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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Studying Two Series of Ternary Deep Eutectic Solvents (Choline Chloride–Urea–Glycerol) and (Choline Chloride–Malic Acid–Glycerol), Synthesis and Characterizations

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Abstract Deep eutectic solvents are a recent class of solvents that started to get attention to replace the ionic liquids and, of course, the traditional organic solvents. In this work, two series mixtures of choline chloride–urea–glycerol and choline chloride–malic acid–glycerol, liquids at room temperature, were synthesized in different molar ratios and their properties were studied. Electrochemical characterization test was performed using Pt/C catalyst and the results showed an interesting electrochemical stability for choline chloride–urea–glycerol mixture within the potential range of −1 to 1 V. The viscosity was reported as a function of temperature for mixtures which behaved as Newtonian fluids and as a function of shear rate for those which behaved as non-Newtonian fluids. For instance, 1–1–1 choline chloride–urea–glycerol viscosity was decreased from 706.8 to 26.9 cP when the temperature was increased from 20 to 80 °C, respectively. While for the same mixture at 10 °C, it was decreased from 30,933 to 3948 cP by increasing the shear rate from 0.03 to 0.38 S^{-1}, respectively. Thermogravimetric analysis, differential scanning calorimeter and density measurements were all reported in detail in this paper.

Keywords Deep eutectic solvent · Choline chloride · Non-Newtonian · Viscosity · Cyclic voltammetry and shear rate

1 Introduction

Deep eutectic solvents (DESs) can be defined as mixtures of two components: One of them is a hydrogen bond donor (HBD) and the other is a hydrogen bond accepter (HBA) [1,2]. The HBA is usually an ammonium or phosphonium salt that react with the HBD, by the hydrogen bond interaction, to form a mixture that possess lower melting point than its raw materials [3]. In general, the DESs are liquids at temperatures below 100 °C, containing a group of them liquids at room temperature [4–6]. Deep eutectic solvents have the advantages of being good solvents with low flammability, almost no vapor pressure, environmentally friendly, wide thermal and electrical windows, water tolerant, biodegradable, inexpensive, easy to make and benign [7,8]. Those advantages have increased the opportunity for studying DESs to be used in different applications [3]. In 2003, Abbott et al. reported that by mixing choline chloride (ChCl) and urea, their melting points are 302 and 133 °C with a 1–2 molar ratios, respectively, and the product was a eutectic solvent with a melting point of 12 °C [9]. Since then, many efforts were contributed to study the DESs [3].

After the success that the DESs achieved to be good candidates for many applications, studying their physical and chemical properties became extremely important [10]. Choline chloride, urea, glycerol and malic acid, the materials which were selected for this work, are safe, inexpensive and non-toxic [2]. ChCl–urea and ChCl–glycerol binary mixtures are very common DESs that were investigated

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by many researchers [5,9–17]. Malic acid was reported as a HBD that participated with different HBAs, including choline chloride. It was found that mixing 1.2–1, 1–1, 1–1.2 molar ratios of ChCl and malic acid, respectively, leaded to form liquid phase DESs at room temperature. While the ratios of 1–2 or 21 produced solid products [7,18]. Therefore, selecting the components ratios is effecting the product and its properties. In addition, the need of a third component which helps in forming lower melting point DES is obvious.

The hydrogen bonding is the key for DESs forming, in which HBD and HBA react and the specious charge delocates [3]. The H bonding is very unique comparing with other bonding types. H bonding can have different bonding forces and lengths depending on the ambient conditions for the same component. For instance, the H bond in water can be many times stronger when the PH increases or decreases, but they would be shorter. This behavior gave a wide range of products even when the same raw materials were used [19].

Ternary deep eutectic solvents (TDESs) have been reported in order to increase the DESs range toward their applications [20]. One hot topic where TDESs were applied at was CO_2 capturing. Leonhard et al. reported the use of three carbon dioxide capturing materials that formed TDESs mixtures with choline chloride and glycerol [21]. On the other hand, Dai et al. synthesized TDESs using natural materials, which were plant's primary metabolites materials [22]. These contribution studies made a clear evidence that the DESs have great flexibility in forms, synthesis and applications.

In this paper, two TDESs mixtures of choline chloride–urea–glycerol with molar ratios of (1–1.5–1.5, 1–2–2, 1–0.5–1.5, 1–1–1), respectively, and choline chloride–malic acid–glycerol with molar ratios of (1–0.5–1.5, 1–1.5–0.5, 1–1–1, 1–1–2, 1–2–1), respectively, were synthesized and studied. Cyclic voltammetry (CV), viscosity, thermogravimetric analysis (TGA), differential scanning calorimeter (DSC) and density characterizations were reported. However, those characterizations were selected because of their importance in engineering applications, such as pumping system, electrochemistry, stirring and thermal limits. Electrochemical stability was studied over Pt/C catalyst at room temperature for mixtures of 1–1–1 molar ratio. Viscosity was studied as a function of temperature for Newtonian fluids, while studied as a function of shear rate for non-Newtonian fluids at constant temperature. A range of temperatures,10 to 80 °C, was applied to investigate the viscosity change for the same mixture. TGA technique was used to study mixtures' degradation as a function of temperature. DSC was used to measure the melting points, glass transition temperatures, and crystallization temperatures. Finally, density was studied as a function of molar ratio for both mixtures.

2 Experimental Methodology

2.1 Materials

Choline chloride (ChCl) >99% was purchased from Chem-Impex Intel Inc., USA. Urea (99.4%), and glycerol (99.5%) were obtained from Fisher Scientific Company, USA. Malic acid (99+ %) was obtained from Sigma-Aldrich. The commercial Pt/C catalyst (19.7% Pt over Vulcan XC-72ETEK) was supplied by De Nora, North America. Ultrapure deionized water type 1 (DI) water Direct-Q-3UV was used for all experiments.

2.2 TDESs Preparation

TDESs samples were prepared in different molar ratios of choline chloride–urea–glycerol of 1–1.5–1.5, 1–2–2, 1–0.5–1.5 and 1–1–1, respectively, and choline chloride–malic acid–glycerol with molar ratios of 1–0.5–1.5, 1–1.5–0.5, 1–1–1, 1–1–2 and 1–2–1, respectively. The pure choline chloride was dried at 65 °C under vacuum for 24 h as a pretreatment to remove any possible moisture and stored in a dry place for further use. TDESs mixtures were synthesized under atmospheric pressure, by mixing choline chloride, urea and glycerol, and choline chloride, malic acid and glycerol at 80 °C in different molar ratios [20,21]. These mixtures were stirred under heating until homogeneous colorless liquids formed. DES samples were dried at 80 °C under vacuum overnight in order to eliminate any moisture before characterizations.

2.3 Characterizations

2.3.1 Electrochemical Characterization

The electrochemical test, cyclic voltammetry (CV), occurred at room temperature using electrochemical workstation model CHI651E. Two selected ternary mixtures (choline chloride–urea–glycerol 1–1–1 and choline chloride–malic acid–glycerol 1–1–1 molar ratios) were examined in three electrode cell with 0.196 cm^2 glassy carbon electrode (GC) as a working electrode. Ag/AgCl was used as a reference electrode and a platinum wire was used as a counter electrode [23,24]. A GC electrode was polished first with alumina slurry with size of 1 µm and then ultrasonically washed by DI water. The experiments performed using Pt/C catalyst within the potential range of −1 to 1 V for both mixtures. The ink of the catalyst was prepared by ultrasonically dispersion of 1 mg Pt/C catalyst in 1 ml ethanol for one hour. 10 µl of this ink was pasted on the polished GC electrode and left for drying. Later, 10 µl of 0.05% Nafion solution was dropped and left to dry on the catalyst to bind it with the electrode surface, and then, the samples were examined.

2.3.2 Viscosity

The viscosity of the present prepared TDESs mixtures was measured using Brook Field DV O Ultra Program Rheometer cone/plate with attached spindle #42 [21]. Viscosity was studied as a function of temperature for Newtonian fluids and as a function of shear rate for non-Newtonian fluids. In this test, 1 ml of each sample was placed individually in the viscometer cone and the viscosity was measured at different rotating speeds with range of temperatures 10 to 80 °C. The temperature was controlled by using external water bath circulator type of ISOTEMP. All viscosity measurements were taken at atmospheric pressure condition.

2.3.3 Thermogravimetric Analysis (TGA)

TDESs thermal stability and the thermal decomposition temperatures were examined using thermogravimetric analyzer device model Q500 from TA Instruments-Waters LLC. The samples were placed individually in platinum pan as a sample holder under nitrogen atmosphere flow rate of 40 ml min^{-1}. All samples were heated form 10 to 600 °C with heating rate increasing of 10 °C/min [20].

2.3.4 Differential Scanning Calorimeter (DSC)

Phase transition temperatures, including freezing point (Tm), glass transition temperature (Tg), crystallization temperature and heat flow rates(mW) were measured using differential scanning calorimeter DSC [20] model Q20 from TA Instruments-Waters LLC. All measurements are taken by placing 10 mg of the sample in an aluminum hermetic pan. The pan and sample were first cooled to temperature about −80 °C with liquid nitrogen and then heated to 100 °C at a rate of 10 °C/min. The heat flow rate was examined as a function of time and temperature with a reference nitrogen flow rate of 40 ml/min.

2.3.5 Density

The densities of the presented systems were measured by manual weighing using a glass density meter (2-ml glass tube Gay-Lussac method) at room temperature. To avoid measurement errors, the densities were measured three times and the averages were taken for each sample. In this measurement, the glass vial weight was taken when it was empty and filled with the liquid, then the weight difference divided by the glass vial volume will be equal to the density [9].

3 Results and Discussion

3.1 Cyclic Voltammetry (CV)

The cyclic voltammetry for 1–1–1 choline chloride–glycerol–urea mixture showed interesting electrochemical stability toward oxidation and reduction reactions, within the potential range of −1 to 1 V as shown in Fig. 1. This DES is a highly electrical conductive solvent confirming that the ionic species can move independently. In liquid phase, the high viscosity is recommending this DES as a good electrolyte [23]. It was noted that the mixture is stable in the anodic bath and started to slightly oxidize at potentials higher than 600 mV and reached its maximum current density (0.1 mA cm^{-2}) at a potential of 1000 mV. This mixture showed an important stability in the cathodic bath as well and started to reduce at potentials lower than −600 mV and reached its maximum reduction current −0.1 mA cm^{-2} at a potential of

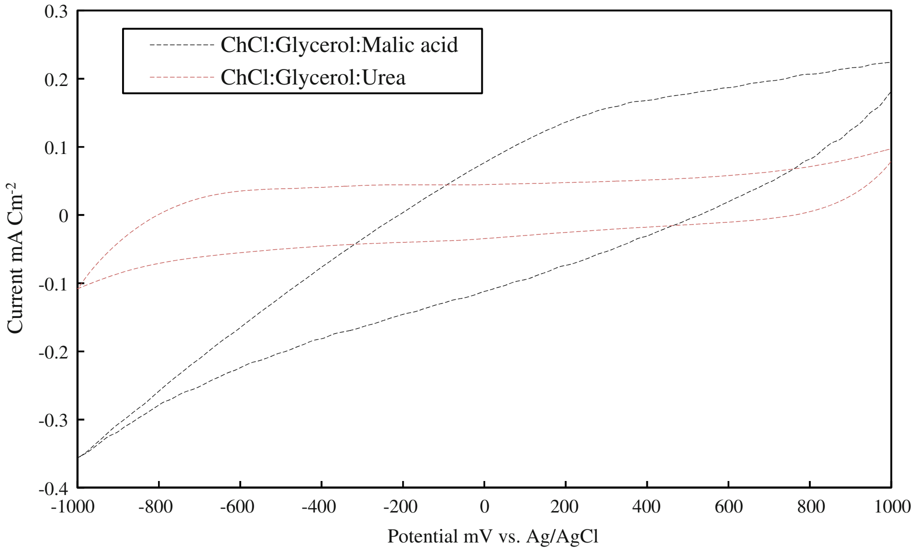


Fig. 1 Cyclic voltammetry for two DESs (ChCl–glycerol–malic acid (1–1–1) and ChCl–glycerol–urea (1–1–1)) over Pt/C catalyst at scan rate of 50 mV s^{-1}

−1000 mV. The window of urea mixture is narrower than malic acid mixture and the current is very low, which could be attributed to chlorine gas evolution. CV for 1–1–1 choline chloride–malic acid–glycerol mixture showed more sensitivity toward oxidation and reduction reactions. It was noted that the current density for this mixture was higher and the potential window was larger, the mixture oxidized and reduced continuously and reached its maximum oxidation and reduction current densities at 0.22 and −0.35 mA cm^{-2}, respectively. The reason for this situation could be that malic acid is highly sensitive toward the oxidation and reduction reactions within the potential range of −1 to 1 V, which showed lower electrochemical stability than the other mixture. Within the potential range of −600 to 600 mV, no peaks were observed which implies no electroactive impurities. By extending the potential limits to either more positive or negative, a very tiny irreversible reduction and oxidation peaks were observed prior to maximum current increase. These peaks are attributed to the reduction of water traces and its effect on the glycerol's oxidation mechanism [25].

3.2 Viscosity

Viscosity is a temperature- and mole ratio-dependent property. It is important to establish a viscosity database due to the direct relation of this physical property in fluid flow calculations and equipments design. By finding such data at the design stage, the DES mixture can be formed to achieve lower viscosity value. Moreover, by knowing the temperature effect on viscosity, the required energy for processing these fluids can be reduced [25]. Generally, ILs have exponentially diminishing viscosity–temperature profiles [26]. Figures 2 and 3 show the viscosity as a function of temperature and mole ratio for choline chloride–urea–glycerol and choline chloride–malic acid–glycerol mixtures, respectively. It is clear to note that the viscosity decreased with temperature increasing for both mixtures; this effect is due to the higher mobility of the ions. The decrease in the internal resistance of the molecules causes an easy movement of the molecules to flow with less viscosity [27] according to Arrhenius equation. From Fig. 2, it can be seen that the viscosity decreased by increasing urea and glycerol percentages. The higher molar amount of HBDs in the DES mixture, the lower viscosity values. But this effect decreased at high HBD compositions. Urea has a higher effect on viscosity than glycerol due to higher viscosity of urea system and the amide type, which leads to form self-hydrogen bonds between HBD and chloride ion [28]. Comparing these findings to the viscosity of pure components (urea and glycerol) at different temperatures [29], it gave similar pattern of variation. The viscosity started to be almost the same at 30 °C and above for all ratios. For the mixture of 1–1–1 choline chloride–urea–glycerol, it was hard to measure the viscosity at low temperature since the mixture behaved as non-Newtonian fluid. Thereby, it was necessary to study the viscosity as a function of shear rate at the same temperature. Section 3.2.1 is illustrating this non-Newtonian behavior. Figure 3 shows that the viscosity of choline chloride–malic acid–glycerol mixture is highly depends on malic acid ratios. Whenever malic acid percentage increased, the viscosity increased due to the higher viscosity of malic acid. In general, the acidity of ionic liquids is managed by the strength of the cation, anion or both [30]. The viscosity of DESs is influenced by two factors, the salt to hydrogen bond donor interaction and their ability for coordinating [27]. As was mentioned above, the non-Newtonian behavior was associated with most of choline chloride–malic acid–glycerol mixtures but at high temperatures. This behavior is not common and was studied in detail and reported in Sect. 3.2.1 for 1–1–1 ChCl–malic acid–glycerol mixture. In addition, the same behavior was

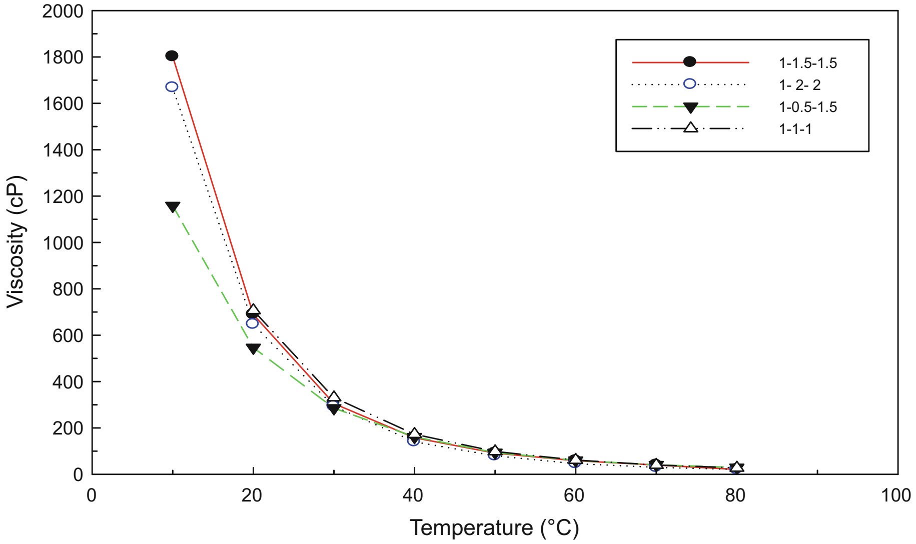


Fig. 2 Viscosity as a function of temperature for choline chloride–urea–glycerol mixture at different mole ratios

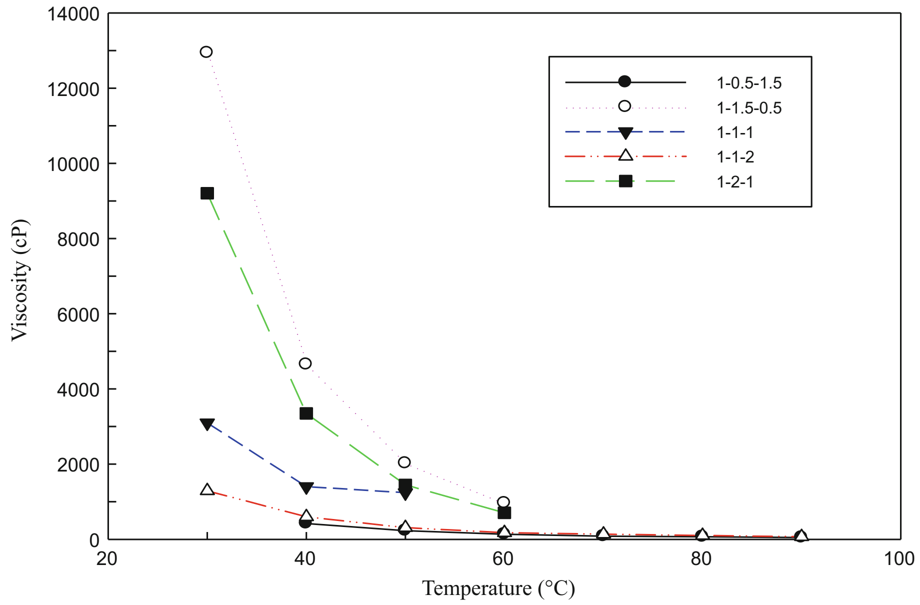


Fig. 3 Viscosity as a function of temperature for choline chloride–malic acid–glycerol mixture at different mole ratios

observed for 1–0.5–1.5 choline chloride–malic acid–glycerol at 30 °C.

3.2.1 Shear Rate

Viscosity can be defined as the ratio of shear stress and shear rate ($\boldsymbol{\eta} = \boldsymbol{\sigma}/\boldsymbol{\gamma}$) where η is the apparent viscosity Pa s, σ is the shear stress Pa and γ is shear rate s^{-1}. The shear rate is the velocity gradient within the flowing liquid. The effect of shear rate on viscosity or shear stress points out whether the fluid is Newtonian or non-Newtonian. Liquids were classified as Newtonian if the relation above was linear otherwise non-Newtonian [31,32]. Figure 4 shows the shear rate effect started from 0.01 to 0.4 S^{-1} on viscosity for 1:1:1 choline chloride–urea–glycerol mixture. The non-Newtonian behavior appeared only at low temperatures at 10 and 15 °C due to higher viscosity of the mixture at low temperature. It was observed that whenever the shear rate increased, the viscosity decreased. In non-Newtonian fluid, the shear stress is not directly proportional to the deformation rate. So that, the shear stress/strain rate relation is not linear and the viscosity changed with the shear rate. Typically, the viscosity decreases at high shear rates; this phenomenon is known as shear thinning [33].

For 1–1–1 choline chloride–malic acid–glycerol mixture, non-Newtonian behavior is illustrated in Fig. 5. The shear rate effect appeared at shear rates of 0.5 and 12 S^{-1} at high temperatures 60, 70, 80 and 90 °C. This surprising result could be attributed to the solubility lack of acids in glycerol and glycerol-based DESs. At high temperatures, glycerol could react with malic acid to form some kinds of esters, such as monoester or diesters, which increased the mixture's viscosity and effected the shear rate. Abbott et al. reported that lauric acid can form monoester or diester at high temperature in glycerol-based DES mixture [13]. Figure 6 presents the viscosity as a function of shear rate started from 0.3 to 1.6 S^{-1} for 1–0.5–1.5 choline chloride–malic acid–glycerol at 30 °C.

Figures 7 and 8 show the relations between natural logarithm of viscosity and temperature are inverse for both mixtures at different mole ratios. From these two figures, the linear regression and activation energy can be calculated depending on Arrhenius equation, which describes the relation between viscosity and temperature:

$$\ln(V) = \ln(V_o) + \frac{E_v}{RT} \tag{1}$$

where V_o is a constant, R is the universal gas constant, T is the temperature in (K) and E_v is the activation energy. These figures show that most of the data obey this equation except 1–1–1 choline chloride–malic acid–glycerol mixture, which has non-Newtonian behavior. Table 1 lists the activation energy, intercept and linear regression values for all molar ratios. It is shown from the table that the activation energy increased with the urea and glycerol mole ratios for choline chloride–urea–glycerol, while it was increased with malic acid mole ratio for choline chloride–malic acid–glycerol mixture.

3.3 Thermogravimetric Analysis

Thermal stability results for both mixtures at different molar ratios are presented in Figs. 9 and 10. The thermal decomposition onset was defined by 10% weight loss and the thermal decomposition temperatures are listed in

Fig. 4 Viscosity as a function of shear rate for choline chloride–urea–glycerol mixture (1–1–1) mole ratio at 10 and 15 °C

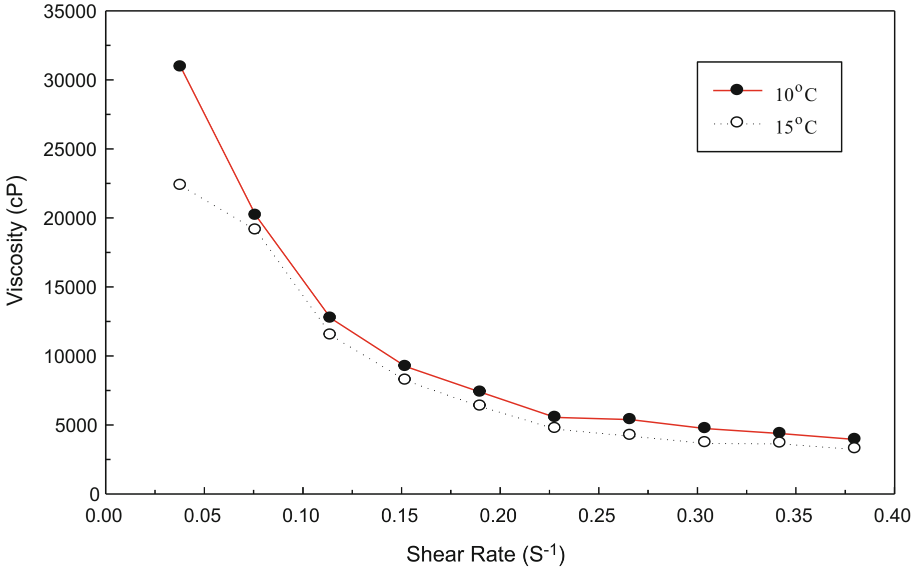


Fig. 5 Viscosity as a function of shear rate for choline chloride–malic acid–glycerol (1–1–1) mole ratio mixture at different temperatures

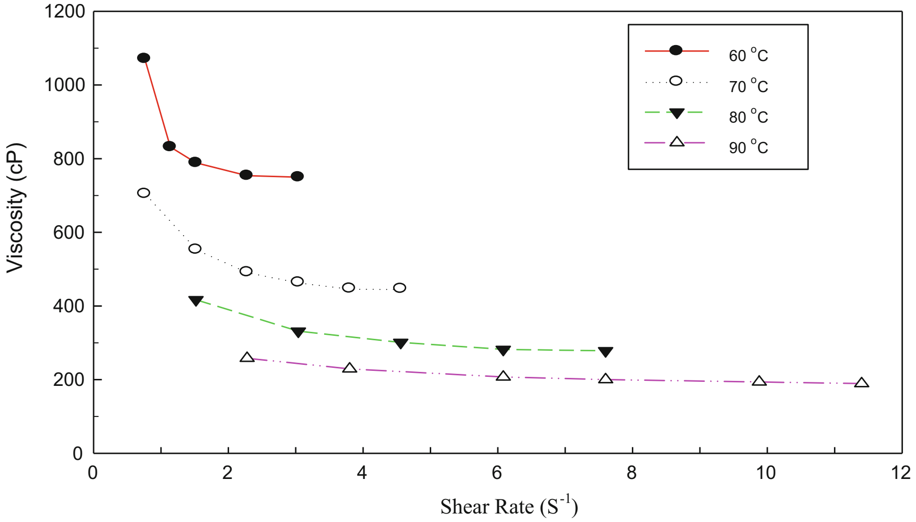


Fig. 6 Viscosity as a function of shear rate for choline chloride–malic acid–glycerol (1–0.5–1.5) mole ratio mixture at 30 °C

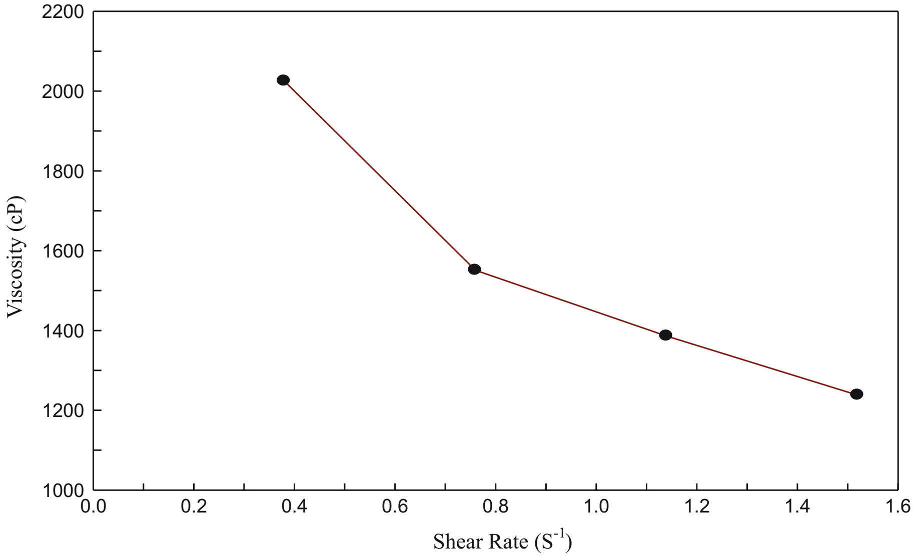


Fig. 7 ln(v) versus 1/T for choline chloride–urea–glycerol mixture at different mole ratios

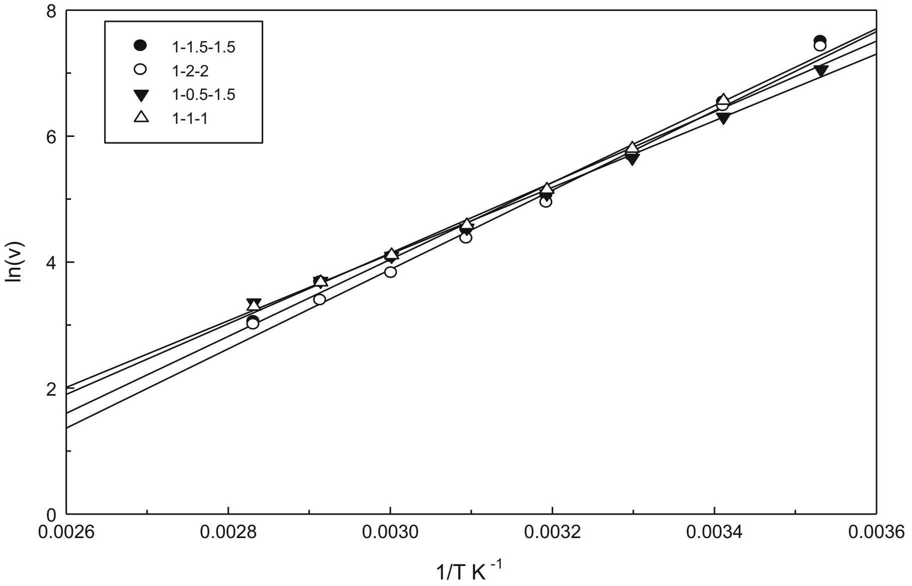


Fig. 8 ln(v) versus 1/T for choline chloride–malic acid–glycerol mixture at different mole ratios

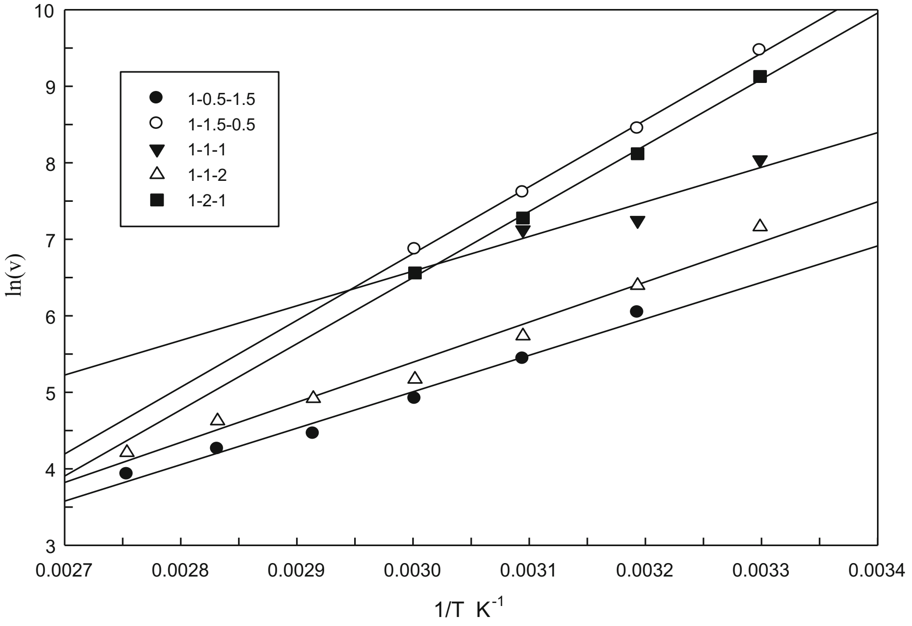


Table 1 Activation energy for both mixtures at different mole ratios

Mixture	$\ln V_0$	Ea (kJ mol^{-1})	r^2
1ChCl–1urea–1glycerol	−12.689	46,643.892	0.995
1ChCl–1.5urea–1.5glycerol	−14.271	50,748.015	0.992
1ChCl–2urea–2glycerol	−15.009	52,350.639	0.993
1ChCl–0.5urea–1.5glycerol	−11.749	43,999.026	0.996
1ChCl–0.5malic acid–1.5glycerol	−9.289	39,616.176	0.982
1ChCl–1.5malic acid–0.5glycerol	−19.386	72,608.198	0.998
1ChCl–1malic acid–1glycerol	−6.997	37,632.614	0.863
1ChCl–1malic acid–2glycerol	−10.330	43,573.981	0.978
1ChCl–2malic acid–1glycerol	−19.432	71,862.724	0.998

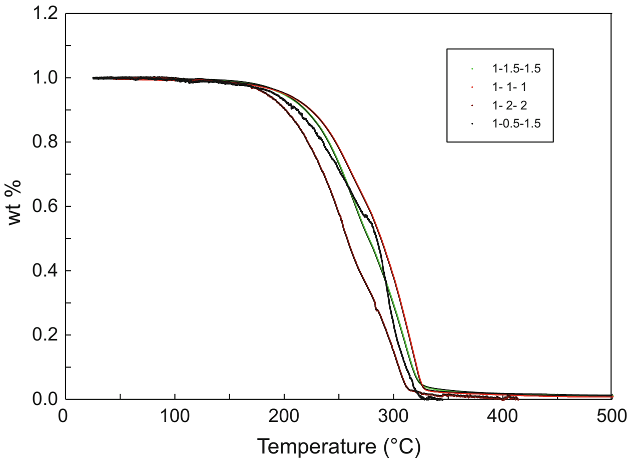


Fig. 9 TGA plot for choline chloride–urea–glycerol mixture at different mole ratios

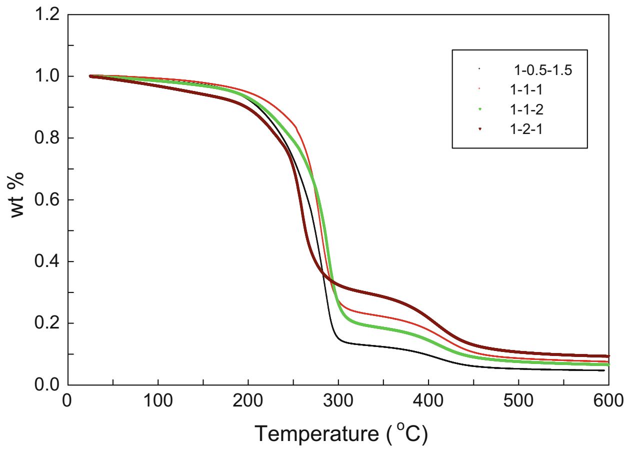


Fig. 10 TGA plot for choline chloride–malic acid–glycerol mixture at different mole ratios

Table 2 Thermal properties of ternary DES from TGA and DSC

DES	Decomposition temperature (°C)	Glass transition temperature (°C)
1ChCl–1urea–1glycerol	224	–
1ChCl–1.5urea–1.5glycerol	219	–
1ChCl–0.5urea–1.5glycerol	212	–
1ChCl–2urea–2glycerol	200	–
1ChCl–1malic acid–1glycerol	226	–
1ChCl–1malic acid–2glycerol	214	–
1ChCl–0.5malic acid–1.5glycerol	209	−54
1ChCl–2malic acid–1glycerol	192	−52

Table 2. The order of thermal decomposition temperatures for choline chloride–urea–glycerol was [1–1–1] (224 °C) > [1–1.5–1.5] (219 °C) > [1–0.5–1.5] (212 °C) > [1–2–2] (200 °C), while for chloride–malic acid–glycerol was [1–1–1] (226 °C) > [1–1–2] (214 °C) > [1–0.5–1.5] (209 °C) > [1–2–1] (192 °C). The results indicated that the highest thermal stability appeared when the molar ratios were equal for both mixtures, and it decreased by changing the molar ratio. It can be seen that the thermal decomposition temperatures are very close to each other, which means the thermal stability for both mixtures is close to each other. It can be observed that the thermal decomposition occurred in one stage for choline chloride–urea–glycerol, while in two stages for chloride–malic acid–glycerol. The second stage of the decomposition could be attributed to the polymers formation, such as monoester and diester due to the reaction between glycerol and malic acid [13]. Temperature of thermal decomposition indicates the stability of the mixtures. The increase in thermal decomposition temperatures could be related to the coordinating nature of the ions and intermolecular interaction [34]. In these stages, the components were converted to gases leaving a black material as a residue. It was very difficult to study choline chloride–malic acid–glycerol (1–1.5–0.5) due to the high amount of malic acid. These acids are lacking solubility in glycerol; therefore, the ratio of glycerol has to be higher than malic acid ratio [13]. The presented results demonstrated that the change in mole ratio played an important role to determine the thermal stability for ternary DES.

3.4 Differential Scanning Calorimeter (DSC)

DSC was used to determine the phase transition temperatures, including melting point (T_m), glass transition temperature (T_g) and crystallization temperature. The glass transition temperatures of 1–0.5–1.5 and 1–2–1 choline chloride–malic acid–glycerol mixture exhibited at −54 and −52 °C, respectively. The glass transition temperatures might be formed due to the long-chain network bonded between atoms or due to the complex molecular structure formation, which has high viscosity. This behavior is consistent with the glassy materials, that goes through glass transition temperature, but not melt and crystallize upon heating [20]. Based on the results presented in Figs. 11 and 12, it was not possible to observe melting points and crystallization temperatures for all mixtures. Essentially, the melting temperature happens at crystalline region, whereas the glass transition temperature occurs at amorphous region. Based on the literature, it was reported that no glass transition temperature for ChCl and urea DESs [34].

3.5 Density

The density test results are listed in Table 3. The densities increased by the HBDs increasing. This could be attributed to the strength of hydrogen bonds between the molecules [22].

Fig. 11 DSC results plot for choline chloride–urea–glycerol mixture at different mole ratios

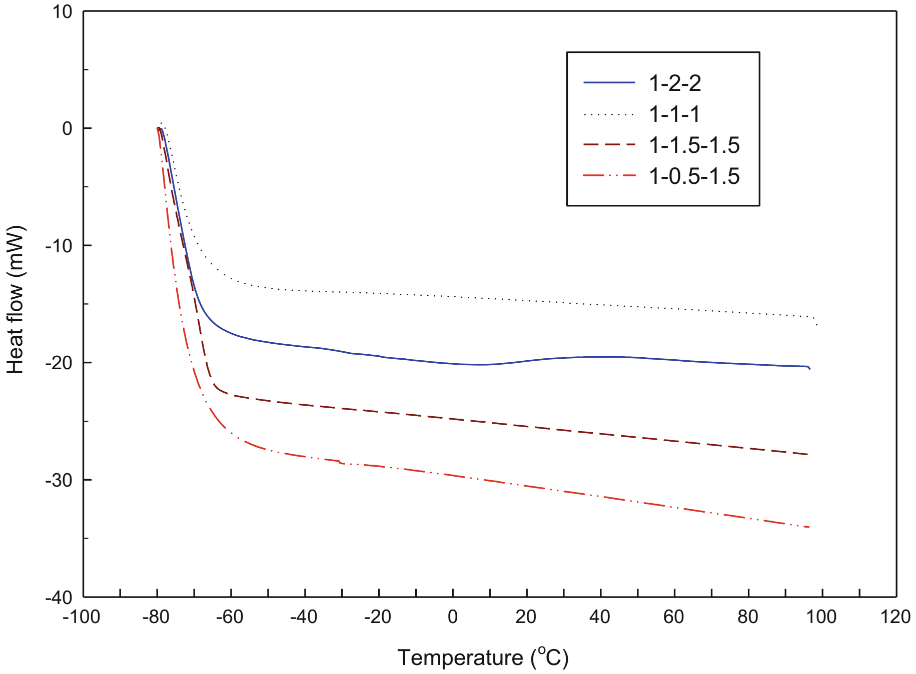
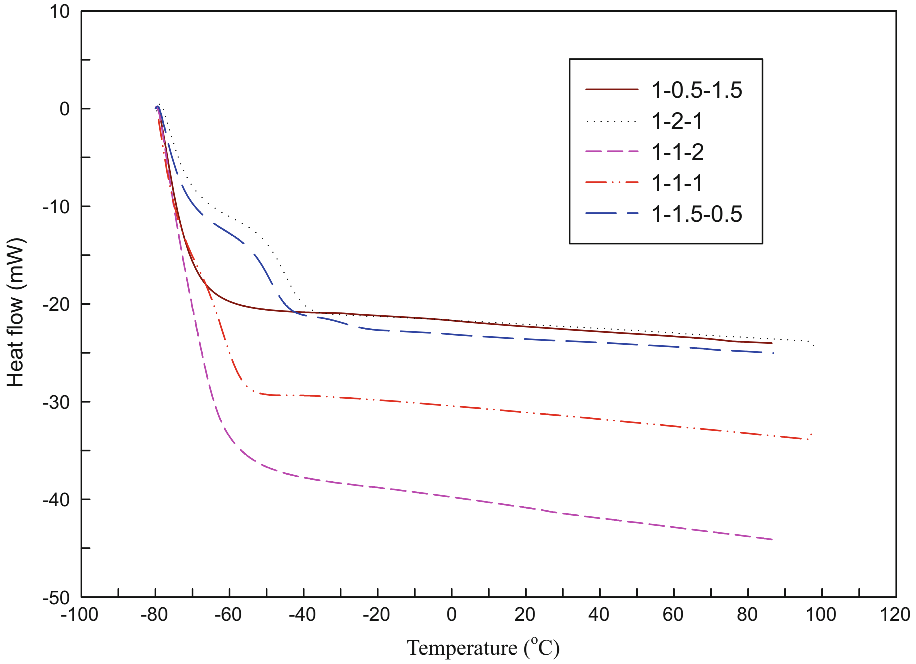


Fig. 12 DSC results plot for choline chloride–malic acid–glycerol mixture at different mole ratios



Apart from that, malic acid has higher effect on density than other materials (urea and glycerol) due to the higher density of malic acid ($1.6\,\mathrm{g\,cm^{-3}}$).

4 Conclusion

Cyclic voltammetry, viscosity, TGA, DSC and density were investigated for two ternary deep eutectic solvent mixtures (choline chloride–urea–glycerol and choline chloride–malic acid–glycerol). The results have indicated different properties for both mixtures. Choline chloride–urea–glycerol mixture has a higher electrochemical stability than the other mixture over Pt/C catalyst. Choline chloride–urea–glycerol mixture behaved as a Newtonian liquid at low temperatures (10 and 15 °C) for all molar ratios except at the equal one, where it behaved as a non-Newtonian liquid. Choline chloride–malic acid–glycerol mixture behaved as a Newtonian liquid at ≥30 °C for all ratios except the equal molar ratio at 60, 70, 80 and 90 °C, in which it behaved as a non-

Table 3 Ternary DES densities

Mixture	Choline chloride–urea–glycerol				Choline chloride–malic acid–glycerol				
Mole ratio	1–2–2	1–1.5–1.5	1–1–1	1–0.5–1.5	1–1–1	1–2–1	1–1–2	1–0.5–1.5	1–1.5–0.5
Density (g/ml)	1.246	1.183	1.160	1.148	1.254	1.263	1.184	1.148	1.279

Newtonian liquid. The thermogravimetric analysis showed that the thermal stability depended on the molar ratio for both ternary mixtures. DSC results showed the glass transition temperature only for choline chloride–malic acid–glycerol at two mole ratios. Density results indicated that the density depends on mole ratio for both mixtures. The most important property that reported in this work is the non-Newtonian behavior of those mixtures. Choline chloride–urea–glycerol mixtures seem to be less viscous than choline chloride–malic acid–glycerol mixtures.

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