POTENTIAL APPLICATION OF DEEP EUTECTIC SOLVENTS IN HEAT TRANSFER APPLICATION

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Abstract

Glycol based conventional fluids are generally used as coolants and anti-freezing agents in industrial applications. Thus, this paper explores the possibility of utilizing DES as a heat transfer fluid due to their enhanced thermal stability compared to conventional fluids. Thermal conductivity of four types of DES comprising of methyl triphenyl-phosphonium-bromide (MTPB) and choline chloride (ChCl) as salts, and ethylene glycol (EG) and triethylene glycol (TEG) as the hydrogen bond donor (HBD), are measured from 25°C to 50°C using KD2 Pro thermal properties analyser. The obtained results show that the presence of salt lowers the thermal conductivity of the pure organic fluids. As the temperature increases, the thermal conductivity of the DESs increase compared to the thermal conductivity of pure organic solvents that does not change with temperaure. At higher temperature (50°C), the thermal conductivity decreased by 9.9% for MTPB:EG-DES, 5.4% for MTPB:TEG-DES and 5.4% for ChCl:EG-DESs. In addition to the thermal conductivity, the viscosity of the DES was also measured and found to be higher than the pure organic solvents. DES synthesized from MTPB salt shows higher viscosity as compared to ChCl due to higher hydrogen bonding between the salt and HBD. As the temperature increases, the viscosity of the DES converges closer to the viscosity of the pure organic fluids. Therefore, DES at high temperature will pose negligible increase in pumping power. With the addition of salt, the DES has lower freezing point compared to the pure EG and TEG due to the highly energetic hydrogen bonding.

Keywords: Deep eutectic solvents, Thermal conductivity, Glycol.

1. Introduction

Deep eutectic solvent (DES) (a type of ionic liquid - IL) is a mixture of two or more economic components that are formed by the hydrogen bond interactions resulting in an eutectic mixture [1, 2]. In general, DES is synthesized by incorporating organic halide salts and hydrogen bond donors (HBD) in a particular molar ratio. The particular molar ratio should allow the mixture to reach eutectic point [1, 2]; hence, DES. The molar ratio of the salts and HBD is dependent on the amount of HBD molecules required for each halide ion in the mixture [3]. For instance, the eutectic point of choline chloride (ChCl) and carboxylic acid is detected at the molar ratio of 1 mole ChCl and 2 moles carboxylic acids (which is equivalent to 67mol% of carboxylic acid). This indicates that two moles of acid are needed to develop complex with each mole of halide ion; in order to produce the eutectic mixture [4]. The discovery of DES as a substitute to ILs was introduced by Abbott et al. [5] with the production of the first generation DESs from quaternary ammonium salts and amines or carboxylic acids as the hydrogen bond donors [3, 5, 6]. The resulting DES exist in liquid phase at temperature below 100℃ due to the reduction in freezing point as a result of hydrogen bonds formation [2]. The conventional applications of DES are metal oxides dissolution [3,4], electro-polishing [7, 8], catalysis [9, 10], extraction [11-13] and electrodeposition [2].

Fang et al. [14] has reported application of DES (ammonium and phosphonium-based) as a base fluid with the dispersion of graphene nanoparticles. Results shows that the phosphonium-based DES has lower thermal conductivity at temperature below 50°C, but has higher thermal conductivity at 70°C compared to the pure organic fluid (up to 200%) [14]. This shows great potential of DES in high temperature application. In addition, it was also reported that the nanofluid synthesized from DES shows higher thermal enhancement compared to IL as base fluid in the graphene based nanofluid [14]. Due to limited literature of DES in the heat transfer field the following literatures reviewed will be on the ILs in the heat transfer field. Till date there are literatures available that studies DES as heat transfer fluid are almost non-existent [15]. However, since DES belongs to a class of ionic liquid; research done on ionic liquid can be used as reference to explore the potential of DES in heat transfer application. In the past few years, ionic liquids (ILs) have been researched as a viable replacement of the present working heat transfer fluid. In comparison to the conventional heat transfer fluid, ILs has wide liquid temperature range, high heat capacity, high density, high thermal and chemical stability, and low vapor pressure [16]. The application of silicon oil and diphenyloxide/biphenyl as working heat transfer fluid are limited by various disadvantages such as low density, high vapor pressure, low chemical stability, and low decomposition temperature [17].

Studies conducted by Valkenburg et al. [18] show ILs are able to overcome the various disadvantages of silicon oil and diphenyloxide/biphenyl, and serve as a more suitable working heat transfer fluid. In addition, it is reported that the sensible heat transfer of the ionic liquid is 2 to 3 times higher than the minimum heat transfer requirement [18]. Another study by He et al. [16] on the heat transfer performance of 1-hexyl-3-methylimidazolium tetrafluoroborate in microfin tubes has shown that the initial decomposition of the IL is 440.6°C which overcomes the low decomposition temperature of silicon oil and

diphenyloxide/biphenyl as working heat transfer fluid. This implies that the IL is suitable to be used in mid to high temperature applications. Additionally, from the study, thermal conductivity of the IL measured increased by 25% when temperature is increased from 30°C to 180°C. Fox et al. [19] investigated the thermal stability of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate by using thermogravimetric analysis (TGA). The result shows that the IL starts to decompose at the temperature of 200°C, which is a lot higher when compared to conventional heat transfer fluid such as water and ethylene glycol.

In the application of solar thermal application, Paul et al. [20] has investigated the potential of N-butyl-N,N,N-trimetylammoniumbis(trifluorme thylsulfonyl)imide and reported the thermal conductivity of IL to be lower than de-ionized water by 20% at room temperature. Additionally, it is also indicated that the thermal conductivity of the IL decreases with temperature which ultimately reduces the heat transfer coefficient of the IL in solar thermal application. In absorption heat transformer application, mixture of water and lithium bromide was used as the working heat transfer fluid. This is due to exceptional properties of the mixture such as non-toxic, non-flamable, and high latent heat [21]. However, the presence of corrosion inhibitors, low thermal stability, high volatility, high vapor pressure of water and the occurrence of crystallization in this mixture limited the use of absorption heat transformers to only air-conditioning applications [22]. Besides water and lithium bromide, ammonia and water, and 2,2,2-trifluoroethanol and tetraethylene glycol dimethyl ether are also some of the conventional working heat transfer fluid used in heat absorption [23, 24]. However, these working heat transfer fluids also poses impractical application due to the high vapor pressure of water and low system performance [22, 23]. Therefore, ILs can be used in this application to overcome the conventional constraint of organic working heat transfer fluid such as thermal instability and high volatility.

Hence, the objective of this paper is to explore the potential of DES (methyl triphenyl-phosphonium-bromide and choline chloride as halide salt and ethylene glycol and triethylene glycol as hydrogen bond donor) in the heat transfer application and as a replacement for conventional heat transfer fluid by measuring thermal conductivity, viscosity, and freezing point with respect to DES molar ratio and temperature. This would open up more research opportunity to the scientific community to work on DES for future application. The novelty of this research is the studies of DES in the field of heat transfer which can be used to overcome the limitation the conventional heat transfer such as high vapor pressure, low thermal stability, low chemical stability, oxidation, and corrosion [22, 23]. In addition, DES is an alternative to IL due to the fact that DES resemble various unique characteristics of IL such as viscosity, conductivity, and surface tension but offers less expensive cost, easier to synthesize and has higher green solvents aspect compare to IL [2].

2. Research Methodology

2.1. Materials

In this study, methyl triphenyl-phosphonium-bromide and choline chloride were selected as the salts while ethylene glycol and triethylene glycol were

used as HBDs. These chemicals are purchased from Merck, Malaysia with purity more than 99% and can be used directly for the synthesis of DESs without any further processing. Table 1 below shows the necessary physical information of the chemicals used in this research according to the MSDS.

Table 1. Materials used.

Chemicals	Abbreviation	Molecular Weight (kg/kmol)	Density (kg/m^3)
Methyl-triphenylphosphonium-bromide	MTPB	357.23	1200
Choline Chloride	ChCl	139.62	1100
Ethylene Glycol	EG	62.07	1110
Triethylene Glycol	TEG	150.17	1100

2.2. Synthesis of deep eutetic solvents

The DESs are prepared according to the molar ratio as shown in Table 2.

The mass of the halide salt and HBD is measured using electronic weight balance with a precision of 1mg. salt and HBD were transferred in universal laboratory bottle containing magnetic stirrer. The bottle is sealed with parafilm to prevent any contamination from atmospheric moisture which may interfere with the hydrogen bonding process of the DES synthesis. The mixture is then heated on hot plate stirrer (IKA C-MAG HS 7) at 120°C and 600 RPM continuously for three hours until a homogeneous and colorless liquid appeared [3].

Table 2. Molar ratio of synthesized DESs.

Salt	HBD	Molar Ratio (Salt : HBD)	Abbreviations
MTPB	EG	1:3	DES 1
		1:4	DES 2
		1:5	DES 3
	TEG	1:4	DES 4
		1:5	DES 5
ChCl	EG	1:3	DES 6
		1:4	DES 7
		1:5	DES 8
	TEG	1:3	DES 9
		1:4	DES 10
		1:5	DES 11

2.3. Thermophysical properties

This section reports the methodology used in the thermal conductivity, viscosity and freezing point depression studies. Thermal conductivity and viscosity

measurements are carried out at 25°C, 40°C 50°C. The temperature was limited to 50°C because unwanted convection starts to occur above 50°C, which results in high error to the thermal conductivity measurement [25, 26]. To be consistent, the viscosity was also measured at the same temperature values.

2.3.1. Thermal conductivity

The thermal conductivity was measured using the KD2 Pro thermal properties analyzer (Decagon Devices, Pullman WA, USA) with an accuracy of ± 5% and measuring range up to 2 W/m.K. In this study, the thermal conductivity of the DESs was measured using a single 6 cm long in a 25 mL vial to ensure 80% of the needle is immersed into the sample. In order to measure the thermal conductivity at different temperature, the nanofluids were placed in a thermal jacket which is connected to a circulating thermostat bath (BL-720D). Silicon oil is used to fill the thermal jacket in which the DES samples were placed. In addition, the measurements were carried outside a non-operating fume hood to isolate the sample from the influence of the ambient temperature fluctuation and external vibration that causes forced convection in the sample. Before any measurements were taken, the needle was calibrated using standard glycerine at 20°C. The measurement of thermal conductivity was recorded at an interval of 15 minutes until 5 stable measurements were recorded and the average thermal conductivity was calculated. Graphs of thermal conductivity against temperature for different DES were plotted. The percentage of thermal enhancement was calculated using the following equation [27]:

$$Thermal\ Enhancement\ (\%) = \frac{k_{DES} - k_{base\ fluid}}{k_{base\ fluid}} \times 100\% \tag{1}$$

2.3.2. Viscosity

The dynamic viscosity was measured using rheometer (Model AR2000 Rheometer, TA Instruments) with standard double gap concentric cylinders geometry (System MK2 992291) at $1000s^{-1}$ shear rate. The rheometer was operated using air pump with 30Psi air pressure and water pump with the set temperature. The geometry was mapped via precise method, recalibrated for the new geometry inertia and reset the datum via zero gap activation for every viscosity measurement to ensure the accuracy of the measurement. Approximate 11.65mL of sample was injected into the concentric cylinder. After each viscosity measurement, the geometry was uninstalled from the rheometer and cleaned thoroughly with acetone and distilled water.

2.3.3. Freezing point

Freezing point of DES was measured using the differential scanning calorimeter (Model DSC-60 Plus, Shimadzu) with a temperature measuring range of -140°C to 600°C. The weight of the sample was recorded beforehand and approximate 5mg of sample was placed in an aluminium pan. The aluminium pan was then sealed with a crimper. Empty pan was used as a reference material. Both the sample pan and reference pan were placed inside the furnace. First, the samples were cooled down to -120°C using liquid nitrogen. Then, the samples were heated at a rate of 5°C/min to 25°C and purged with argon gas at 150mL/min.

3. Results and Discussion

3.1. Thermal Conductivity

It was observed that MTPB:EG-DESs exhibited negative enhancement (approximate 20%) in thermal conductivity when compared to pure EG. In Fig. 1, the thermal conductivity of the DESs corresponds to the amount of salt (MTPB). With decreasing salt content in the DES, thermal conductivity of the MTPB:EG-DES increased as a result of reduction in the general mobility and the amount of effective charge carriers due to aggregation of ions which causes the DES to have higher thermal conductivity [28]. This is also because the salt generally has lower thermal conductivity. At 25°C, MTPB:EG-DES shows negative thermal conductivity enhancement (DES 1: -20.5%, DES 2: -16.9%, DES 3: -13.2%). However, as the temperature increases to 50°C, the thermal conductivity of the DESs increase and reduces the negative thermal conductivity enhancement (DES 1: -15.2%, DES 2: -14.3%, DES 3: -9.9%). Overall, thermal conductivity of MTPB:EG-DES decreases by approximate 9.9% to 20.5% at the temperature range of 25°C to 50°C. This results is consistent with the finding on phosphonium-based DES from the studies conducted by Fang Y.K et al. (2016) which shows lower thermal conductivity at temperature below 50°C [14]. Similar results were observed for MTPB:TEG-DESs as shown in Fig. 2. The thermal conductivity increased with the decrease in salt content. On other hand, pure organic solvents such as EG shows constant thermal conductivity (0.211W/m.K) with increasing temperature as shown in Figs. 1 and 3 [29]. Similarly, pure TEG also has a constant thermal conductivity with increasing temperature [30].

MTPB:TEG-DES shows negative thermal conductivity enhancement of 20.2% (DES 4) and 9.7% (DES 5) over the pure TEG at room temperature (25°C). However, MTPB:TEG-DES makes up for the loss in thermal conductivity enhancement at higher temperature (50°C) and reduces the negative thermal conductivity enhancement to 5.4% higher thermal conductivity in DES 5. In DES 4, higher salt content is likely to inhibit any recovery of loss in thermal conductivity as TEG forms more hydrogen bonding with MTPB.
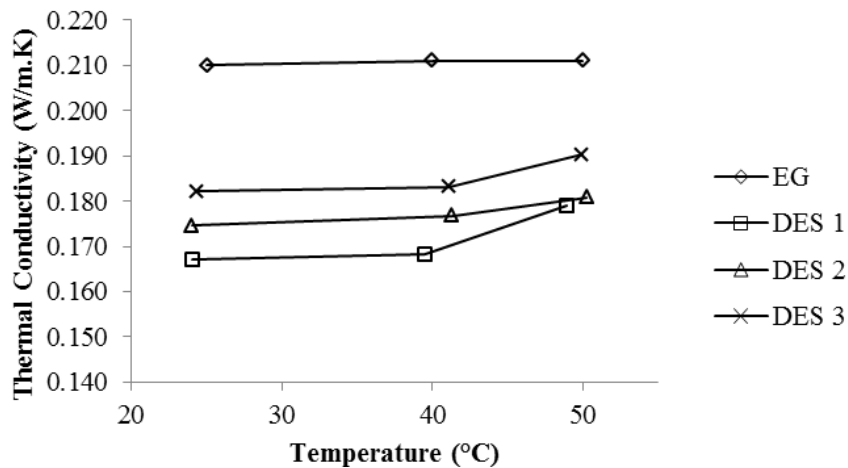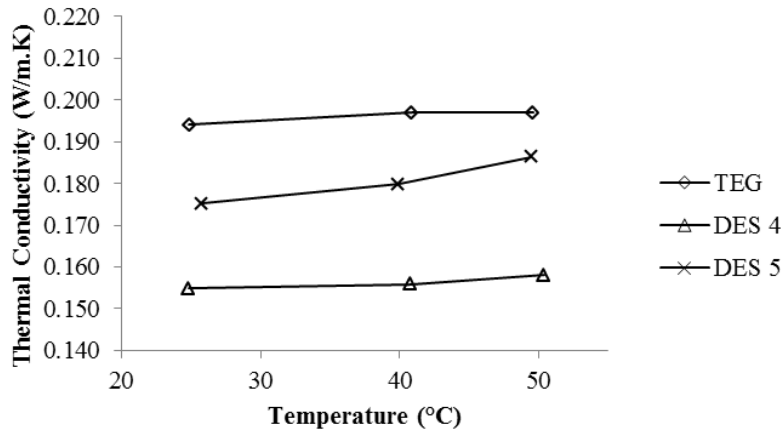

Fig. 1. Thermal conductivity of MTPB: EG with respect to temperature.

Fig. 2. Thermal conductivity of MTPB:TEG with respect to temperature.

As for ChCl:EG-DESs, thermal conductivity measurement shows relatively lower decrement in thermal conductivity (approximately 5.4% to 7.6%) when the temperature rises from 25°C to 50°C as shown in Fig. 3. Similarly with the pure EG, ChCl:EG-DES shows constant thermal conductivity with increasing temperature [31]. This is most likely due to the small difference in molecular weight between the ChCl (139.62 g/mol) and EG (62.07 g/mol) as compared to MTPB (357.23 g/mol) and EG. The big difference in the molecular weight caused the thermal conductivity behaviour of the DESs to behave different as the hydrogen bonding and interaction between the HBD and salt decreases [32]. This explains the increasing the amount of ChCl salt which leads to higher negative thermal conductivity enhancement of the resulting DES. In term of thermal conductivity enhancement, ChCl:EG-DES does not show a lot of negative thermal conductivity enhancement (DES 6: -7.6%, DES 7: -6.7%, DES 8:-5.4%).

ChCl:TEG-DESs shows even smaller negative thermal conductivity enhancement (approximately 1.3% to 4.5%) when the temperature rises from 25°C to 50°C as shown in Fig. 4. As explain in the earlier paragraph, this is most likely due to the higher molecular weight of TEG (150.17 g/mol) which eventually leads to smaller mass of salt was added to synthesized the DES with similar molar ratio as compared to ChCl:EG-DESs. As observed in the previous three DESs mixture, lower salt content ultimately reduces the negative thermal conductivity enhancement, which is consistent with the observation of the ChCl:TEG-DESs results. ChCl:EG-DES does not show a lot of negative thermal conductivity enhancement (DES 9: -7.6%, DES 10: -6.7%, DES 11:-5.4%). In general, the thermal conductivity of the resulting DES is most likely due to the influence due to the nature of the anion or halide salt [33]. This suggests that different halide salt in DES will cause the DES to behave differently in thermal conductivity. This also explains the degree of thermal conductivity reduction in DES with MTPB as halide salt and ChCl as halide salt, in which MTPB-DESs show higher thermal conductivity reduction whereas ChCl-DESs show lower thermal conductivity reduction.
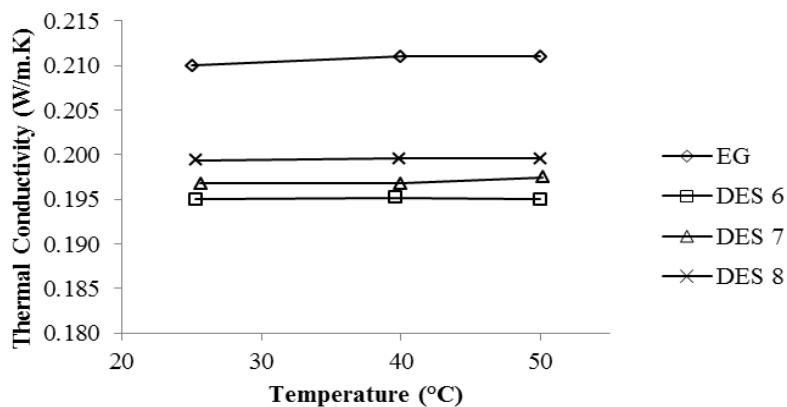
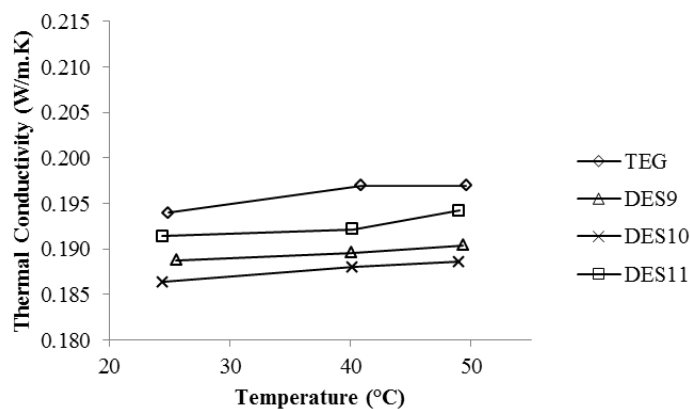**Fig. 3. Thermal conductivity of ChCl:EG with respect to temperature.**

Fig. 4. Thermal conductivity of ChCl:TEG with respect to temperature.

3.2. Viscosity

Viscosity of the DES is a crucial property that is required for heat transfer as it would affect the required pumping power to circulate the DES. Shown in Fig. 5 to Fig. 8, higher temperature reduces the viscosity of the DES which indicates that the DES follows the Arrhenius behaviour [4]. This trend is in a good agreement with the reported trend in literature [32]. This decreasing viscosity trend is due to higher intermolecular forces at higher temperature and it is observed that the DES mixture begins to converge into the viscosity of the pure HBD.

It is also observed that most of the DES has viscosity higher than 25cP at room temperature which is higher than the pure organic solvents, EG and TEG. This is because the extensive and complex hydrogen bonding between the salt and HBD causes the DES to be less mobile and have higher viscosity [2, 15, 32]. The increment in viscosity is highly due to the chemical nature of its component such as the molar ratio, type of halide salt and the HBD [4]. This explains, for every DES variation, the increased in viscosity with decreasing molar ratio (1:5 to 1:3). This is also in agreement with the results obtained in literature that shows higher viscosity for lower molar ratio [4, 32, 34].

DES synthesized from the MTPB salt has higher viscosity compared to the DES synthesized from ChCl salt. This is because the DES synthesized from MTPB salt requires more salt to achieve the desired molar ratio whereas DES synthesized from ChCl salt requires lesser salt at the similar molar ratio. This is generally generates more extensive hydrogen bonding between the halide salt and HBD which leads to higher viscosity [32].
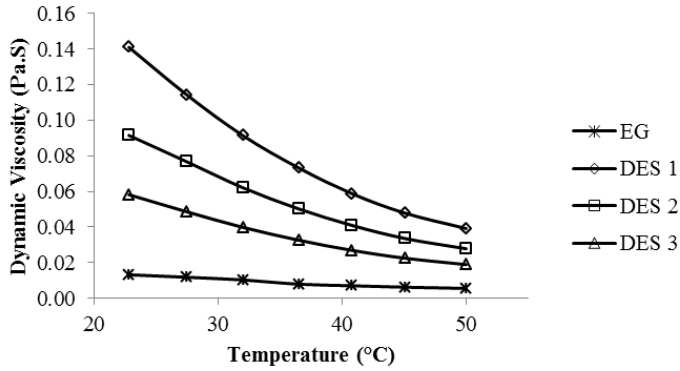
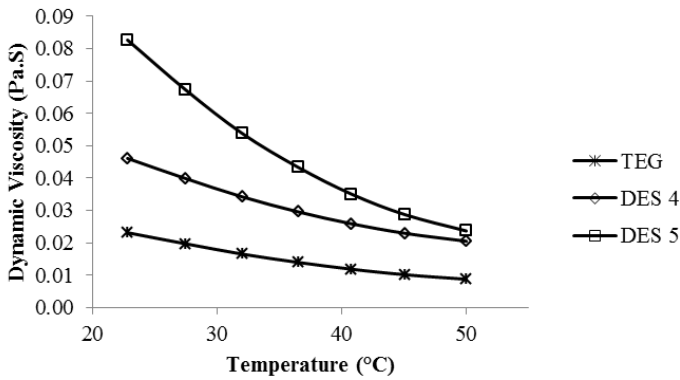**Fig. 5. Viscosity of MTPB:EG with respect to temperature.**

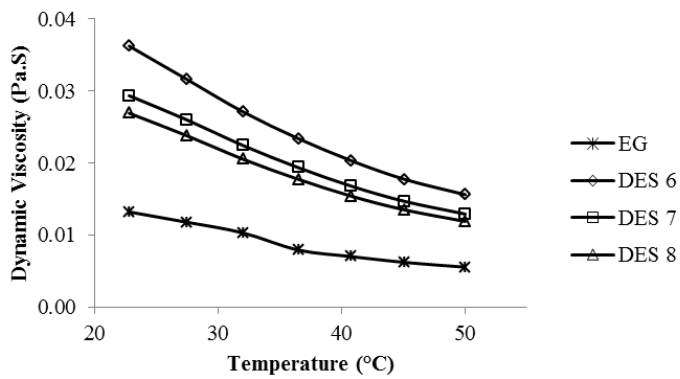**Fig. 6. Viscosity of MTPB:TEG with respect to temperature.**

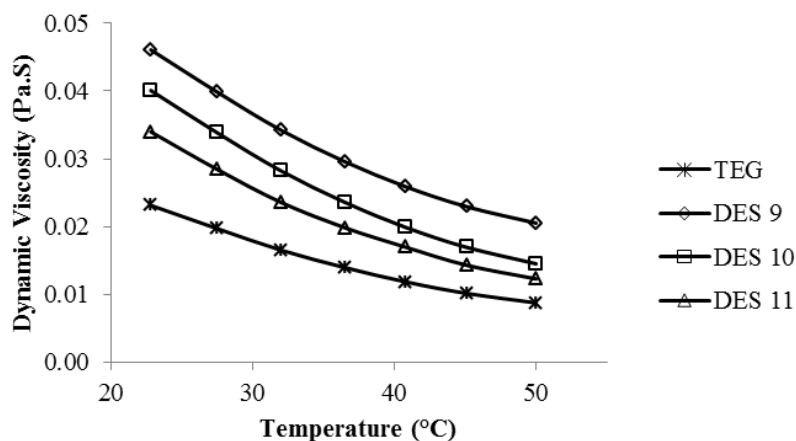**Fig. 7. Viscosity of ChCl:EG with respect to temperature.**

Fig. 8. Viscosity of ChCl:TEG with respect to temperature.

3.3. Freezing point

The formation of liquid DES from solid halide salt is a result of freezing point depression due to the highly energetic hydrogen bonding between the halide salt and HBD in comparison to the lattice energies of the pure components [35]. This explains the lower freezing point of the DES shown in Table 3 in comparison to the pure EG (-12.9°C) and pure TEG (-7°C).

With low freezing point, DES becomes an attractive fluid as cheap and safe solvents in various fields. The freezing point depressed further with increasing molar ratio (1:3 to 1:5) as shown in Table 2. This is because the halide salt has higher freezing point, MTPB is 234°C and ChCl is 302°C [32]. Therefore, when lower amount of halide salt is present in the DES mixture, the freezing point will depressed further. This trend is consistent with the finding available in literature for similar halide salt and HBD combination [36-38].

Table 3. Freezing of the synthesized DESs.

DES	Ratio of HBD to one molar of salt	Freezing point (°C)
1	3	-46.25
2	4	-48.55
3	5	-49.34
4	4	-18.85
5	5	-21.55
6	3	-115.51
7	4	-116.68
8	5	-117.71
9	3	-87.00
10	4	-87.99
11	5	-89.29

4. Conclusions

This study attempted to measure the important physical property (thermal conductivity, viscosity and freezing point) of DES to explore its potential in heat transfer application. The thermal conductivity measurement was limited to below 50°C as unwanted natural convection starts to occur within the sample. In this study, all the synthesized DESs showed negative thermal conductivity enhancement over the pure organic fluids. However, at higher temperature (50°C), the negative thermal conductivity enhancement reduces. In addition, DES with molar ratio of 1:5 shows the least negative thermal conductivity enhancement (9.9% for MTPB:EG and 5.4% for MTPB:TEG at 50°C). When the type of salt is changed from MTPB to ChCl, the overall negative thermal conductivity enhancement reduces (from approximate 20% to 7%). The synthesized DES also shows higher viscosity compared to the pure organic fluids at lower temperature, and decreases with increasing temperature which slowly converges to the viscosity of the pure organic solvent. Lower salt concentration (molar ratio 1:5) would give lower negative thermal enhancement and lower viscosity increment; therefore, molar ratio 1:5 was recommended to synthesize DES for heat transfer application. Addition of the halide salt depressed the DES freezing point, and the freezing point was further depressed with higher molar ratio. This makes DES with high molar ratio a promising heat transfer fluid. As the type of salt influences the thermal enhancement, more detailed work is required to further measure the other thermo-physical properties of such DESs with different halide salt. Besides that, some future studies on the usage of nanoparticles such as carbon nanotube to enhance the thermal conductivity of the DESs will be conducted.

Acknowledgement

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