

## Characteristics and intermolecular interaction of eutectic binary mixtures: Reline and Glyceline

Farouq Sabri Mjalli<sup>†</sup> and Omar Umar Ahmed

Petroleum and Chemical Engineering Department, Sultan Qaboos University, Oman

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**Abstract**—Deep Eutectic Solvents are promising greener and cheaper alternatives to ionic liquids. The applications involving these solvents depend largely on their physical and chemical properties. However, a DES may possess both desirable and undesirable properties for a certain application. In such situations, mixing two DESs, each possessing a unique set of properties, may yield one with a more suitable set of physical and chemical properties for the same application. In this work, the variation in the physical properties of Reline upon addition of Glyceline was investigated. While a positive deviation of excess molar volume was observed, a negative deviation of viscosity was recorded with the increase in Glyceline mol% indicating a disruption of the ordered structure of Reline. The highest deviation in both cases was observed at 30 mol% Glyceline. The physical properties measured were density, viscosity, pH, RI and conductivity. The Glyceline molar percentage studied was 0 to 100 mol% while temperature was varied within the range of 20 °C to 80 °C.

Keywords: Mixture, Eutectic, Reline, Glyceline, Molar Volume, Ionic Liquids

### INTRODUCTION

Investigation into the properties of deep eutectic solvents (DES) is a growing research area. Not only do they possess the potential for application in a variety of fields [1-4], but they are easily synthesized, cheap and to a large extent green. DESs have been systematically categorized into four types by Abbott and co-workers [5]. Type I DESs are synthesized by the combination of a quaternary salt of a heteroatom with a metal halide, while Type II DESs are synthesized by mixing a quaternary salt of a heteroatom with hydrated metal halide. Mixing the quaternary salt of a heteroatom or metal halide with hydrogen bond donor to form liquids generates Type III or Type IV DESs, respectively.

The huge interest in studying the properties of DESs stems from the fact that there is a huge variety of these DESs and each has a unique set of physical and chemical properties. In certain cases, DES possessing, to a great extent, the right set of properties for an application in a particular field can be formulated. For instance, Glyceline (1 choline chloride: 2 glycerol) containing 3% (v/v) water was successfully used along with cross-linked subtilisin for transesterification of N-acetyl-L-phenylalanine ethyl ester using 1-propanol. Glyceline was preferred as compared to Reline (1 choline chloride: 2 Urea) because of its relatively low viscosity and that the glycerol component is less denaturant than urea for proteases [6].

In other cases, a DES may possess almost all the right properties except a few that can be adequately replaced by another DES with similar properties. It has been shown that in presence of lyophilized *Candida antarctica* lipase B (CLAB), Reline aids in the con-

version (>90%) of ethyl valerate to butyl valerate. The yield of butyl valerate at 60 °C was obtained as 99%. Employing Glyceline, the yield obtained was 96%. Although Reline is slightly more efficient, Glyceline is less viscous than Reline and therefore more suitable [7].

However, many cases exist where the performance of the DES depends strongly on its constituents. For instance, Reline has a potential application in surface cleaning and metallurgy due to its ability to dissolve metals and metal oxides [8]. The active material in this study was urea, which in its neutral or anionic form binds with the surface of the metal/metal oxide and thereby enhances the dissolution of the metal [9]. Likewise, the ability of Reline to catalyze the electrophilic substitution of 1-aminoanthra-9-10-quinone derivatives in the presence of bromine was suspected to be due to the basic nature of the DES together with the ability of urea to stabilize transition state [8,10]. In the ionothermal synthesis of materials such as aluminophosphates, the chemical composition of the DES influences the structure of the synthesized material [10]. Application of Reline as the reaction medium for the ionothermal synthesis of  $[Zn(O_3)PCH_2CO_2] \cdot NH_4$  structure indicates an *in situ* generation of  $NH_4^+$  by partial decomposition of urea. The formed  $NH_4^+$  aids in the formation of the targeted material [11]. Although the presence of urea is required in the aforementioned applications, Reline does not possess certain physical properties (such as viscosity) suitable for the same applications. We thereby may seek the synthesis of a DES that contains the component required for certain application while possessing the physical properties suitable for such application. As applied to the aforementioned literature, we seek a DES that contains urea which is required for certain application while possessing a low viscosity similar to that of Glyceline while not significantly altering its performance.

One way this can be done is by mixing two or more DESs that

<sup>†</sup>To whom correspondence should be addressed.

E-mail: farouqsm@yahoo.com

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have the different properties suitable for a particular application. Mixing Reline and Glyceline, for example, allows one to retain an active material (urea) and at the same time lower the viscosity of the resulting solvent. How these physical properties are affected upon mixing is dependent on the strength and type of the intermolecular attraction between the components of the mixture. Upon mixing two DESs, a series of physical bond formation and breakage is expected with a consequent rearrangement of molecules and packing. This results in varying of the physical properties of the mixture such as density as compared to the pure DESs, respectively. The extent of this variation can be evaluated by using the excess thermodynamic properties. The excess thermodynamic properties of liquids mixtures are related to the intermolecular interactions between the constituents of the mixture. Excess thermodynamic properties have been successfully employed in evaluating the variation in properties of ionic liquid (IL) mixtures [12,13], aqueous mixtures of ILs and mixtures of molecular solvents with IL [14-16]. Studies of variations in physical properties using excess properties have also been carried out on aqueous mixture of DESs [17-20]. However, extensive studies on the variation of the intermolecular forces and thus physical properties of a DES upon mixing using excess thermodynamic properties have not been carried out.

The aim of this work is to study the physical properties of Reline-Glyceline mixtures and characterize their variation from the pure DESs using the excess thermodynamic properties.

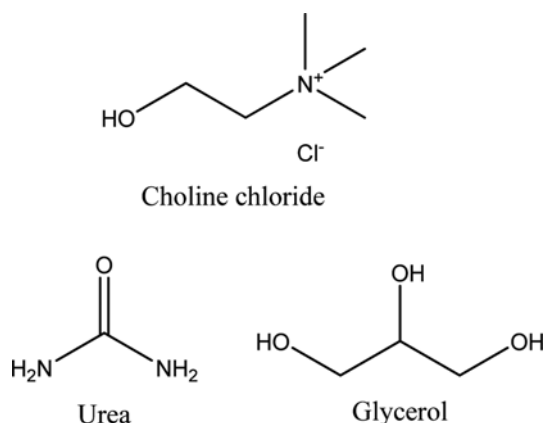
## EXPERIMENTAL METHODS

### 1. Chemicals

Choline chloride (ChCl), glycerol and urea (>98%) were supplied by Merck Chemicals (Darmstadt, Germany). Scheme 1 shows the chemical structure of the chemicals used in this work. It was ensured that DESs prepared contain low moisture level by drying the chemicals in an oven for at least 3 hours prior to use.

### 2. DES Preparation

Reline and Glyceline were prepared by mixing choline chloride (ChCl) with urea and glycerol, respectively. The syntheses were carried out in an incubator shaker (Brunswick Scientific Model INNOVA 40R). The chemicals were mixed at a mixing rate of 400rpm and temperature of 80 °C for 2 hours or until a homogeneous trans-



Scheme 1. Chemical structure of the DES components.

parent liquid was formed. The incubator shaker was operated at atmospheric pressure under tight control of moisture. The molar ratio of ChCl to either urea or glycerol was maintained at 1 : 2. DES mixtures were synthesized by adding Glyceline to Reline to make up the following: 0, 10, 30, 50, 70 100 mol% Glyceline. The prepared mixtures were stored in air-tight vials prior to physical property measurement.

### 3. Physical Property Measurement

The physical properties of interest in this work include melting point, density/molar volume, viscosity, refractive index, pH and conductivity. Excluding melting point, the measurements of physical properties were carried out in the temperature range of 20 °C–80 °C as follows.

Anton Paar DMA4500M and Anton PaarRheolabQc, each equipped with Techne-Tempette TE-8A external water-circulator for controlling temperature, were used for the measurement of density and viscosity, respectively. The standard uncertainty in the measurements of density was determined as 0.0001 g/cm<sup>3</sup>, while 5% was determined for the viscosity measurement. The refractive indices of the DESs and their mixtures were measured using Bellingham and Stanley Abbe refractometer (model 60/ED) equipped with a sodium D1 line. Before each measurement, deionized water was used for calibration and the standard uncertainty in the measurement was determined as 0.001. Jenway conductivity meter (model 4520) was used for determining the conductivity of DES/mixture, while the thermo Scientific 3 star pH Bench top meter equipped with Julabo Labortechnik water circulator for temperature control was used for measuring the pH of the synthesized DES/mixture. The pH meter was calibrated with the aid of standard pH buffers. TA-Q20 differential scanning calorimeter (DSC) equipped with an auto-sampler was used for measurement of the melting point of the synthesized DES/mixture. The standard uncertainties of the measurement of conductivity, pH and melting point were 5 μS/cm, 0.05 and 0.01°C, respectively.

## RESULTS AND DISCUSSION

### 1. Melting Point

The melting points of some of the DES mixture were determined as 10.12 °C, –2.85 °C and –1.82 °C for the mol% Glyceline of 10%, 70% and 90%, respectively. However, melting points of 30 and 50 mol% Glyceline were not detected. In general, the detected melting points indicate that as Glyceline is added, the melting point decreases to a certain minimum. Pure Reline has a melting point of 12 °C, while there is no apparent melting point for Glyceline [21]. At a mixture molar composition of 70% Glyceline, the amount of melting point decrease reaches 14.85 °C. This indicates that the intermolecular forces existing between the Reline constituent molecules are affected as more Glyceline is added to the mixture. This interaction is so complicated that within the different tested mixture molar ratios, some showed clear melting points while others did not. The urea and glycerol hydrogen bond donors (HBD) interactions disturb the hydrogen bonding between the DES salt and HBD molecules. This effect is demonstrated in its extreme at DESs molar ratios away from the pure DESs. These interactions can be studied using molecular level simulations to determine the h-bonding

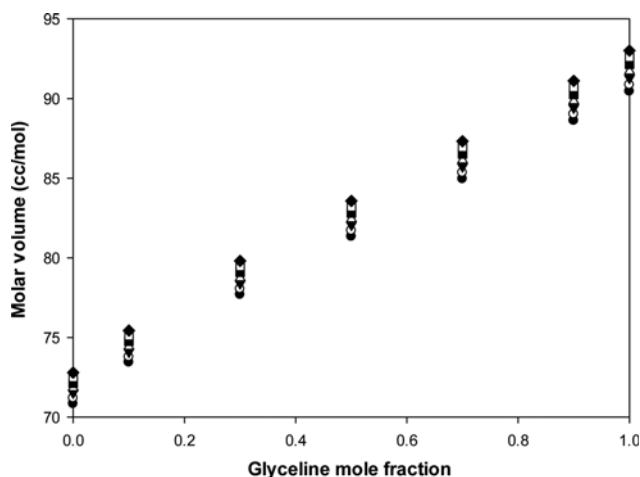


Fig. 1. Plot of molar volume as a function of Glyceline mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

strength between the choline chloride and the two HBDs.

## 2. Molar Volume

The molar volume of Reline-Glyceline mixture was studied and presented in Fig. 1. Pure Reline has a molar volume of  $70.83 \text{ cm}^3/\text{mol}$ , while pure Glyceline has a molar volume of  $90.44 \text{ cm}^3/\text{mol}$  at  $20^\circ\text{C}$ . The lower molar volume of pure Reline suggests a more compact structure and a more extensive hydrogen bond network as compared to pure Glyceline [8]. This is supported by the fact that the freezing point depression of Reline ( $121^\circ\text{C}$ ) with respect to urea is greater than that of Glyceline ( $57^\circ\text{C}$ ) with respect to glycerol. Therefore, upon addition of Glyceline to make up 10 mol%, the strong hydrogen bond interaction between  $\text{ChCl}:\text{urea}$  is expected to be weakened in order to accommodate more  $\text{ChCl}$  and glycerol. Since the hydrogen bond length is dependent on the strength of the hydrogen bond (HB) interaction between the components of the DES [22], a weakened or distorted HB network will consequently lead to larger molar volume. In agreement with the discussion above, the molar volume of the mixture increased by  $2.62 \text{ cm}^3/\text{mol}$  with respect to pure Reline. In fact, an increase in the molar volume with respect to pure Reline by  $2.57\text{--}2.64 \text{ cm}^3/\text{mol}$  was observed throughout the temperature range considered. The opposite effect was observed when Reline was added to pure Glyceline to make up 10 mol% (90 mol% Glyceline). In this case, the molar volume decreased by  $1.84\text{--}1.90 \text{ cm}^3/\text{mol}$  for all measured temperatures. Similarly, HB breakage and formation upon addition of Reline results in lower volume. This is largely due to the ability of urea to form stronger HB network with the available  $\text{ChCl}$  molecules leading to shorter bond length with a slightly more compact molecular arrangement.

Fig. 1 also shows that the molar volume of the pure DES and their mixtures increases with increase in temperature. For pure Reline, the molar volume increased by  $1.97 \text{ cm}^3/\text{mol}$  from  $70.8 \text{ cm}^3/\text{mol}$  at  $20^\circ\text{C}$  to  $72.80 \text{ cm}^3/\text{mol}$  at  $80^\circ\text{C}$ . For pure Glyceline, molar volume increased by  $2.56 \text{ cm}^3/\text{mol}$  from  $90.44 \text{ cm}^3/\text{mol}$  at  $20^\circ\text{C}$  to  $93.01$  at  $80^\circ\text{C}$ . This increase in the molar volume of the mixtures with temperature appears to be dependent on the concentration of

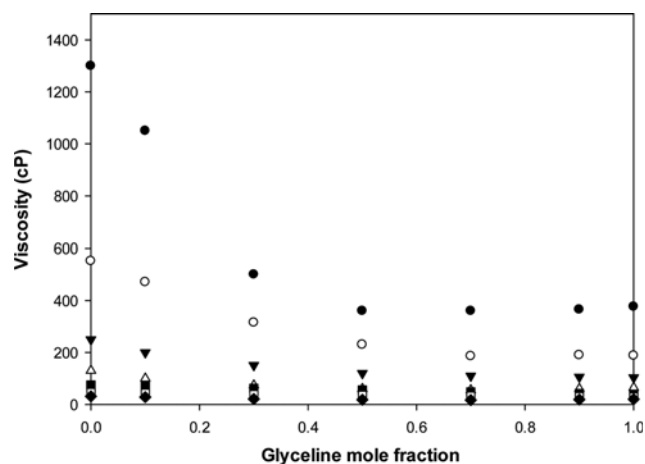


Fig. 2. Plot of viscosity as a function of Glyceline mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

the Glyceline in the mixture as follows: 1.99, 2.11, 2.24, 2.36 and  $2.50 \text{ cm}^3/\text{mol}$  for 10, 30, 50, 70 and 90 mol%, respectively. The observed increase in molar volume with temperature can be assumed to be as a result of the change in the kinetic energy of the molecules with temperature. As temperature is increased, the molecules possess more kinetic energy, which weakens the HB strength. The weakened HB strength translates into increased bond length and consequently larger molar volume.

## 3. Viscosity

The viscosity of the pure Reline decreased significantly with increase in concentration of Glyceline in the mixture up to a mol% of about 30. When the concentration of the Glyceline was about 30 mol% and above, the viscosity values of the mixture only marginally decreased and were similar to those of pure Glyceline (Fig. 2). The implication of this is that as Glyceline is added to pure Reline, the physical bond breakage and formation leads to comparatively weaker interactions between the constituent molecules. The less rigid hydrogen bond network allows for more mobility of the molecules and thereby the apparent reduction in viscosity. Upon addition of Glyceline beyond 30 mol%, no further distortion of hydrogen bond network takes place as the rigidity of the whole network becomes similar to that of pure Glyceline. At  $20^\circ\text{C}$ , the viscosity of DES mixture decreased from  $1,300 \text{ cP}$  (pure Reline) to  $1,050 \text{ cP}$  (10 mol% Glyceline). This decreased to  $500 \text{ cP}$  upon addition of more Glyceline (30 mol%). The viscosity further decreased to a value of  $376 \text{ cP}$  (100 mol% Glyceline). Adding Glyceline (90 mol%) to pure Reline results in reduction of viscosity by  $935 \text{ cP}$ ,  $362 \text{ cP}$ ,  $144 \text{ cP}$ ,  $70 \text{ cP}$ ,  $33 \text{ cP}$ ,  $16 \text{ cP}$  and  $12 \text{ cP}$  at  $20^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $60^\circ\text{C}$ ,  $70^\circ\text{C}$ , and  $80^\circ\text{C}$  respectively.

The effect of the increase in concentration of Glyceline is more pronounced at lower temperature. This is because at high temperature, the effect of temperature on the viscosity of the DESs/mixture outweighs the effect of the individual DES component. The viscosity also decreases with temperature. This can be attributed to the corresponding increase in internal energy of the constituent's molecule with temperature. This will result in weakening interac-

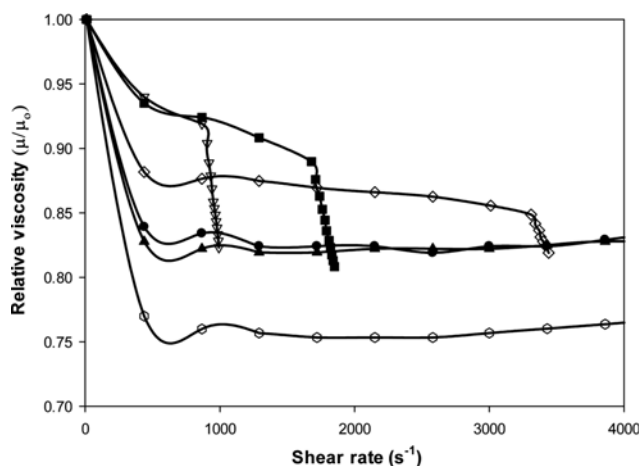


Fig. 3. Viscosity variation for the (1 : 1 molar ratio) Reline:Glyceline mixture as a function of shear rate at different temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

tions and increase in mobility of the constituents and thereby reduction in viscosity.

Next, the effect of shear rate on the viscosity of the two DES mixtures was investigated. The behavior of viscosity under shear rates within the range of 0–4,000 s<sup>-1</sup> indicates similar rheological properties of these DES mixtures at different compositions and temperatures. Fig. 3 shows the relative variation in the viscosity of the DES mixtures at different shear rates ( $\mu$ ) to the viscosity of the mixture at the minimum shear rate tested ( $\mu_0$ ). It is noticed that high temperature increases the mobility of the two DES molecules, increasing its fluidity and exhibiting a stable Newtonian-like fluid behavior. On the other hand, as the temperature is reduced, the molecular mobility is reduced and consequently viscosity increases. At conditions close to the room conditions, there exists clear reduction in the viscosity as a function of shear rate, which indicates some shear thinning behavior. This variation in liquid behavior as a function of shear rate indicates the sensitivity of the viscosity of these mixtures to pumping or mixing conditions. Consequently, when using these fluids at conditions close to room temperature, special precautions need to be considered in the design and operation of the pumping and mixing equipment.

#### 4. Intermolecular Interaction

Using the DESs binary mixture density data, we used Eq. (1) to calculate excess molar volumes  $V_m^E$  of the mixtures:

$$V_m^E = V_m - \sum_{i=1}^2 x_i V_{m,i} \quad (1)$$

where  $V_m$ : molar volume of the mixture,  $x_i$ : mole fraction,  $V_{m,i}$ : molar volume of component  $i$ , respectively.

Fig. 4 shows the variation in the excess molar volume of DES mixtures with mole fraction and temperature. The variation in excess volumes is attributed to three types of interactions between the molecules present in the mixtures [23]: (a) structural contribution due to difference in size and shape of the component molecules present in the mixture, (b) chemical or specific interaction, and (c) weak dipole-dipole interaction. The interactions mentioned in (a) and (b)

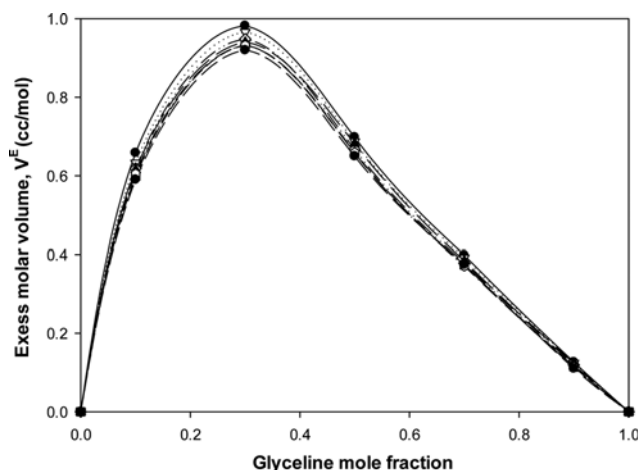


Fig. 4. Plot of excess molar volume as a function of Glyceline mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

above result in a negative contribution to the excess molar volume, while the interaction mentioned in (c) above results in a positive contribution to the molar volume. A positive contribution was observed on adding Glyceline, which indicates a weak dipole-dipole interaction between the constituents' molecules of the mixture. Furthermore, the positive contribution is attributed to the disruption of the ordered structure of pure the component during the formation of the mixture [24]. This means that there is a disruption of the ordered structure of pure Reline on addition Glyceline as mentioned earlier.

The variation of excess molar volume increases with increase in mol% Glyceline and a maximum was observed at 30 mol%. Further increase in Glyceline reduces the variation. Going by the aforementioned description of the meanings of the variation of the excess molar volume with mol%, the structure of pure Reline can be assumed to be disrupted upon addition of Glyceline. This disruption reaches its maximum at 30 mol% and further increase in Glyceline does not affect the structure of the mixture. This is in agreement with observed decrease in molar volume and viscosity with increase in Glyceline concentration. The variation of excess volume was observed to decrease with temperature.

The variation of excess molar volume with mole fraction was calculated using Eq. (2) (Redlich-Kister)

$$V_{m,RK}^E = x_R x_E \sum_{i=0}^m a_i (1 - x_E)^i \quad (2)$$

where  $x_R$ : Reline mole fractions,  $x_E$ : Glyceline mole fractions and  $a_i$ 's : model parameters. The parameters for each temperature studied are given in Table 1.

Genetic algorithms technique was used for the optimization of the objective function presented in Eq. (3):

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (V_{m,exp}^{E,i} - V_{m,RK}^{E,i})^2}{(n-m)}} \quad (3)$$

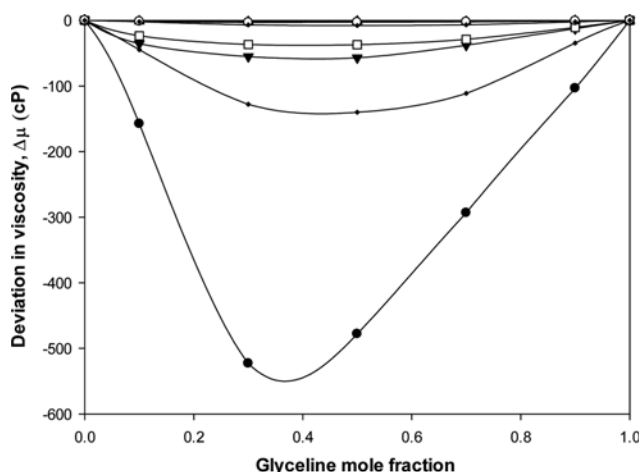
Very small values of  $\sigma$  were obtained during optimization and the regression coefficients were very close to 1 for all considered tem-

**Table 1. Redlich-Kister model parameters for the excess volume ( $V_m^E$ ) of Reline+Glyceline mixtures**

Temp. (°C)	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$	$R^2$
20	2.84	-3.40	2.47	-0.47	0.015	0.998
30	2.81	-3.38	2.30	-0.24	0.018	0.994
40	2.71	-3.31	2.10	-0.07	0.02	0.999
50	2.74	-3.36	2.26	-0.17	0.019	0.999
60	2.78	-3.41	2.38	-0.26	0.016	0.995
70	2.70	-3.31	2.15	-0.15	0.019	0.999
80	2.74	-3.43	2.30	0.00	0.016	0.994

**Table 2. Redlich-Kister model parameters for the viscosity variation ( $\Delta\mu$ ) of Reline+Glyceline mixtures**

Temp. (°C)	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$	$R^2$
20	-1950.67	1299.93	784.97	-1443.04	0.387	0.999
30	-579.50	108.14	180.52	-58.28	5.653	0.999
40	-219.95	85.32	-56.82	114.09	2.334	0.998
50	-146.87	33.07	-63.39	87.22	0.326	0.999
60	-6.59	0.93	-6.85	4.63	0.345	0.969
70	-10.98	5.09	-2.64	-0.58	0.227	0.994
80	-32.22	1.39	11.50	-3.47	0.469	0.997


**Fig. 5. Deviation of viscosity from linear additivity for the Reline-Glyceline mixture as a function of composition and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.**

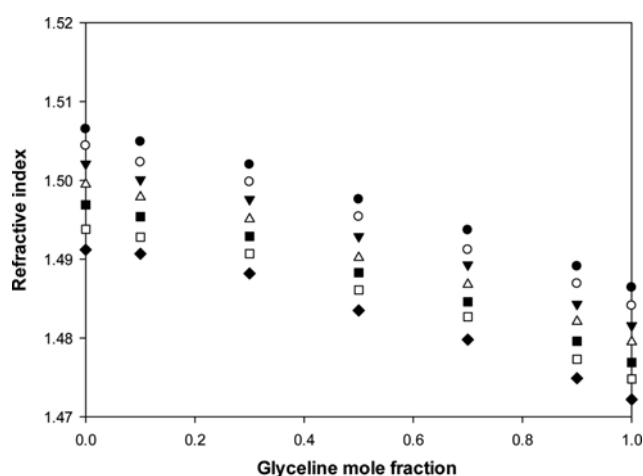
peratures. Both experimental and fitted excess volume profiles are shown in Fig. 4.

Variation of viscosity can be determined from Eq. (4)

$$\Delta\mu = \mu - \sum_{i=1}^2 x_i \mu_i \quad (4)$$

where  $\Delta\mu$ : viscosity deviation,  $\mu_m$ : molar volume of the mixture,  $x_i$ : mole fraction,  $\mu_i$ : molar volume of component  $i$ , respectively.

While Eq. (4) was used for calculating the variation in viscosity of the mixture, Fig. 5 shows negative deviation for all mole fractions measured. Since the deviation in viscosity is approximately proportional to the strength of interaction [25], the decrease in the negative deviation of excess viscosity indicates weakening interactions. This further validates the assumption made that the addition of Glyceline results in distortion of hydrogen bond network. It suggests that the structure of pure Reline becomes less compact in the presence of Glyceline due to weakening interactions and thereby the molecules become more mobile. Consequently, the viscosity of the mixture is reduced. The highest deviation was observed at around 30 to 40 mol%. The deviation of viscosity with mole fraction is more pronounced at lower temperature possibly due to larger temperature effect as compared to the effect of mole fraction. Fig. 5 also shows the fitted viscosity variation profiles, which was modeled


**Fig. 6. Variation of RI as a function of Glyceline mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.**

using a four parameters Redlich-Kister model similar in form to that of Eq. (2). Table 2 shows the parameters for each temperature studied. The regression coefficient was above 0.998 for all considered temperatures.

## 5. Refractive Index (RI)

The variation of refractive indices as a function mole fraction and temperature was measured and presented in Fig. 6. The RI, which is the measure of the ratio of speed of light in vacuum to the speed of light in the liquid of interest, appears to decrease with increase in concentration of Glyceline. RI is linearly proportional to density for materials with density  $\ll 1 \text{ g/cm}^3$  and although the linearity disappears for dense material, density is still the primary determinant of the RI [26]. Therefore, as Glyceline is added to pure Reline, the molar volume of the DES mixture increases as shown in Fig. 1. This in turn results in decreasing in density and consequently decreasing RI. The RI of pure Reline was determined as 1.5065, while the RI of pure Glyceline was determined as 1.4864. The RI values decreased by approximately 0.020 for all temperatures measured.

RI was also observed to decrease with the increase in temperature. For pure Reline, the RI at 20 °C was determined as 1.5065, while the RI decreased by 0.015 to 1.4912 at 80 °C. The decrease from 20 °C to 80 °C was obtained as approximately 0.014 for all the other mixtures tested.

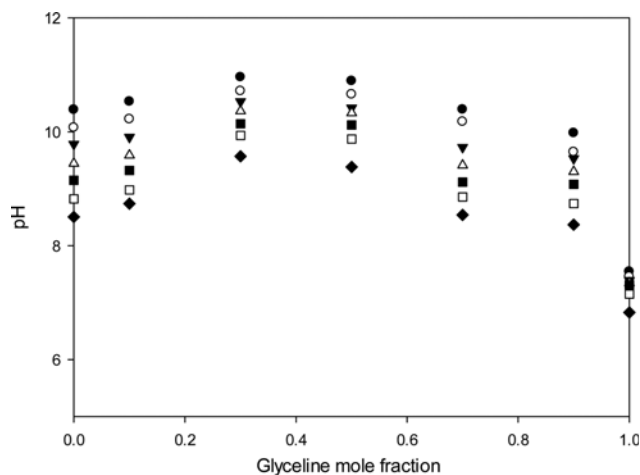


Fig. 7. Plot of pH as function of mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

## 6. pH

Fig. 7 shows the variation of pH as a function mole fraction and temperature. Pure Reline was found to be alkaline with a pH of 10.3870, while Glyceline was found to be only slightly alkaline with a pH of 7.5430 at 20 °C. From Fig. 7, Reline has more effect on the pH of the DES mixtures as the pH value remains close to the value of pure Reline up to 70 mol% Glyceline. This is true for all temperatures. It is also interesting that at 30 mol% the pH reaches a maximum of 10.9590, 10.7150, 10.5310, 10.3660, 10.1420, 9.9360 and 9.5710 at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C, respectively. This coincides with the mole fraction at which the highest disruption of the hydrogen bond network was assumed to occur. Since pH is an indication of the concentration of  $\text{OH}^-/\text{H}^+$  ions in solution, the alkaline nature of pure Reline means that there is a relatively high concentration of  $\text{OH}^-$  ions, while pure Glyceline has very little amount of these ions. Therefore, upon addition of the Glyceline, the subsequent physical bond breakage and formation results in more  $\text{OH}^-$  ions available in the mixture as these ions no longer participate in hydrogen bond formation. As more Glyceline is added, the hydrogen bond network gets further distorted and consequently more  $\text{OH}^-$  ions are released. This continues until no more  $\text{OH}^-$  ions can be released (30 mol%). Adding Glyceline beyond 30 mol% results in a reversal effect as  $\text{OH}^-$  ions will participate in forming new bond with the incoming glycerol molecules. Consequently, the pH values decreases. However, these changes in  $\text{OH}^-$  ion are marginal.

The pH of DESs mixture decreased with the increase in temperature (Fig. 7). The pH of pure Reline decreased from 10.3870 at 20 °C to 8.5050 at 80 °C. The corresponding decrease for pure Glyceline was from 7.5430 to 6.828. The pH decreased with increase in temperature (20 °C–80 °C) by 1.7920, 1.3880, 1.5090, 1.8500 and 1.6090 for 10, 30, 50, 70 and 90 mol% Glyceline, respectively. The corresponding decrease in pH with temperature suggests disappearance of the  $\text{OH}^-$  ions. But increase in temperature also results in distortion of hydrogen bond network, as discussed above. Therefore, it can be assumed that increase in temperature results in the

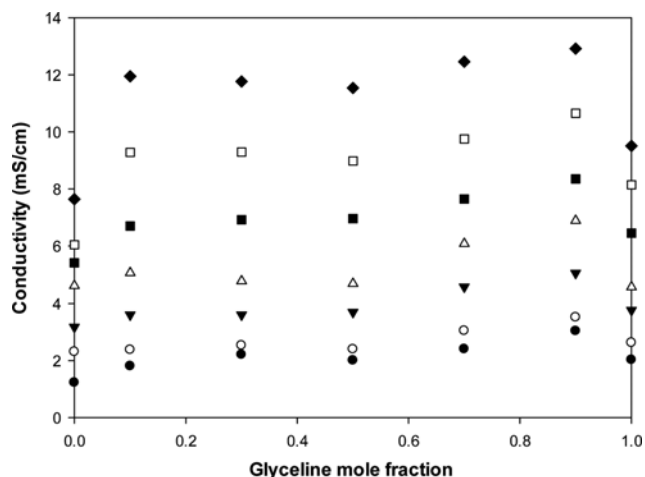


Fig. 8. Variation of conductivity as a function of Glyceline mole fraction and temperature. Symbols represent different temperatures as follows: ● 20 °C, ○ 30 °C, ▼ 40 °C, △ 50 °C, ■ 60 °C, □ 70 °C and ◆ 80 °C.

dissociation of more  $\text{H}^+$  ions in the mixture, which thereby reduces the concentration of the  $\text{OH}^-$  ions with a consequent reduction in pH.

## 7. Conductivity

The conductivity of Reline-Glyceline mixture was studied and presented as Fig. 8. As can be seen, the conductivity of the DES mixture increased slightly from 1.23 mS/cm (pure Reline) to 1.81 mS/cm (10 mol% Glyceline) at 20 °C. A further increase in conductivity was observed up till 30 mol% Glyceline (2.21 mS/cm). Upon addition of more Glyceline, the conductivity of the mixture decreased to 2.01 mS/cm (50 mol%). The conductivity of the mixture then began to increase by adding more Glyceline to make up 70 and 90 mol%. The conductivity of DES at 90 mol% Glyceline was found to be greater than that of pure Glyceline (2.03 S/cm). This pattern remained virtually the same for all temperatures measured. Conductivity is normally expected to increase with decrease in viscosity as the mobility of ionic species tends to be retarded in a viscous medium. Therefore, an increase in conductivity with increase in concentration of Glyceline was expected. Although the observed trend indicates that the viscosity plays a role in the conductivity value of the mixture, it is not governed by the viscosity of the formed DES alone.

For each DES mixture, the conductivity values increases with temperature. For pure Reline, conductivity increased from 1.23 mS/cm to 7.64 mS/cm. For pure Glyceline, conductivity increased from 2.03 mS/cm to 9.51 mS/cm. An increased of conductivity in the range of 9.53 mS/cm to 10.14 mS/cm was observed for all the DES mixtures. The increase in conductivity can be attributed to increase in mobility due to decrease in viscosity as temperature is increased.

## CONCLUSION

Deep eutectic solvents (DES) of Reline and Glyceline were synthesized and mixed to form DES mixtures of 0, 10, 30, 50, 70, 90 and 100 mol% Glyceline. The physical properties of mixtures were

investigated. The variation of excess volume and viscosity with mole fraction and temperature was analyzed to gain a better understanding of the change in intermolecular interactions upon mixing.

The molar volume of the Reline-Glyceline mixture increased linearly with increase mol% of Glyceline and temperature, possibly due to weakening hydrogen bond strength, which results in increase in bond length. In contrast, the viscosity of the mixtures was found to decrease with increase in Glyceline mol% and temperature, which suggests that the DES structure has become less compact and molecules have become more mobile. Studying the variation of excess molar volume and viscosity validates the assumption that the addition of the Glyceline to pure Reline results in the disruption of its structure. Therefore, positive and negative deviations were observed for the study involving excess molar volume and viscosity, respectively. The maximum deviation in both cases was observed at about 30 mol% Glyceline. The investigation into the effect of Glyceline mol% on the RI reveals a reciprocal relationship while pH reaches a maximum at 30 mol% Glyceline. Although viscosity affects conductivity of the mixture, the variation in conductivity with mol% Glyceline was not only governed by the viscosity of the mixture.

It was shown that by mixing two DESs with different set of properties, a new DES that possesses certain attributes belonging to the individual DES component can be formed.

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