added (Figure 1-a). The reaction was carried out at 80 °C and stirred for 48 h under nitrogen atmosphere. The product was washed with ethyl acetate and the remaining solvent was removed under vacuum then dried in vacuum oven at 80°C for 48 h to form a clear viscous gel product [$P_{8,8,814}$]Cl. Then, [$P_{8,8,814}$]Cl was dissolved in 30 ml of acetone and mixed with 0.04 mol sodium dioctylsulfosuccinate (Figure 1-b). The mixture was stirred at room temperature for 48 h followed by filtration of the solid. The product was washed with ethyl ether and the remaining solvent was removed under vacuum and then dried in a vacuum oven for 48 h to afford the clear viscous gel product [$P_{8,8,8,14}$]DOSS.

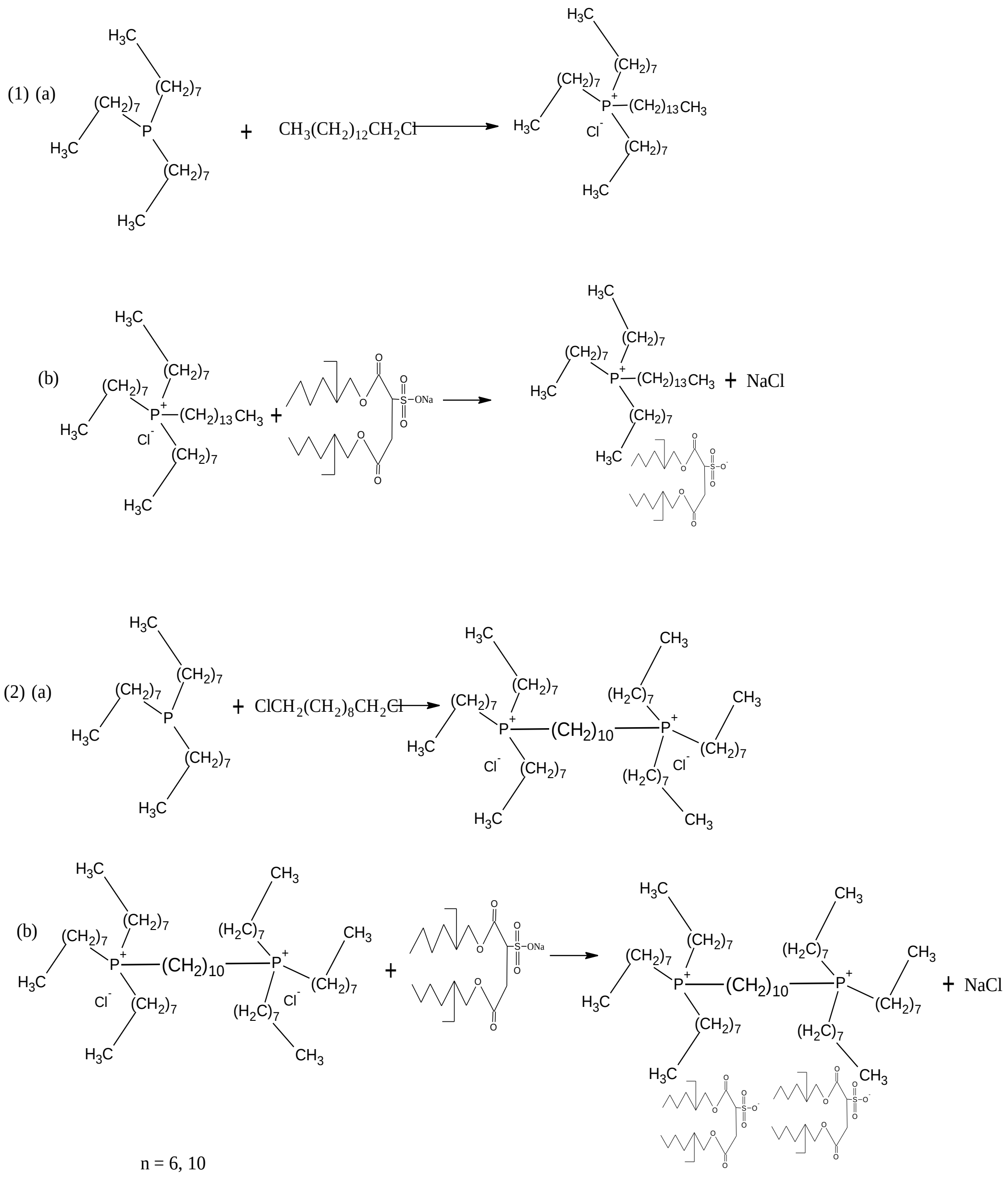

Figure 1. Synthesis of ionic liquids (1) synthesis of monocationic ionic liquid (MIL) (2) synthesis of symmetrical dicationic ionic liquids (DILs)

Synthesis of 1,6-bis(trioctylphosphonium)hexane dioctylsulfosuccinate $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS

1,6-bis(trioctylphosphonium)hexane dioctylsulfosuccinate; $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS was synthesized in two steps. First, 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 (0.041 mol, 18.7ml) 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 ºC to remove any volatile components. The product was then cooled to room temperature and washed with acetone, then 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 $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]Cl_2$. Secondly, stoicheometric amounts of $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]Cl_2$ and sodium dioctylsulfosuccinate were mixed in diethyl ether and stirred for 48 h followed by separation of the solid. The product was washed with acetone and the remaining solvent was removed at 70 °C under vacuum and then dried in a vacuum oven at 80°C for 48 h to afford the clear viscous gel product $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS.

1,10-bis(trioctylphosphonium) decane docusate $[P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}]$DOSS was synthesized in a similar manner as $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS except,1,10-dichlorodecane was used instead of 1,6-dichlorohexane.

Characterization and Properties Measurements.

The instruments used for the measurements of the physical properties in the present study were calibrated using Millipore quality water with known density, viscosity and refractive index. The data established by our research group (Ziyada et al. 2010) for the ILs 1-butyl-3-propanenitrile imidazolium bromide; $[C_2CN\ Bim]Br$, bis-(2-hydroxyethyl)ammonium acetate; BHEAA and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[C_6Mim]Tf_2N$ were used for the validation of the accuracy and reproducibility of the instruments.

NMR and Elemental analysis

The ionic liquids of the present study were characterized using CHNS-932 (LECO instruments) elemental analyzer to determine the individual percentage of elements in these ILs. A Burcher Avance 300 spectrophotometer was used to determine the ^1H NMR spectra of the present ILs using deuterated water (D_2O) as solvent (Yunus et al. 2010).

Water and chloride content

A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo) with CombiCoulomat fritless Karl Fischer reagent (Merck) was used to determine the water content of the present ILs. The measurement for each IL was made in triplicate and the average values are reported in Table 1.

Chloride measurements were conducted by ion chromatography (Metrohm Model 761 Compact IC) with (150 X 4.0) mm analytical column (Metrosep A Supp 5-150) and (5.0 X 4.0) mm guard column (Metrosep A Supp 4/5). The samples were diluted by dissolving $0.5cm^{-3}$ of each IL in $10cm^{-3}$ of acetonitrile then the volume was completed to 50 cm^{-3} with deionised water. The analysis of the results was made using Metrodata IC Net 2.3 software.

Densities and Viscosities Measurements

The density and viscosity of all ionic liquids was measured in a temperature range (293.15 to 353.15) K at atmospheric pressure using a Stabinger viscometer (Anton–Paar model SVM3000). The temperature was controlled to within ±0.01°C. The repeatability of measurements were $\pm 5\times10^{-4}\ g.cm^{-3}$ and 0.35% for density and viscosity respectively (Ziyada et al. 2011). The standard calibration fluid provided by the supplier was used for the calibration of the viscometer followed by ionic liquids with known viscosity (Ziyada et al. 2014).

Refractive indices Measurements

ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of $\pm 4\times10^{-5}$ was used to measure the refractive index of various ILs in a temperature range (298.15 to 333.15). The temperature of the apparatus was controlled to within ±0.05°C. The apparatus was calibrated and checked before each series of measurements using pure organic solvents with known refractive indices. Dried samples kept in desiccators were directly placed into the measuring cell. Reproducibility of the results was confirmed by performing three experiments for each IL in the whole temperature range studied in the present work.

RESULTS AND DISCUSSION

^{1}H NMR and elemental analysis were performed to verify the synthesis of the ionic liquids and the results indicated that all samples were obtained correctly. The ^{1}H NMR and elemental analysis (%found (%calculated)) of the ionic liquids are as follows:

[$P_{8,8,8,14}$]DOSS: ^{1}H NMR 300 MHz, ($CDCl_3$): δ 0.88 (t, 24H), 1.29 (br, 76H), 1.66 (br, 8H), 2.35 (t, 2H), 3.25-4.20 (br, 4H), 3.96 (m, 1H).

Analysis % found (% calculated), C, 68.65 (68.98), H 11.87 (11.69), S 3.49 (3.54).

[$P_{8\,8\,8}\,C_6\,P_{8\,8\,8}$]DOSS: ^{1}H NMR 300 MHz, ($CDCl_3$): δ 0.84 (t, 42H), 1.25 (br, 116H), 2.18 (br, 8H), 2.76 (t, 16H), 3.34 (m, 4H), 4.15 (br, 8H), 7.26 (m, 2H).

Analysis % found (% calculated), C, 67.73 (67.66), H 11.28 (11.36), S 3.72 (3.84).

[$P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}$]DOSS: ^{1}H NMR 300 MHz, ($CDCl_3$): δ 0.81 (t, 42H), 1.19 (br, 108H), 1.42 (br, 8H), 2.22 (t, 16H), 3.14 (m, 4H), 3.99 (br, 8H), 7.20 (m, 2H).

Analysis % found (% calculated), C, 68.39 (68.25), H 11.59 (11.45), S 3.65 (3.72).

In consideration of ILs for use in processes where it would be in contact with another phase, ILs impurities (water and halide) may drastically affect the physical properties. The presence of water may have a rather dramatic effect on density, viscosity, refractive index and thermal stability. Also it has a remarkable effect on reactivity, not only in the new biotechnology applications but also in many synthetic schemes using IL as reaction media (Kurnia et al. 2009). The water content value of the present ILs is presented in Table 1. The water content value is comparable with the phosphonium ILs reported (Tariq et al. 2009) where the water content of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide [$P_{6,6,6,14}$][NTf_2], trihexyltetradecylphosphonium acetate [$P_{6,6,6,14}$][OAc] and trihexyltetradecylphosphonium trifluoromethanesulfonate [$P_{6,6,\,6,14}$][OTf] was in the range of $(20 - 150)\cdot10^{-6}$

Table 1. Molecular weight M.W and mass fraction of water w_{H2O} and chlroide w_{HCl} for the ILs

	$[P_{8,8,8,14}]$ docusate	$[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$ docusate	$[P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}]$ docusate
M.W	989.59	1668.57	1724.67
w_{H2O}	$121\cdot10^{-6}$	$142\cdot10^{-6}$	$136\cdot10^{-6}$
w_{HCl}	$41\cdot10^{-6}$	$59\cdot10^{-6}$	$74\cdot10^{-6}$

The effect of the alkyl chain and spacer alkyl chain length on the liquid density of phosphonium-based ionic liquids is shown in Figure 2. The densities of the dicationic phosphonium-based ionic liquids are highest when compare with the monocationuc phosphonium-based ionic liquid. The density of the DCIL with decyl alkyl chain is higher when compare with the hexyl alkyl chain.

The measured density of the present ionic liquid in the range from (0.9579 to 0.9914) g.cm^{-3} and in agreement with the published values for $[P_{6,6,6,14}][NTf_2]$ and $[P_{6,6,6,14}][OTf]$ (Tariq et al. 2009); 1.0654 and 0.9823 g.cm^{-3} respectively, which indicates that the effect of the docusate anion on density is similar to that for $[NTf_2]$ and [OTf] anions. The density of the

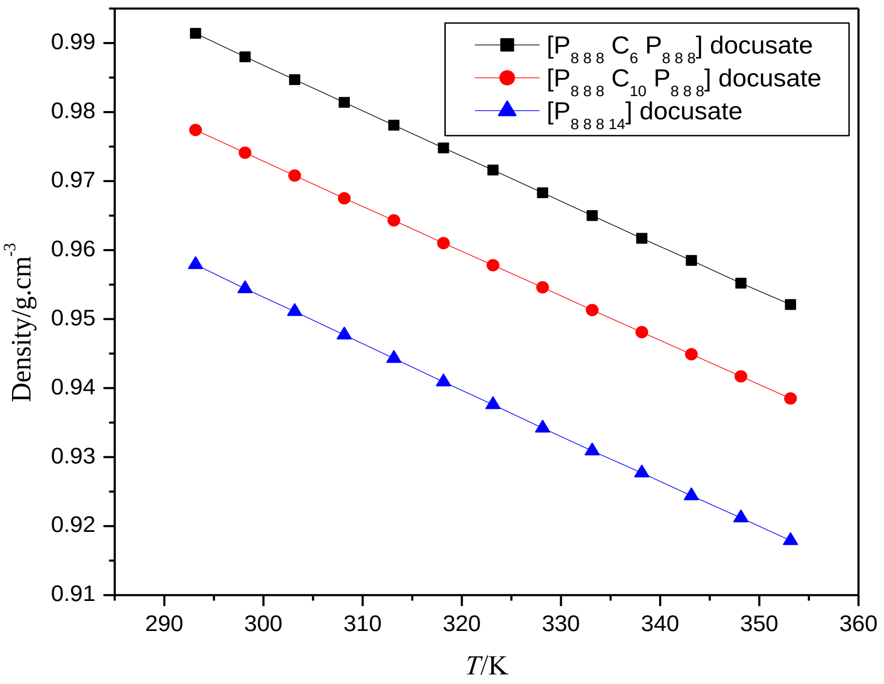

Figure 2. Densities for the present ILs as a function of temperature

present MIL is in agreement with the trioctylphosphonium–based MILs; density for $[P_{8,8,8,8}][NTf_2]$ and $[P_{8,8,8,8}]$ dithiomalenitrile is 1.07 and 0.946 $g\cdot cm^{-1,}$ respectively (Yua et al.2007) but lower compared to the phosphonium ILs with short alkyl chain; 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 (Tariq et al. 2009).

As expected, the density values for the presnt ILs decrease linearly with increasing temperature and also the densities of the DILs decrease with increasing length of the hydrocarbon linkage chain; density of $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS is greater than that of $[P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}]$DOSS. The decrease in density with increasing spacer alkyl chain length has been reported for a large series of DILs (Yua et al. 2007).

The measured viscosity data of the present ILs is presneted in Figure 3. Through the whole range of measured temperatures, $[P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}]$DOSS exhibits the highest viscosity, while the lowest was measured for $[P_{8,8,8,8}]$DOSS. As it can be observed, a rise in temperature caused a significant reduction in the ionic liquids viscosities.

The viscosity values of the present DILs are much higher comparable to MIL. The viscosity values increase as the spacer alkyl chain length increases and the result is in agreement with that observed (Tokuda et al. 2005) for other dicationic ILs. The high viscosity of the DILs was attributed

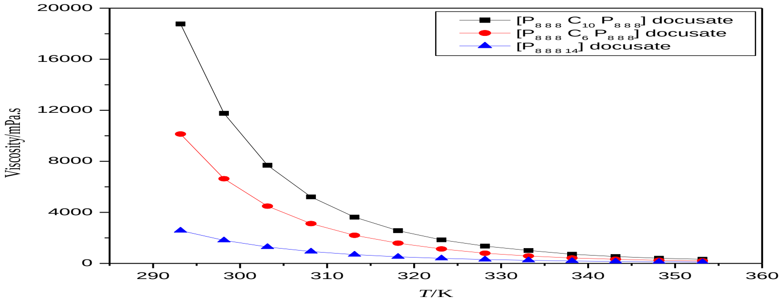

Figure 3 Viscosities for the present ILs as a function of temperature

to an increase in Van der Waals forces, hydrogen bonding between cationic protons and anion and the symmetry of the cations (Huddleston et al. 2001).

The high viscosity of the present ILs when compared to $[P_{6, 6, 6, 14}][NTf_2]$, $[P_{2, 2, 2 ,8}][NTf_2]$ and $[P_{2, 2, 2, 12}][NTf_2]$ is due to the increased Van der Waals interactions whcih result from the long alkyl chains of both the phosphonium cation and the docusate anion. In addition, the high viscosity of the present IL compared to the other phosphonium ILs may be due to the large volume of the DOSS anion which results in low ion mobility (Yao et al. 2010). Increasing the alkyl chain length has two contradictory effects: increases the electron donation into the cationic center which decreases the electrostatic interaction between the cation and anion and hence reducing the viscosity and also it increases the Van der Waal's interactions between the alkyl chains which results in increasing the viscosity.

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 (Yua et al. 2007). Also, the relation between the refractive index and the polarizability constitute a measure of the importance of the dispersion forces to the cohesion of the liquid (solvents with a large index of refraction should be capable of enjoying strong dispersion forces). In addition, the values of refractive index are regarded as a measure of the relative extent of the polar domains in the ionic liquid (Tariq et al. 2009).

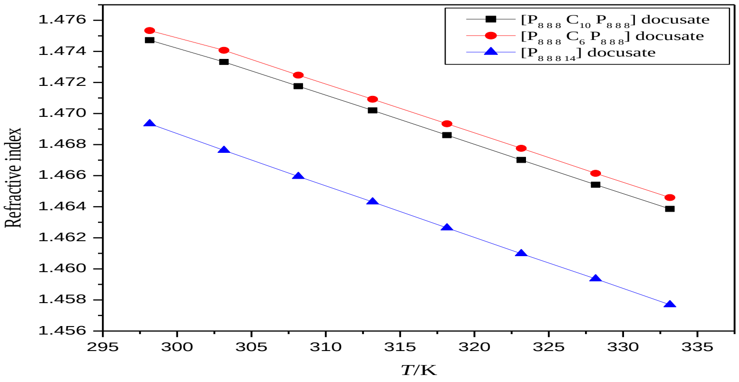

Figure 4. Refractive index for the present ILs as a function of temperature

The refractive indices of the present ILs in the temperature range from (298.15 to 333.15) K are represented in Figure 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 (Tariq et al. 2009). As expected, the refractive index values decrease almost linearly with increasing temperature and also decrease with increasing the alkyl chain length and the spacer alkyl chain length.

The thermal expansion coefficients of $[P_{8,8,8,14}]$DOSS, $[P_{8\,8\,8}\,C_6\,P_{8\,8\,8}]$DOSS and $[P_{8\,8\,8}\,C_{10}\,P_{8\,8\,8}]$DOSS are defined by the following equations (Pereiro et al. 2006):

$$\rho/(\text{g.cm}^{-1}) = A_0 + A_1 T \quad \text{.......................................(1)}$$

$$\alpha_P /(\mathrm{K}^{-1}) = -(1/\rho).(\partial\rho/\partial T)_P$$
$$= -(A_1)/(A_0 + A_1 T) \text{ ....(2)}$$

Where, ρ is density; T is the absolute temperature; A_0 and A_1 are fitting parameters and α is thermal expansion coefficient in K^{-1}. The fitting parameters are estimated using the method of least squares. The estimated thermal expansion coefficient values are reported in Table 2. These values indicate that an increase in the alkyl chain length of the cation tends to decrease the thermal expansion coefficient. The ionic liquids in the present work show weak temperature dependence for the thermal expansion coefficient, $\alpha_p = (6.655 \times 10^{-4}$ to $7.311 \times 10^{-4})$ K^{-1} in the present studied temperature range (293.15 to 353.15) K. These values are high compared with those reported for imidazolium-, pyridinium-, phosphonium- and ammonium – based ILs ($\alpha_p = (5.0 \times 10^{-4}$ to $6.5 \times 10^{-4})$ K^{-1}) (Kilaru et al. 2007).

Table 2: Thermal expansion coefficients α_p for of $[P_{8,8,8,14}]$DOSS, $[P_{8\,8\,8}C_6P_{8\,8\,8}]$DOSS and $[P_{8\,8\,8}C_{10}P_{8\,8\,8}]$DOSS as a function of temperature.

T/K	$10^4\ \alpha_p/(K^{-1})$		
	$[P_{8,8,8,14}]$DOSS	$[P_{8\,8\,8}C_6P_{8\,8\,8}]$DOSS	$[P_{8\,8\,8}C_{10}P_{8\,8\,8}]$DOSS
293.15	7.004	6.667	6.655
298.15	7.029	6.690	6.677
303.15	7.053	6.712	6.700
308.15	7.078	6.735	6.722
313.15	7.103	6.757	6.745
318.15	7.129	6.780	6.768
323.15	7.154	6.803	6.791
328.15	7.180	6.827	6.814
333.15	7.206	6.850	6.837
338.15	7.232	6.873	6.861
343.15	7.258	6.897	6.884
348.15	7.285	6.921	6.908
353.15	7.311	6.945	6.932

Crystal energy of IL is the surface excess energy which is reliant on interaction energy between ions. The low crystal energy is the underlying reason for forming the IL at room temperature. Crystal energies of ionic liquids were estimated according to Glasser theory (Glasser 2004) using the following equation:

$$U_{POT} = 1981.2(\rho/M)^{1/3} + 103.8 \text{ ....(3)}$$

where U_{POT} is the crystal energy in kJ.mol^{-1}. The results showed that the crystal energies of the preseent ILs are much less than that of inorganic fused salts; the minimal crystal energy (U_{POT}) among alkali chlorides is 602.5 kJ.mol^{-1} (Yang et al. 2006). The crystal energies for the present ILs; [$P_{8,8,8,14}$]DOSS, [$P_{8\,8\,8}C_6P_{8\,8\,8}$]DOSS and [$P_{8\,8\,8}C_{10}P_{8\,8\,8}$]DOSS are (300.0, 269.8 and 268.8) kJ.mol^{-1} are lower compared with that of the imidazolium-based

ILs (for [C_nMim]alanine and [C_nMim]glycine (where n=2-6), ranging from 421 to 456 and 429 to 469 kJ.mol^{-1} respectively (Fang 2008).

Experimental refractive index values were used to estimate molar refraction values (the molar refractions is an approximate measure of the total volume without free space of the molecules in one mole of compound) for the present synthesized ILs using the following Lorentz–Lorenz relationships (Glasser 2004).

$$R_M = \frac{N_A \alpha_e}{3\varepsilon_0} = \left(\frac{M}{\rho}\right)\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \qquad \text{...(4)}$$

where, R_M is the molar refraction in cm$^{3}\cdot$mol^{-1}, α_e is mean molecular polarizability (electronic polarizability), ε_0 is the permittivity of free space. The molar refraction values for present ILs present ILs are; 311.32, 489.85 and 491.74 for [$P_{8,8,8,14}$]DOSS, [$P_{8\,8\,8}C_6P_{8\,8\,8}$]DOSS and [$P_{8\,8\,8}C_{10}P_{8\,8\,8}$]DOSS. Till date no results have been reported for the molar refraction of these series of ILs. The molar refraction values of the present ILs at 298.15 K are less high than that reported for [C_4Mim]NTf_2, [C_6Mim]NTf_2, [C_8Mim]NTf_2 and [C_{10}Mim]NTf_2; which are 74.91, 84.23, 93.61 and 102.90 cm$^{3}\cdot$mol^{-}respectively (Glasser 2004). Furthermore, these values are higher than that reported for [C_4Mim]PF_6, [C_6Mim]PF_6, [C_8Mim]PF_6, [C_4Mim]BF_4 and [C_8Mim]Cl which are 51.46, 60.69, 70.29, 47.84 and 67.91 cm$^{3}\cdot$mol^{-}respectively (Kumar 2008).

REFERENCES

Breitbach, Z. S. and D. W. Armstrong (2008). "Characterization of phosphonium ionic liquids through a linear solvation energy relationship and their use as GLC stationary phases." Anal. Bioanal. Chem. 390(6): 1605-1617.

Earle, M. J. and K. R. Seddon (2000). "Ionic liquids. Green solvents for the future." Pure Appl. Chem. 72 1391–1398.

Fang, D. W., Guan, W., Tong, J., Wang, Z. W., Yang, J.Z. (2008). "Study on Physicochemical Properties of Ionic Liquids Based on Alanine [$C_n$mim]Ala (n = 2,3,4,5,6)." J. Phys. Chem. B. 112 7499–7505.

Freire, M. G., P. J. Carvalho, *et al*. (2007). "Surface tensions of imidazolium based ionic liquids: Anion, cation, temperature and water effec. ." J. Colloid Interface Sci. 314: 621–630.

Glasser, L. (2004). "Lattice and phase transition thermodynamics of ionic liquids " Thermochim. Acta 421: 87–93.

Huddleston, J. G., A. E. Visser, *et al*. (2001). "Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation." Green Chem. 3(4): 156-164.

Kilaru, P., G. A. Baker, *et al.* (2007). "Density and surface tension measurements of imidazolium-, quaternary phosphonium-,and ammonium-based room-temperature ionic liquids: data and correlations." J. Chem. Eng. Data 52(6): 2306-2314.

Kumar, A. (2008). "Estimates of Internal Pressure and Molar Refraction of Imidazolium Based Ionic Liquids as a Function of Temperature " J. Sol. Chem. 37 203–214.

Kurnia, K. A., C. D. Wilfred, *et al*. (2009). "Thermophysical properties of hydroxyl ammonium ionic liquids " J. Chem. Thermodyn. 41 517-521.

Lopes, J. N. C., T. C. Cordeiro, *et al*. (2005). "Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion." J. Phys. Chem. B 109 3519-3525.

Pereiro, A. B., F. Santamarta, *et a*l. (2006). "Temperature Dependence of Physical Properties of Ionic Liquid 1,3-Dimethylimidazolium Methyl Sulfate " J. Chem. Eng. Data 51 952 – 954.

Tariq, M., P. A. S. Forte, *et al*. (2009). "Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: Effect of temperature, alkyl chain length, and anion." J. Chem. Thermodyn. 41: 790–798.

Tokuda, H., K. Hayamizu, *et al*. (2005). "Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation." J. *Phys. Chem. B. 109(13): 6103-6110.*

Yang, J.-Z., Q.-G. Zhang, et al. (2006). "Study on the Properties of Amino Acid Ionic Liquid EMIGly " J. Phys. Chem. B. 110 22521- 22524.

Yao, M., M. Fan, *et al*. (2010). "Imidazolium hexafluorophosphate ionic liquids as high temperature lubricants for steel–steel contacts." Wear 268 67–71.

Yua, G., S. Yana, *et al*. (2007). "Synthesis of dicationic symmetrical and asymmetrical ionic liquids and their tribological properties as ultrathin films." Tribology Letters 25: 197-205.
Yunus, N. M., M. I. A. Mutalib, *et a*l. (2010). "Thermophysical properties of 1-alkylpyridinum bis(trifluoromethylsulfonyl)imide ionic liquids." J. Chem. Thermodyn. 42: 491–495.
Zhong, Y., H. Wang, *et al*. (2007). "Densities and excess volumes of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at T = (298.15 to 313.15) K." J. Chem. Thermodyn. 39 291–296.
Ziyada, A. K., M. A. Bustama, *et al*. (2011). "Densities, viscosities and refractive Indices of 1-Hexyl-3-propanenitrile imidazolium Ionic Liquids Incorporated with Sulfonate –based Anions." Journal of Chemical & Engineering Data 56: 2343–2348.
Ziyada, A. K. and C. D. Wilfred (2014). "Effect of Temperature and Anion on Densities, Viscosities, and Refractive Indices of 1-Octyl-3-propanenitrile Imidazolium-Based Ionic Liquids." Journal of Chemical & Engineering Data.
Ziyada, A. K., C. D. Wilfred, *et al*. (2010). "Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K." J. Chem. Eng. Data 55: 3886-3890.

التحضير والخواص الفيزيوحرارية لسوائل ايونية مشتقة من ثلاثي اكتيل الفوسفونيوم ذات انيون ثنائي اكتيل سلفوسكسينات عند درجة حرارة الغرفة

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تم تحضير سلسلة جديدة من السوائل الأيونية عند درجة حرارة الغرفة أحادية الكاتيون وثنائية الكاتيون مشتقة من ثلاثي اكتيل الفوسفونيوم وذات انيون ثنائي اكتيل سلفوسكسينات، وهي: ثلاثي اكتيل تترادكيل فوسفونيوم ثنائي اكتيل سلفوسكسينات $[P_{8,8,8,14}]$DOSS, ثنائي (ثلاثي اكتيل فوسفونيوم) ديكان ثنائي اكتيل سلفوسكسينات $[P_{8,8,8}\ C_{10}\ P_{8,8,8}]$DOSS وثنائي (ثلاثي اكتيل فوسفونيوم) هكسان ثنائي اكتيل سلفوسكسينات $[P_{8,8,8}\ C_{6}\ P_{8,8,8}]$DOSS. تم تشخيص هذه الايونات السائلة باستخدام الرنين النووي المغناطيسي وتحليل العناصر وتم قياس خواصها الفيزيائية مثل الكثافة، اللزوجة ومعامل الانكسار عند درجات الحرارة (353.15–293.15) K عند الضغط الجوي. السوائل الايونية أحادية الكاتيون أظهرت كثافة اقل ولزوجة اعلي مقارنةً بالسوائل الايونية أحادية الكاتيون ذات السلاسل الكربونية القصيرة. يرجع السبب في اللزوجة العالية لهذه السوائل الأيونية لزيادة قوي ڤان درڤال الناتجة من السلاسل الطويلة للكاتيون، بالإضافة للحجم الكبير للانيون مما ينتج عنه قلة في الحركة نسبةً للتجاذب الالكتروستاتيكي بين الكاتيون والانيون. تم حساب معامل التمدد الحراري، طاقة البلورة الانحراف المولي من النتائج المعملية للكثافة ومعامل الانكسار. أظهر معامل التمدد الحراري لهذه السوائل الأيونية تأثراً ضئيلاً بالحرارة كما وجد ان طاقة البلوره لها منخفضة.