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Thermophysical Properties of Trihexyltetradecyl Phosphonium Octylsulfosuccinate Ionic Liquid

[1]A.K. Ziyada, [1]Z. Man, [1]T. Murugesan, [1]M.A. Bustam and [2]C.D. Wilfred
[1]Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia
[2]Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

Abstract: In this study, trihexyltetradecylphosphonium octylsulfosuccinate [$P_{6,6,6,14}$][docusate] was synthesised by anion metathesis using sodium octylsulfosuccinate salt. The molecular structure of the synthesised IL was confirmed by using ^{1}H NMR and elemental analysis and also physical properties such as density, viscosity and refractive index were studied as a function of temperature at the atmospheric pressure. The experimental values of density and refractive index decrease linearly with increasing temperature. The density, refractive index and viscosity of the present IL at 298.15 K are 0.9631 g cm^{-3}, 1.47190 and 1806.1 mPa.s respectively. The results show that this IL possesses higher viscosity, similar density and refractive index compared to the other trihexyltetradecylphosphonium ILs.

Key words: Octylsulfosuccinate, phosphonium ionic liquids, physical properties

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 (Seddon and Earle, 2000; Welton *et al*., 2007). 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; Pieraccini and Chiappe, 2004), easy recycling, make these compounds attracting a considerable attention in many fields (Pieraccini and Chiappe, 2004). The tenability properties make them obtain 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 (Yu *et al*., 2001) and in biocatalysts (Zhong *et al*., 2007) with great advantages. The diverse cationic and anionic components of the ILs will facilitate the choice of ionic liquid with task-specific properties (Canongia *et al*., 2005).

Quaternary phosphonium based ILs have been receiving a great deal of attention in terms of application to electrochemical systems (Hagiwara *et al*., 2009). Compared to the other ILs, the remarkable features of phosphonium ILs are their chemical, thermal and electrochemical stabilities and also some phosphonium ionic liquids exhibit lower melting points and lower viscosities which are practical advantages for various applications (Hagiwara *et al*., 2009; Sugiya and Tsunashima, 2007).

However, reliable experimental data of physical properties are required for a better understanding of the IL behavior and also are related to the engineering components associated with a process (densities and viscosities will determine important parameters including mass transfer, rates of liquid-liquid phase separation, power requirements for mixing and pumping) (Huddleston *et al*., 2001). Many researchers have synthesised and studied the physiochemical properties of trihexyltetradecylphosphonium-based Ils with several anions and reported their physiochemical properties, but thermophysical properties of trihexyltetradecylphosphonium octylsulfosuccinate [$P_{6,6,6,14}$][docusate] IL has not been studied. Hence, an attempt was made to by our group to synthesise and

Corresponding Author: A.K. Ziyada, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia

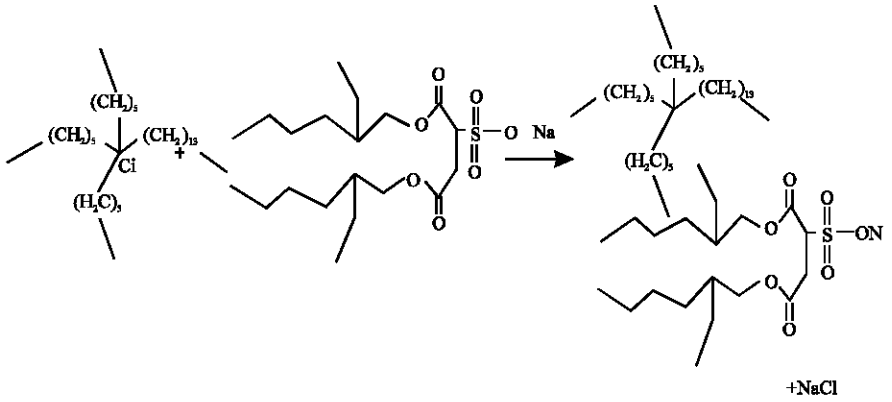

Fig. 1: Synthesis of Trihexyltetradecylphosphonium octylsulfosuccinate [$P_{6,6,6,14}$][docusate]

study the thermophysical properties of trihexyltetradecylphosphonium octylsulfosuccinate.

The present study involves the synthesis of a trihexyltetradecylphosphonium octylsulfosuccinate [$P_{6,6,6,14}$][docusate] ionic liquid. The IL was synthesised by reacting trihexyltetradecylphosphonium chloride with sodium octylsulfosuccinate (Fig. 1). The structure of the products was verified with ^{1}H-NMR and elemental analysis.

The physical properties of the ionic liquid such as density, viscosity and refractive index were carried out. In addition to this, thermal expansion coefficient, molar refraction, molar volume, entropy and crystal energy of the synthesised IL were estimated.

MATERIALS AND METHODS

Materials: The source and grades of the chemicals used for the synthesis of the IL are: trihexyltetradecylphosphonium chloride (Aldrich 95%), sodium octylsulfosuccinate (Aldrich 98%), anhydrous diethylether (Sigma-Aldrich 99%) and acetone (Sigma-Aldrich 99.9%).

Synthesis of ionic liquid: Trihexyltetradecylphosphonium octylsulfosuccinate was synthesised by mixing stoichiometric amounts of trihexyltetradecylphosphonium chloride and sodium octylsulfosuccinate 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 for at 80°C for 48 h to afford the clear viscous gel product trihexyltetradecylphosphonium octylsulfosuccinate.

Characterisation: The synthesised IL was characterized by using Bruker Avance 300 spectrometer, ^{1}H NMR spectra was taken in $CDCl_3$ solvent. CHNS-932 (LECO instruments) was used for elemental analysis (Murugesan *et al*., 2010).

A coulometric Karl Fischer titrator, DL 39 (Mettler Toledo) was used to determine the water content of the synthesised IL, using Hydranal coulomat AG reagent (Riedel-de Haen) (Huddleston *et al*., 2001). All measurements were made for IL in triplicate to ensure their reproducibility. DL-55 autotitrator (Mettler Toledo) with 0.005 M $AgNO_3$ as the titrant was used to determine the chloride content of the IL (Muhammad *et al*., 2008).

Perkin-Elmer, Pyris V-3.81 thermal gravimetric analyzer was used to measure the start and onset temperatures. The samples (5.0-10.0) mg were placed in aluminum pans under a nitrogen atmosphere at a heating rate of 10°C min^{-1} (Murugesan *et al*., 2010; Muhammad *et al*., 2008; Wilfred *et al*., 2009).

Stabinger viscometer (Anton-Paar model SVM3000) (Xiaa *et al*., 2010) was used for the measurements of density and viscosity of the present IL at a temperature range (293.15 to 353.15) K. The temperature was controlled to within ±0.01°C. The repeatability of measurements were 0.35%, $\pm 5\times10^{-4}$ gcm^{-3} and ±0.02°C for viscosity, density and temperature respectively (Murugesan *et al*., 2010; Muhammad *et al*., 2008; Wilfred *et al*., 2009).

ATAGO programmable digital refractometer (RX-5000 alpha) with measuring accuracy of $\pm 4\times10^{-5}$ and a controlled temperature to within ±0.05°C was used to measure the refractive index of the synthesised IL in the temperature range (298.15 to 333.15) K (Murugesan *et al*., 2010; Wilfred *et al*., 2009). Dried samples kept in desiccators were directly placed into the measuring cell. The apparatus was calibrated before each series of measurements and checked using pure organic solvents with known refractive indices (Muhammad *et al*., 2008). Reproducibility of the results was confirmed by performing at least three experiments for each sample.

RESULTS AND DISCUSSIONS

^{1}H NMR and elemental analysis (CHNS) were used to confirm the compound. The results confirmed the desired structure. The ^{1}H NMR and elemental analysis results are as follows: ^{1}H NMR ($CDCl_3$): δ 0.89 (24H, t, CH_3); 1.26-1.41 (64H, br, CH_2); 2.2-2.3 (8H, br, CH_2-P); 3.10 (2H, t, CH_2COO); 3.90-4.20 (4H, br, CH_2-O); 5.10 (1H, s, CO-CH). Elemental analysis: % found (% calculated) C, 68.23 (68.98); H, 11.57 (11.69): S, 3.47 (3.54). Chloride content is 69 ppm.

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 affect on density, viscosity, refractive index and thermal stability. Also it has a remarkable affect on reactivity, not only in the new biotechnology applications but also in many synthetic schemes using IL as reaction media (Huddleston *et al*., 2001).

The water content value of trihexyltetradecyl phosphonium octylsulfosuccinate [$P_{6,6,6,14}$][docusate] synthesised is presented in Table 1. The water content value is comparable with the phosphonium ILs reported by Tarig *et al*. (2009), where the water content of trihexyltetradecylphosphoniumbis (trifluoromethylsulfnyl) 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 ppm.

Thermal stability of ILs is of practical importance for various applications. The start temperatures for weight loss (T_s) and onset temperatures (T_d) of trihexyltetradecylphosphonium octylsulfosuccinate are 294 and 368°C respectively. The start and onset temperatures of this series of ILs are affected slightly by the size of the alkyl chain of the cation, the decomposition temperature decreases as the alkyl chain increases (Zhao *et al*., 2004). The decomposition temperature of the present IL is lower compared to other phosphonium ILs with cshort alkyl chain, for [$P_{2,2,2,8}$][NTf_2] and [$P_{2,2,2,12}$][NTf_2] are 380 and 400°C, respectively (Sugiya and Tsunashima, 2007).

Table 1 and Fig. 2 presents the densities of trihexyltetradecyl phosphonium octylsulfosuccinate of [$P_{6,6,6,14}$][docusate] IL in the temperature range from (293.15 to 353.15) K. The density of the IL is lower compared with the imidazolium Ils reported by (Zhao *et al*., 2004), the densities of [C_2CN Mim]BF_4, [C_3CN Mim]BF_4 and [C_4CN Mim]Cl are 2.15, 1.87 and 1.61 g cm^{-3}, respectively.

The measured density of the present ionic liquid in the range from (0.9287 to 0.9664)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] (Tarig *et al*., 2009). The density of [$P_{6,6,6,14}$][NTf_2] and [$P_{6,6,6,14}$][OTf] are 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 presnt IL is 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. As expected, the density values for [$P_{6,6,6,14}$] [docusate] decrease linearly with increasing temperature. The linear behavior is common to ionic liquids and is a consequence of the large temperature difference between their working temperature range and their critical temperatures Tarig *et al*. (2009).

Table 1 and Fig. 3 presents the viscosity for [$P_{6,6,6,14}$][docusate] IL. The viscosity increases with increasing molecular weight or alkyl chain (Tarig *et al*., 2009). The high viscosity of the present IL when compared to [$P_{6,6,6,14}$][NTf_2] and [$P_{6,6,6,14}$][OTf] is due to the long alkyl chain of the docusate anion which results in increasing the electrostatic interaction between the cation and anion. Further the higher viscosity of the present IL when compared to [$P_{2,2,2,8}$][NTf_2] and [$P_{2,2,2,12}$][NTf_2] is due to the increased Van der Waals interactions results 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

Table 1: Density, viscosity and refractive index for Trihexyltetradecylphosphonium octylsulfosuccinate

IL	Density(gcm^{-3})	Viscosity(mPa.s)	Refractive index
[$P_{6,6,6,14}$] [docusate]	0.9631	1806	1.47190

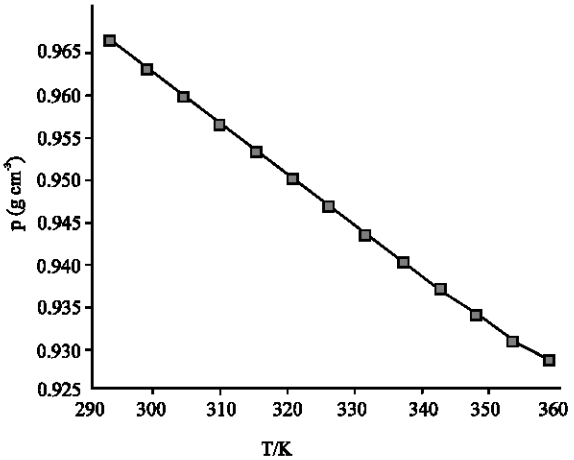

Fig. 2: The density of [$P_{6,6,6,14}$][docusate] IL as a function of temperature

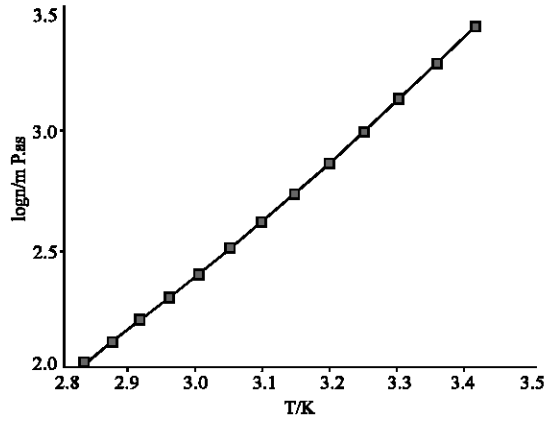

Fig. 3: Log η against T^{-1} for $[P_{6,6,6,14}]$[docusate] IL as a function of temperature

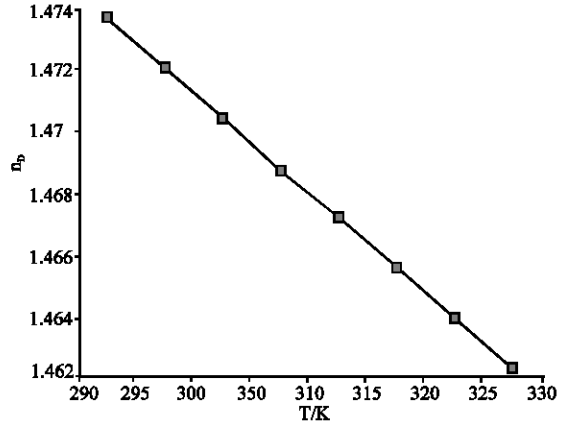

Fig. 4: Refractive index of $[P_{6,6,6,14}]$[docusate] IL as a function of temperature

phosphonium ILs may due to the large volume of the docusate anion which results in low ion mobility (Xiaa *et al*., 2010). Increasing the alkyl chain length has two contradictory effects:

- Increase the electron donation into the cationic centre which decreases the electrostatic interaction between the cation and anion and hence reducing the viscosity
- Increase the Van der Waal's interactions between the alkyl chains which results in increasing the viscosity

The relation between the refraction index and the polarisability 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). Also the values of refractive index are regarded as a measure of the relative extent of the polar domains in the ionic liquid Tarig *et al*. (2009).

The measured refractive index values in the temperature range from (298.15 to 333.15) K for $[P_{6,6,6,14}]$[docusate] is represented in Fig. 4. Table 1 show that the refractive index values of the present IL is in agreement with other phosphonium ILs, the refractive index of $[P_{6,6,6,14}][NTf_2]$ and $[P_{6,6,6,14}][OTf]$ is 1.4587 and 1.4585 as reported by (Tarig *et al*., 2009). As expected, the refractive index values decrease almost linearly with increasing temperature.

CONCLUSION

The experimental values of density and dynamic viscosity at temperature range from (293.15 to 353.15) K and refractive index from (298.15 to 343.15) K were measured and reported for the trihexyltetradecylphosphonium octylsulfosuccinate $[P_{6,6,6,14}]$][docusate] ionic liquid.

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