Journal of Molecular Liquids 252 (2018) 439–444

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermophysical properties of glycerol and polyethylene glycol (PEG 600) based DES

Amarpreet Singh [a], Rashmi Walvekar [a,*], Mohammad Khalid [b], Wai Yin Wong [c], T.C.S.M. Gupta [d]

[a] Energy Research Group, School of Engineering, Taylor's University, Taylor's Lakeside Campus, Jalan Taylor's, Subang Jaya 47500, Selangor, Malaysia
[b] Graphene & Advanced 2D Materials Research Group (GAMRG), Research Centre for Nano-materials and Energy Technology (RCNMET), School of Science and Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, 47500 Subang Jaya, Selangor, Malaysia
[c] Fuel Cell Institute, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia
[d] Research and Development, Apar Industries Limited, Mumbai, India

A R T I C L E I N F O

Article history:
Received 29 June 2017
Received in revised form 16 September 2017
Accepted 5 October 2017
Available online 6 October 2017

Keywords:
Deep eutectic solvent
Ionic liquid
Glycerol
Polyethylene glycol
Viscosity

A B S T R A C T

In this study, the Deep Eutectic Solvent (DES) is prepared based on glycerol and polyethylene glycol 600 (PEG) as hydrogen bond donor and choline chloride (ChCl) as hydrogen bond acceptor. The glycerol based DESs were formed with ratio of 1:2, 1:3, 1:4 and 1:5 whereas three-component DESs of ChCl, PEG and glycerol were synthesized with ratio 1:3:2, 1:4:2 and 1:5:2. The DESs were subjected to DSC, Karl Fishcer, thermal conductivity, viscosity and density testing. The melting temperature (T_m) for PEG based DESs were found to in the region of 18 °C. The moisture content in DESs were identified through Karl Fishcer testing was found to be <1% which is desired when synthesizing a DES. The thermal conductivity of glycerol based DESs decreases with respect to pure glycerol whereas for PEG based DESs shows positive enhancement of thermal conductivity at temperatures below 60 °C. The viscosity of glycerol DESs decreases with increasing temperature and the value of PEG DESs' viscosities was found to be higher than the pure PEG. All the DES samples have linear decrease across a temperature range with highest density achieved at 1.2155 g/cm^3 with temperature of 25 °C for molar ratio of ChCl to glycerol of 1:4 (DES 4).

1. Introduction

Ionic Liquids (ILs) are relatively new type of solvents that have gained huge attention in the scientific world and due to their promising nature, ILs are extensively explored in industrial level applications. Currently, ILs have been applied in food science, separation, nanomaterial processing and may other industries. ILs are a type of liquid salt that consist of ions and ions pair which have relatively low melting points due to the asymmetrical structure between ions. The type of anions and cations determine the physical and chemical properties of IL. The common type of cations are imidazolium, ammonium, and pyridinium whereas anions are PF_6^-, BF_4^-, and others [1].

There are plenty of advantages of using ILs which makes ILs favourable to replace conventional solvents but unfortunately there are also certain disadvantages. In the usage of anions such as PF_6^- and BF_4^- imidazolium salts can lead to reaction with water which results in formation of hydrogen fluoride (HF). The unwanted formation can greatly affect the surroundings and result in corrosion of metals [2]. Some ILs showed severe corrosiveness towards copper metal strips when tested at elevated temperatures [3]. The decomposition of ILs in the presence of air and moisture results in corrosion. The occurrence of corrosion on the lubricating surface will reduce the lifespan of the equipment causing failure and increased cost due to replacement of the specific part.

The limitations of ILs are overcome by the discovery of DES. DES is a type of mixture formed by two or more components which have similar properties as ILs but is different in composition and structure. The physical properties of DESs and ILs are similar but the chemical properties are different. The difference in chemical properties allows wider potential application of DESs in different areas compared to ILs. DES is formed with a quaternary ammonium salt and hydrogen bond donor which has charge delocalization in the form hydrogen bonding. The hydrogen bond is formed between halide ion and Hydrogen Bond Donor (HBD) having lower melting point compared to the individual component [4]. The HBD can be amide, acid, alcohol and other suitable compound that is capable of forming hydrogen bond. DESs are produced by simple mixing process which is relatively cheap in order to obtain a eutectic mixture [5]. This process is even cheaper than the production of ILs which makes it more feasible to replace ILs with DES.

DES has lower melting point than the individual component due to formation of complex anion that decreases the lattice energy [6]. The components are prepared by mixing and heating to produce the required DES. The melting point or freezing point of the DES is achieved

* Corresponding author.
E-mail address: rashmigangasa.walvekar@taylors.edu.my (R. Walvekar).

https://doi.org/10.1016/j.molliq.2017.10.030
0167-7322/

by eutectic composition of the mixture of the two component. Eutectic point is achieved by varying the molar ratio of the salt and HBD.

Abbot et al. (2014) reported a study on four different types of DESs which used a common salt and different HBDs. The DESs used ChCl [$(CH_3)_3$-N^+-CH_2-OH Cl^-] as salt and four different HBD which were urea (1:2), ethylene glycol (1:2), glycerol (1:2) and oxalic acid (1:1). DESs together with imidazolium based ILs were tested for the corrosive nature towards metals. All the DES have extremely low freezing point except for urea based DES. The latter DES has the tendency to decompose at high temperature and form ammonia whereas oxalic acid based DES has high corrosiveness towards mild steel. Thus, ChCl and glycerol showed promising properties with low corrosivity and good viscosity profile. Similarly, all the DESs were tested with different type of metals such as Iron (Fe), Aluminium (Al) and Nickel (Ni) together with water to observe the corrosive nature of ChCl based DES. The outcome showed low corrosion of DESs towards these metals except for oxalic acid based DES. The least corrosion was observed for glycerol based DES [7].

Polyethylene glycol (PEG) is a form of polymer that consist of ethylene glycol monomers that has formula of HO-$(CH_2CH_2OH)_n$-H and widely used in synthetic based lubricants formulation. PEG is non-toxic and is classified according to the molecular weight of the product [8]. Therefore, the formation of PEG based DES would be a new innovation and the physical properties can be investigated. The formation of glycerol and PEG based DES will allow to investigate the resultant thermophysical properties with respect to the individual HBDs whether DES formation has positive effect or negative effect on thermophysical properties. The effect and properties would be further studied to use DESs as potential base fluids for lubrication industry and the behavior to the surrounding specially corrosion.

2. Experimental

2.1. Materials

Choline Chloride (ChCl) [$HOC_2H_4N(CH_3)_3Cl$] was purchased from Merck with purity 99.0% was used as the common salt for both the DESs. The industrial glycerol [$C_3H_8O_3$] with purity of 97% was purchased together with polyethylene glycol 600 (PEG) [HO-$(CH_2CH_2OH)_n$-H] of R&M chemicals from Wataka Trading. PEG 600 was selected because it exists in liquid form at room temperature.

2.2. Preparation of DES

Glycerol based DESs were prepared with four different molar ratio whereas the PEG based DESs were prepared with three different molar ratios as shown in Table 1. The glycerol based DESs were synthesized by mixing the components based on the molar ratio at 120 °C, with constant stirring at 300 rpm for 2 h to form a colourless liquid. The molar ratio for glycerol based DESs were found from the earlier reported studies [7,11] whereas the inability of PEG to form two component DESs lead to three component DESs. The three component PEG based DES was formed by initially adding ChCl in the PEG according to the respective molar ratios and stirred at 300 rpm with heating at 120 °C C for 2 h. Later glycerol was added to the mixture with continues stirring to synthesize the PEG based DESs.

Table 1
DESs with different molar ratios.

Salt	HBD 1	HBD 2	Molar ratio	Abbreviation
ChCl	Glycerol	–	1:2	DES 1
			1:3	DES 2
			1:4	DES 3
			1:5	DES 4
	PEG 600	Glycerol	1:3:2	DES 5
			1:4:2	DES 6
			1:5:2	DES 7

2.3. Properties measurement

In order to measure the moisture content of DESs, Mettler Toledo Karl Fischer was used. The melting point was measured using DSC-60 Plus, Shimadzu which has the range as low as −140 °C. The Fourier Transform Infrared Analysis (FTIR) was conducted using the Perkin Elmer Spectrometer 100 with range of 4000–650 cm^{-1}. Thermal conductivity was measured as a function of temperature by using the KD2 Pro Decagon Device with uncertainty of ±5% and jacketed circulating water bath. The thermal conductivity was measured at 25 °C, 40 °C, 60 °C, 80 °C and 100 °C. The viscosity was measured using Haake Mars III Rheometer from Thermo Scientific with spindle plate size of P35 Ti L and lower plate TMP 35. The viscosity was measured at 25 °C, 40 °C and 100 °C with two different shear rates of 10 s^{-1} and 500 s^{-1}. The dynamic viscosity was obtained by taking the average viscosity of the two different shear rate at the particular temperature. The density was measured by using the Anton Par DMA 4500 M at temperature of 25 °C, 40 °C and 90 °C. The viscosity was measured at temperature of 100 °C which was selected due to limitation of the equipment and as the highest temperature to observe the behavior of DES at extreme temperature whereas the heating element of DMA 4500 M limits the temperature to 90 °C to prevent any damage to the U-tube thus the DESs were measured at that particular temperatures.

3. Results and discussion

3.1. Melting point

The melting point (T_m) of newly synthesized PEG based DES is shown in Table 2. The lowest T_m was found for DES 7 with 17.5 °C and the highest among the three different molar ratios was DES 5 with 18.8 °C. The freezing point (T_f) of glycerol based DESs has been extensively studied and were found to be −36.15 °C for molar ratio 1:2 and −32.65 °C for 1:3 M ratio [5].

3.2. Moisture content

The synthesis of DES might lead to some absorbance of moisture from the surroundings even when the mixing process was conducted in a controlled environment. The experiment was conducted in the fume hood and parafilm was used to further seal the container of the mixture to reduce exposure of surrounding air. The highest percentage of moisture was found in DES 1 with 0.73% whereas the lowest percentage was for DES 6 with 0.48% (Fig. 1). Higher moisture content can lead to alteration in physical properties such as density, surface tension and viscosity. However, some researches focus on the influence of DESs-water mixture and their respective application such as metal electrodeposition [9]. The moisture content should be as low as possible as water is also known as the simplest HBD thus to prevent any changes to occur on the eutectic composition [10]. Moreover, the low water content is preferable to prevent corrosion from occurring. In a study conducted by Abbott et al. glycol based DESs are relatively insensitive to the water addition in terms of corrosion compared to urea and oxalic acid based HBDs for common metals. Thus, DES 1 to DES 7 having water

Table 2
Melting point (T_m) for PEG DES samples.

Sample	Melting point, T_m (°C)
DES 5	18.8
DES 6	18.4
DES 7	17.8

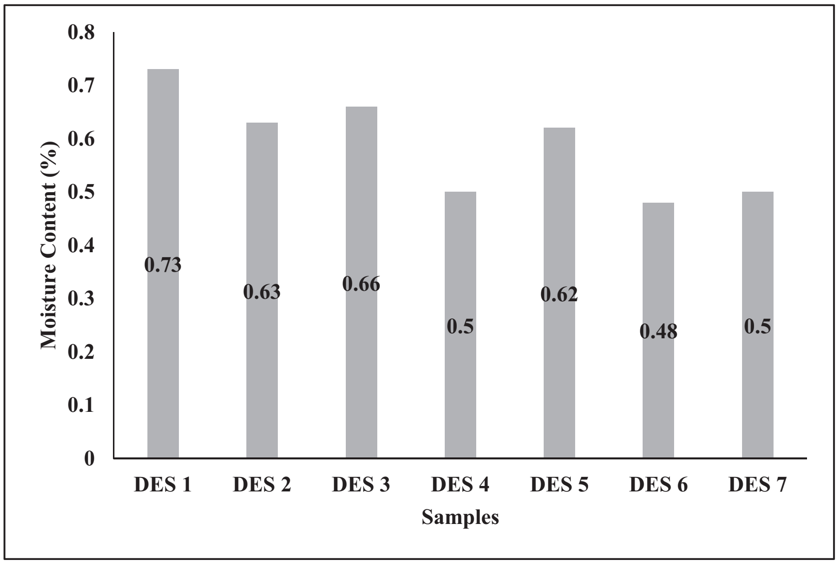

Fig. 1. Moisture content of DESs.

content < 1% signifies high purity DES which does not significantly affect physical properties of DES which increases the potential of DES.

3.3. Fourier transform infrared analysis (FTIR)

From Fig. 2, the FTIR analysis showed the lowest peak at the region of 3400 cm^{-1} to 3300 cm^{-1} which shows the presence of OH group and NH group. The significant presence of OH group was due to the formation of hydrogen bonding in the DES as well as the OH group contributed by the structure of glycerol which has three OH group attached in a single molecule. The peak becomes bigger as the molar ratio except for DES 2 which signifies higher network of hydrogen bond. Besides that, NH group exist within the peak because of the NH bond in ChCl salt. The second lowest peak was found at the region of 1000 cm^{-1} due to the presence of CN group and CO group. ChCl structure attributes to the CN group and the CO group which comes from the bonding of the C—O single bonds. Similarly the peak becomes bigger with the increasing molar ratio as the amount of HBD increases. From Fig. 3, the lowest peak was obtained at 1090 cm^{-1} which represent the CO group. This is due to the structure of PEG compound which has oxygen atom attached to the carbon chain. The second highest peak was found at 2870 cm^{-1} shows the CH which forms majority of the PEG 600 molecules structure. A small and board peak was observed at the region of 3300 cm^{-1} which shows the OH group coming from the hydrogen bonding as well as the addition of glycerol.

3.4. Thermal conductivity

Thermal conductivity is an important physical property, which determines the amount of heat that passes through a certain material. Pure glycerol has relatively high thermal conductivity and the DESs derivative exhibit similar pattern. From Figs. 4 and 5, DES 1 has the lowest thermal conductivity followed by DES 2 while DES 3 has the highest

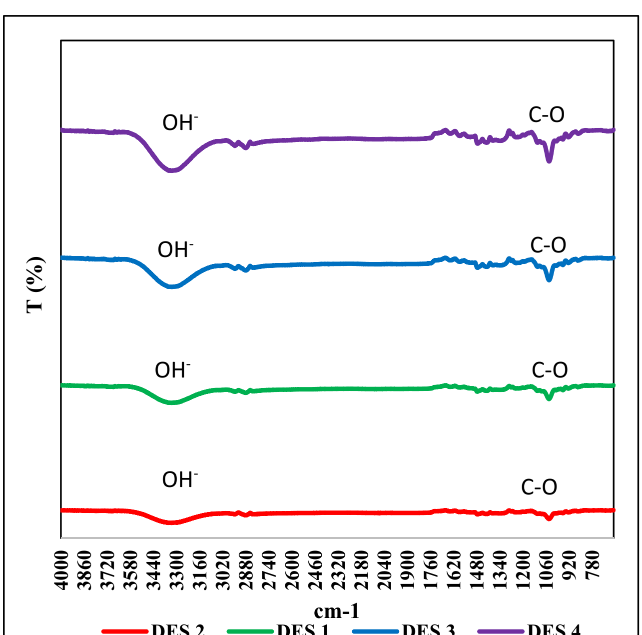

Fig. 2. FTIR of glycerol based DESs.

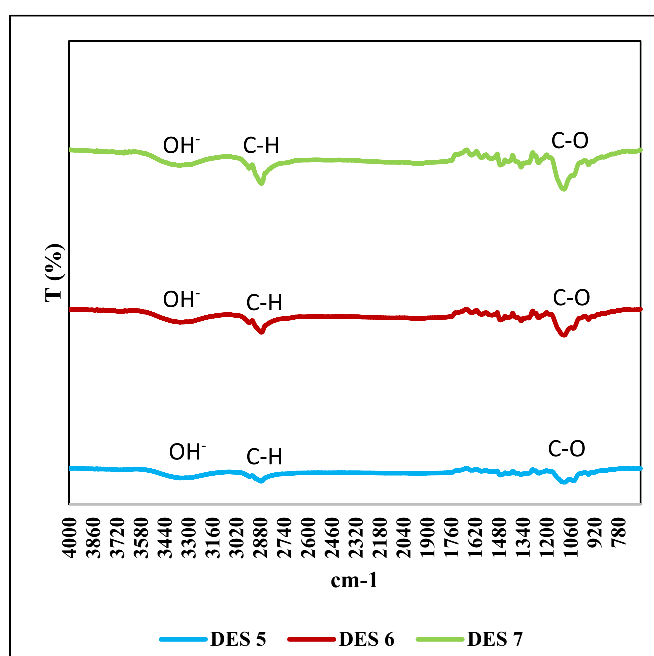

Fig. 3. FTIR of PEG based DESs.

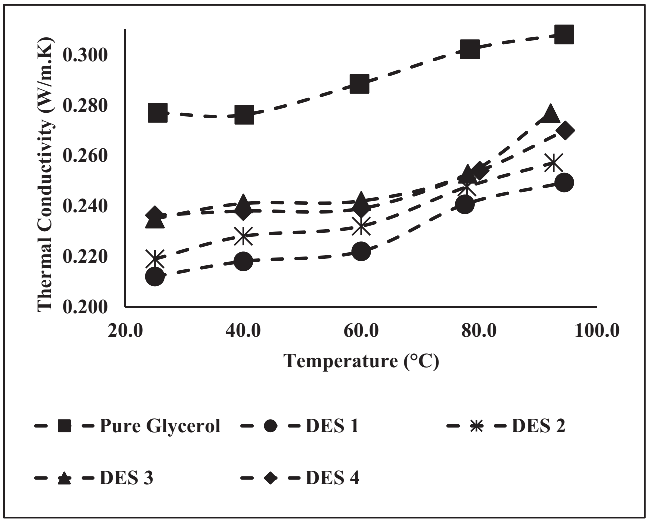

Fig. 4. Thermal conductivity of glycerol based DESs.

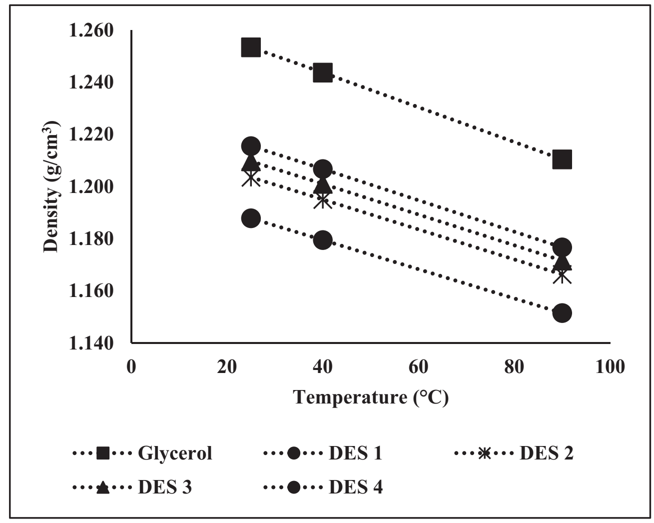

Fig. 6. Density of glycerol based DESs with respect to temperature.

conductivity whereas DES 4 has slightly lower conductivity than DES 3. The difference in thermal conductivity is closely related to the molar ratio of the DES. Glycerol is known for high thermal conductivity but when hydrogen bond is formed with salt the conductivity is reduced due to nature of the ChCl. The PEG based DESs showed very less variation of thermal conductivity compared to glycerol based DESs. At low temperatures, the PEG based DESs similar values but as the temperature increased above 80 °C, DES 7 showed highest thermal conductivity.

The comparison of pure glycerol and its DESs derivatives showed that the thermal conductivity decreases with the formation of DES whereas pure PEG and its DESs derivatives showed increase in thermal conductivity. Thus, it can be concluded that the amount of salt acts as the important factor which determines the resultant thermal conductivity. As the amount of salt content decreases with the increasing molar ratio, the enhancement of thermal conductivity improves [11]. The type of salt used influences the thermal conductivity outcome of the DES [12].

3.5. Density

Density of the DESs depends on the type of the HBD and salt as well as the molar ratio. Pure glycerol has the highest density with 1.253 g/cm^3 at 25 °C and 1.210 g/cm^3 at 90 °C. It is noted from Fig. 6 that DES 1 has the lowest density followed by DES 2, DES 3 and finally DES 4 with the highest density when comparing the DESs. All the samples were found to decrease linearly as the temperature increases. Thus, as the amount of glycerol (HBD) increases in DES with the molar ratio, higher density was obtained. This is similar in a study found by Francisco et al. where increase in molar ratio contributes to reduction in the free space between the molecules thus increasing density [14]. From Fig. 7, the lowest density observed was for pure PEG while all the DES depicting higher density. The highest density at 25 °C was measured for DES 6 with 1.135 g/cm^3 followed by DES 5 and the lowest density was DES 7 with 1.132 g/cm^3. The difference between densities of PEG based DESs were found to be smaller compared to glycerol based DESs but with respect to the temperature, the PEG based DESs have a higher drop in densities with percentage ranging from 4.52% to 4.57%. The glycerol based DESs were found to be lower than pure component whereas the PEG based DESs showed opposite effect with enhancing the density of the PEG based DESs in comparison with the pure component. The enhancement occurred due to the presence of glycerol based component in the DES and in a study done by Hayyan et al. the eutectic phenomena plays a vital role on the resultant density [13]. The enhancement of density was also found in a study conducted by Abbott et al. where the zinc chloride as the common salt with acetamide and urea HBDs showed higher density compared to pure components. The

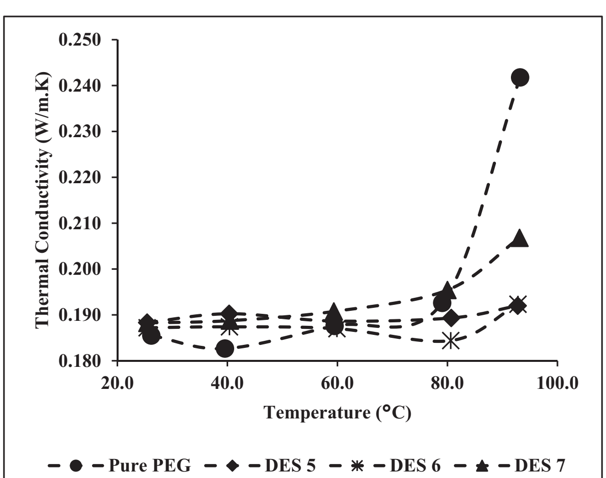

Fig. 5. Thermal conductivity of PEG based DESs.

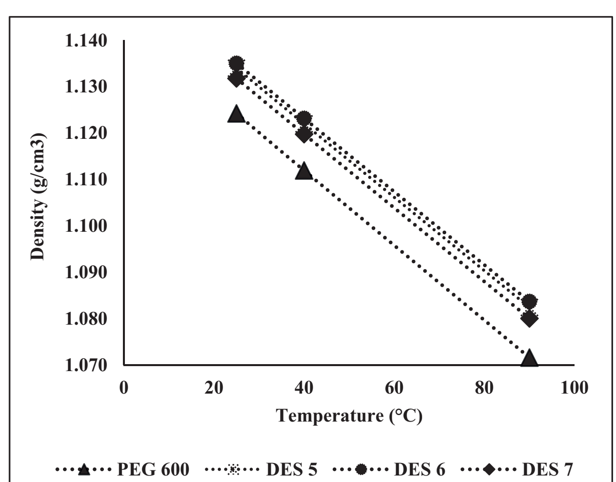

Fig. 7. Density of PEG based DESs with respect to temperature.

resultant DES density is dependent on the packing or the molecular structure of the DES which can be explain by the hole theory [15]. When the salt and HBD were mixed the average hole radius decreases which contributes to more free space thus increasing the density [16]. Overall, the density of the DES could be easily altered with the type of HBDs and the molar ratio to suit a certain application. The PEG based DESs were found to be higher compared to alkylimidazolium dialkyl phosphates ILs which are PEE (1.125 g/cm^3), PBE (1.038 g/cm^3), and POE (1.016 g/cm^3) respectively [17].

3.6. Viscosity

From Fig. 8, glycerol has very high dynamic viscosity (0.7058 Pa·s) at room temperature 25 °C which rapid decreases to 0.01710 Pa·s as the temperature increase 100 °C. The glycerol based DESs exhibit lower viscosity values compared to pure glycerol and has a very small difference at temperature of 100 °C. The lowest viscosity was obtained by DES 1 (0.2002 Pa·s) at 25 °C followed by DES 3 (0.2440 Pa·s), DES 2 (0.2607 Pa·s), and DES 4 (0.3038 Pa·s). The variation of viscosity at 100 °C is small with lowest being DES 3 (0.01271 Pa·s) then DES 1 (0.01339 Pa·s), DES 2 (0.01363 Pa·s), and finally DES 4 (0.01386 Pa·s).

The dynamic viscosity for DES 1 of 0.2002 Pa·s at 25 °C was found to different from the reported values of 0.259 Pa·s [10] and 0.281 Pa·s [18] which could be due to the chemical nature of the component used as well as the moisture content [10]. However, increasing molar ratio which increases the dynamic viscosity behavior was observed for ChCl glycerol DES by study done by Abbott et al. and Chemat et al. [7,20]. When the molar ratio was increased, abundant HBD were available to form hydrogen bonding. The presence of massive hydrogen bond network leads to lower mobility of free species existing in the DES thus increasing the dynamic viscosity [18]. When more HBDs were added to the DES, the resultant viscosity tends to move closer to the pure component but in a study conducted by Mjalli et al. where glycerol HBD was mixed potassium carbonate salt which lead to higher dynamic viscosity than the pure HBD [19]. Therefore, the type of salt used in DES also plays an important contribution towards dynamic viscosity.

On the other hand, it was noted from Fig. 9 that viscosity of pure PEG is lower than PEG based DESs. At 25 °C viscosity of PEG is 0.1282 Pa·s while increases with DES 7 (0.1686 Pa·s), DES 6 (0.1823 Pa·s) and DES 5 (0.1962 Pa·s). An opposite pattern is observed for PEG based DESs compared to the glycerol based DES. This could be to the structure of the three component DES formed where the voids in the liquid are smaller at lower molar ratio compared to higher ratio which resulted in higher dynamic viscosity [20]. The increment of dynamic viscosity

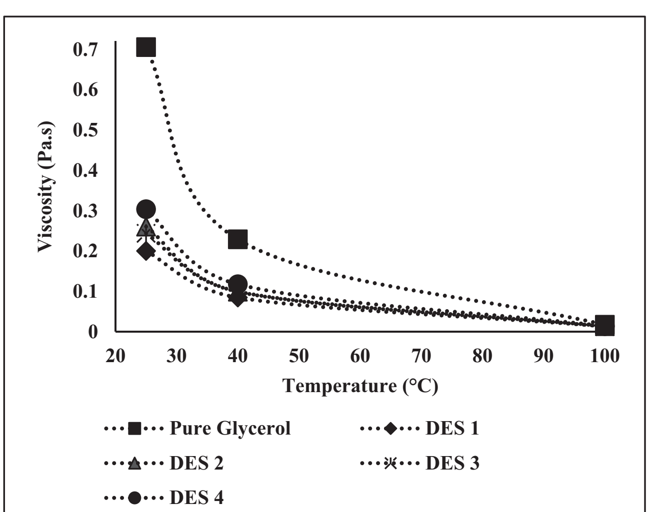

Fig. 8. Dynamic viscosity of glycerol DESs with respect to temperature.

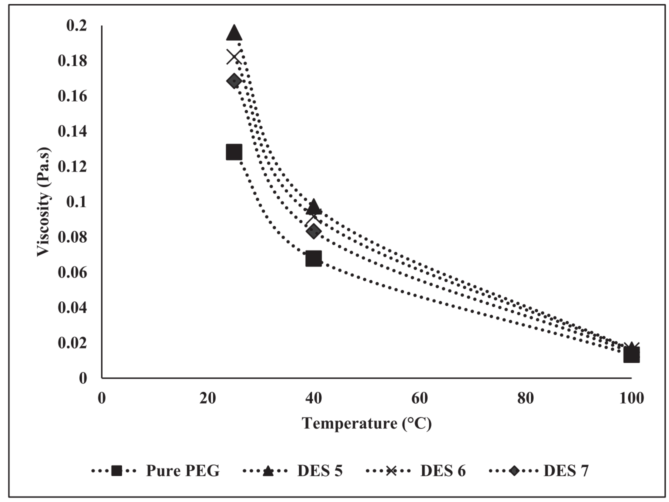

Fig. 9. Dynamic viscosity of PEG based DESs with respect to temperature.

of PEG based DES was similar to the study conducted by Chemat et al. where three component DES consisting of ChCl, glycerol and L-arginine exhibited higher viscosity when DES was formed. As the molar ratio was increased, the dynamic viscosity increases because of the increment of the hydrogen bond formation. From the dynamic viscosity information of DES, the suitable application with respect to an optimum molar ratio can be identified and selected. For certain application such as metal electrodeposition, high viscosity is not a desired factor thus DES synthesis is able to alter the viscosity for the application [13].

4. Conclusion

The glycerol and PEG based DESs were successfully synthesized from ChCl with different molar ratios. The thermophysical properties were investigated showed that the properties of DESs can be altered by changing the type of HBDs and varying molar ratios. All the DESs synthesized showed moisture content lower than 1% which leads to high purity of the solvent. For glycerol based DES, the thermal conductivity, viscosity and density decreases compared to pure glycerol. On the other hand, all this properties showed increased when tested with PEG based DES. Thus, the term of designer solvent suits DES as the properties can be altered and has the potential for wide range of application compared to IL. The process of synthesis of DES is much simpler hence the cost of production is low.

References

[1] Y. Dai, J. Van Spronsen, G.J. Witkamp, R. Verpoorte, Y.H. Choi, Ionic liquids and deep eutectic solvents in natural products research: mixtures of solids as extraction solvents, J. Nat. Prod. 76 (11) (2013) 2162–2173.
[2] K.S. Torimoto, T. Tsuda, K. Okazaki, New frontiers in materials science opened by ionic liquids, Adv. Mater. 22 (11) (2010) 1196–1221.
[3] N. Dörr, I. Gebeshuber, D. Holzer, H.D. Wanzenböck, A. Ecker, A. Pauschitz, F. Franek, Evaluation of ionic liquids as lubricants, J. Microeng. Nanoelectron. 1 (1) (2010) 29–34.
[4] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, Chem. Rev. 114 (21) (2014) 11060–11082.
[5] A. Abo-Hamad, M. Hayyan, M.A. AlSaadi, M.A. Hashim, Potential applications of deep eutectic solvents in nanotechnology, Chem. Eng. J. 273 (2015) 551–567.
[6] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. (Camb.) 1 (2003) 70–71.
[7] A.P. Abbott, E.I. Ahmed, R.C. Harris, K.S. Ryder, Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants, Green Chem. 16 (9) (2014) 4156.
[8] M. Kobayashi, T. Koide, S.-H. Hyon, Tribological characteristics of polyethylene glycol (PEG) as a lubricant for wear resistance of ultra-high-molecular-weight polyethylene (UHMWPE) in artificial knee join, J. Mech. Behav. Biomed. Mater. 38 (2014) 33–38.
[9] V.S. Protsenko, A.A. Kityk, D.A. Shaiderov, F.I. Danilov, Effect of water content on physicochemical properties and electrochemical behavior of ionic liquids containing

choline chloride, ethylene glycol and hydrated nickel chloride, J. Mol. Liq. 212 (2015) 716–722.
[10] S. Khandelwal, Y.K. Tailor, M. Kumar, Deep eutectic solvents (DESs) as eco-friendly and sustainable solvent/catalyst systems in organic transformations, J. Mol. Liq. 215 (2016) 345–386.
[11] E.A. Chernikova, L.M. Glukhov, V.G. Krasovskiy, L.M. Kustov, M.G. Vorobyeva, A.A. Koroteev, Ionic liquids as heat transfer fluids: comparison with known systems, possible applications, advantages and disadvantages, Russ. Chem. Rev. 84 (8) (2015) 875–890.
[12] M.E. Van Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochemistry of ionic liquid heat-transfer fluids, Thermochim. Acta 425 (1–2) (2005) 181–188.
[13] A. Hayyan, F.S. Mjalli, I.M. AlNashef, Y.M. Al-Wahaibi, T. Al-Wahaibi, M.A. Hashim, Glucose-based deep eutectic solvents: physical properties, J. Mol. Liq. 178 (2013) 137–141.
[14] A.P. Abbott, J.C. Barron, K.S. Ryder, D. Wilson, Eutectic-based ionic liquids with metal-containing anions and cations, Chem. Eur. J. 13 (22) (2007) 6495–6501.
[15] A.P. Abbott, R.C. Harris, K.S. Ryder, Application of hole theory to define ionic liquids by their transport properties, J. Phys. Chem. B 111 (18) (2007) 4910–4913.
[16] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev. 41 (2012) 7108–7146.
[17] H.Z. Wang, D. Qiao, S.W. Zhang, D.P. Feng, J.J. Lu, Tribological performance and lubrication mechanism of alkylimidazolium dialkyl phosphates ionic liquids as lubricants for Si_3N_4-Ti_3SiC_2 contacts, J. Nanomater. 2014 (2014) 8.
[18] M.K. Alomar, M. Hayyan, M.A. Alsaadi, S. Akib, A. Hayyan, M.A. Hashim, Glycerol-based deep eutectic solvents: physical properties, J. Mol. Liq. 15 (2016) 98–103.
[19] F.S. Mjalli, J. Naser, B. Jibril, S.S. Al-Hatmi, Z.S. Gano, Ionic liquids analogues based on potassium carbonate, Thermochim. Acta 575 (2014) 135–143.
[20] Y. Liu, Y. Chen, Y. Xing, Synthesis and characterization of novel ternary deep eutectic solvents, Chin. Chem. Lett. 25 (1) (2014) 104–106.