Thermophysical properties in deep eutectic solvents with/without water

Azhar Y M. Al-Murshedī¹, Hasan F Alesary² and Rajaa Al-Hadrawi¹

¹ Chemistry Department, University of Kufa, Najaf, Iraq
² Chemistry Department, University of Kerbala, Kerbala, Iraq

Abstract. Physical properties of pure DESs and DESs mixed with different amounts of water were investigated by different techniques, including, rotational viscometer, Quartz Crystal Microbalance (QCM) and conductivity meter. In order to study heterogeneity of those liquids in nature. Analysis of these data showed some characteristics of heterogeneity, the extent of which depends on the number of hydrogen bond donors in the pure DES.

Key words: Deep eutectic solvents, viscosity, conductivity, Ethaline, Reline, Glyceline, Oxaline.

Introduction:
Deep eutectic solvents (DESs) are a new alternative of ionic liquids (ILs), in 2002 Abbott et al. was the first introduced to DESs. DESs be composed of a quaternary ammonium salts, choline chloride and hydrogen bond donor such as organic acid and amide.¹ DESs have several advantages over traditional ILs such as are easy to prepare, not expensive, high stability, not toxic and not sensitive to water and air such ILs. DESs have been widely used in electrochemistry application due to the high ability to dissolve metal oxides.² In addition, DESs have been used in separation and synthesis of organic compounds.³,⁴ There are four kinds of DESs have been prepared depended of Purpose of use, as a per in Table 1.⁵,⁶

| Type I       | Organic salts+ Metal salts (MClₓ, M= Zn, Fe, Sn) |
|--------------|-----------------------------------------------|
| Type II      | Organic salts+ Hydrated Metal salts (MClₓ.y H₂O) |
| Type III     | Organic salts+ Hydrogen bond donors (CoNH₂, OH, COOH) |
| Type IV      | Metal salts + Hydrogen bond donors              |

Up to now, the research has tended to focus on the physical properties of ionic liquids.⁷-¹⁰ In recent years, there has been an increasing interest in ionic liquids - water mixture to understand at what composition an ionic liquid starts to behave like an aqueous solution. The novelty of this work consists in studying the thermophysical properties of DESs with different water content, which is important to investigate at what composition of water the behavior of DESs become like an aqueous solution.
Experimental part:

Chemicals.

All chemicals were used at this investigation inserted in table 2.1. All work was done at ambient atmosphere. The results were repeated three time and average value was taken.

2.1: List of chemicals were used in this study with source and purity.

| Chemicals                | Source            | Purity% |
|--------------------------|-------------------|---------|
| Choline chloride         | Sigma-Aldrich     | ≥ 98    |
| Glycerol                 | Fischer           | 98      |
| Urea                     | Sigma-Aldrich     | 99      |
| Ethylene glycol          | Sigma-Aldrich     | 99      |
| Oxalic acid dihydrate    | Fischer           | 99      |

Preparation of deep eutectic solvents.

Ethaline, Glyceline and Reline were prepared by mixing 1:2 mole ratio for choline chloride: ethylene glycol, choline chloride: glycerol and choline chloride: urea, respectively. The mixture was heat up at 50ºC and stirred until a clear liquids were formed. Yet, Oxaline was based on a 1:1 composition ratio prepared for choline chloride: oxalic acid and keep it in oven at 50ºC until formed homogeneous solution.

Measurement of thermophysical properties.

1. Viscosity

The viscosity of DES with/without water were measured using two methods. The first one was rotational viscometer (Brookfield DV-E+ Pro) instrument at range of temperatures between (25ºC-75ºC). Second one it was Quartz Crystal Microbalance (QCM) (Agilent Technologies E5061A 300 kHz ENA Series Network Analyzer) at different temperatures (40ºC, 50ºC, 60ºC and 70ºC) using a polished crystal.

2. Conductivity measurements.

The conductivities of the DESs pure and with different content investigate in this work were measured using a Jenway 4510 conductivity meter. As mentioned previously, the conductivity probe was immersed in a liquids at range of temperatures (25ºC-70ºC ).

3. Surface tension and density.

Surface tension and density were done by used ( A KRÜSS Tensiometer K9 model K9MK1). The temperatures were controlled through the use of a thermostat at range from 25ºC to 60ºC.

4. Reflective index measurement.

The refractive indices of the DESs with/without water from 5-95% water were done using (a REFRACTOMETR, RFM 732 automatic digital) at room temperature.
Results and desiccation.

1. Viscosity of DESs using a rotational viscometer.

The viscosities of liquids one of the most important properties because they affect industry field. Previous study has shown that increasing viscosity for liquids useful in some application such as chromatography. Viscosity of ionic liquids tend to be higher than organic solvents due to big size for cation and anion in ionic liquids. Figure 3.1 show viscosities of Ethaline, Glyceline, Reline and Oxaline as a function of temperature. In general, the results induced that with increasing temperature the viscosity of DESs will decreased. Reline shown the highest viscosity than other DESs in this study, however; Ethaline exhibit the lowest viscosity. Interestingly, this correlation is related to change in the number of hydrogen bonding between the liquids under investigation. This finding is in agreement with Stefanovic et al. findings which showed the density of hydrogen bond in Reline is (13.8 bonds nm\(^{-3}\)) than Glyceline (10.8 bonds nm\(^{-3}\)) and finally the Ethaline is (9.4 bonds nm\(^{-3}\)). This behavior due to the urea in Reline, which can form four hydrogen bonds compared with glycerol, which can form three, and ethylene glycol, which can form two.

![Figure 3.1 Viscosity of DESs in four liquids, Ethaline, Glyceline, Reline and Oxaline using rotational viscometer.](image)

\[
\Delta f = -f_0^{3/2} \left( \frac{P_{\text{liq}} \eta_{\text{liq}}}{\rho_q \mu_q} \right)^{1/2} \quad \text{Equation (3.1)}
\]

where \(\Delta f\) is the change in the frequency of the crystal, \(f_0\) is the frequency of the dry crystal, \(P_{\text{liq}}\) is the density of the liquid, \(\eta_{\text{liq}}\) is the viscosity of the liquid, \(\rho_q\) is the density of the crystal (2.648 g cm\(^{-3}\)) and \(\mu_q\) is the sheer modulus of the quartz (2.927\times 1011 g cm\(^{-1}\)s\(^{-2}\)). Rearranging equation above give the viscosity of liquids, as shown in Equation (3.2).
aim of using QCM to study viscosity of DESs is that can be used small sample amount about 1 ml, however; rotational viscometer is require 600 ml. Figure 3.2 show the comparative of viscosities of DESs in the QCM and rotational viscometer as a furcation of temperature. The results inducted that both QCM and viscometer give similar results.

Figure 3.2 viscosity of DESs in four liquids, Ethaline, Glyceline, Reline and Oxaline using QCM.

Previous studies have shown that the viscosity of DESs decreases with increased water content. Figure 3.3 illustrated that viscosities of three DESs: Ethaline, Glyceline and Reline. In general, the viscosity will be decrease with increasing amount of water, yet; the viscosity of DESs do not change between 1-2.5 wt% water. Recently, Edler et al. shown that addition of a 1 molar equivalent of water has an effect on impairment of the interactions between choline-choline, choline-chloride, urea-urea and urea-chloride. Shah and Mjalli argue that the interaction between urea-urea and urea-anion decreased with increase water content by used the radial distribution functions (RDF). This behavior is due to two reasons, firstly; the anion preferably hydrogen bonding to water than urea at lower water fraction. Secondly, The Coulombic attractive interaction in Reline-water mixture was lower than pure Reline. 

Figure 3.3 viscosity of DESs-water mixture.
3. **Surface tension.**

There are many factors that can affect the surface tension of ionic liquids such as, temperature, kind of cations and anions, alkyl chain length and hydrophobic or hydrophilic functional groups. Figure 3.4 presents the experimental data on surface tension as a function of temperature for pure DESs, the results illustrate that the surface tension decreased with increased temperature. Ethaline shows lower surface tension, however; Reline exhibits a higher surface tension in this study due to different intermolecular forces between Ethaline and Reline, the results of surface tension is in accordance with the viscosity data.

**Figure 3.4:** Surface tension of Ethaline, Glyceline, Reline and Oxaline.

**Figure 3.5** shows the surface tension of Ethaline, Glyceline and Reline as a function of water content. In principle, if the mixture of DESs - water is homogeneous the relationship between surface tension and water is linear relationship. Whilees Ethaline and Glyceline shown proximately linear trend, whilst Reline data start at 50 mN m$^{-1}$ than rise rapidly to the value for bulk water 72 mN m$^{-1}$ with addition 2.5 wt% of water. As a result, Reline - water mixture is more heterogeneous than Ethaline and Glyceline.

**Figure 3.5:** Surface tension of DESs - water mixture.
4. **Ionic conductivity**

There is inverse relationship between conductivity and viscosity, high viscosity of DESs can formed problem in electrochemical applications because it leads to high cell resistances. High temperature can be help to reduce the viscosity and rise the ionic conductivity of liquids.\(^{21,22}\) Figure 3.6 provides the results obtained from the conductivity as a function of temperature. As mentioned previously, the conductivity decrease when the temperature increased. Ethaline is highest conductivity, however; Reline is the lower one. The reason behind that is rise temperature will leads to decrease the density and viscosity which enable higher ionic mobility.\(^{23}\)

![Figure 3.6: Ionic conductivity of Ethaline, Glyceline, Reline and Oxaline.](image)

The results obtained from the correlational analysis of DESs- water mixture are set out in Figure 3.7. In general speaking, increasing amount of water leads to increase the conductivity of all three system: Ethaline, Glyceline and Reline due to decreased the viscosity.

![Figure 3.7: Ionic conductivity of DESs- water mixture.](image)

5. **Density.**

The range of density of ionic liquids is between 1.0 to 1.6 g cm\(^{-3}\) because the influence of the ion structure of ILs.\(^{24}\) Figure 3.8 shows densities of pure DESs, density of liquids increase with
temperature decreasing. Reline give the highest density, yet; Ethaline the lower one. This is due to the free volume increase with increasing temperature.

![Density of Ethaline, Glyceline, Reline and Oxaline.](image1)

Figure 3.8: Density of Ethaline, Glyceline, Reline and Oxaline.

Figure 3.9 compares the experimental data on densities DESs-water mixture. As can see from figure the density of all DESs will decrease with increasing amount of water due to the decreased in the free volume in DESs liquids.

![Density of DESs- water mixture.](image2)

Figure 3.9: Density of DESs- water mixture.

6. Reflective index

The phrase of reflective index is means study the bending of light when it passes through different media. Table 3.1 shows the experimental data on reflective indexes of pure DESs and DESs-water mixture. The study was done at room temperature, it clearly that at low water content there is a high reflective index due to the increased ion arrangement and the efficient packing of the ions.
| Water content wt% | Ethaline     | Glyecline    | Reline     |
|-------------------|--------------|--------------|------------|
| 0                 | 1.4590 ± 0.004 | 1.4590 ± 0.004 | 1.4590 ± 0.004 |
| 5                 | 1.4526 ± 0.006 | 1.4526 ± 0.006 | 1.4526 ± 0.006 |
| 10                | 1.4465 ± 0.012 | 1.4465 ± 0.012 | 1.4465 ± 0.012 |
| 20                | 1.4336 ± 0.023 | 1.4336 ± 0.023 | 1.4336 ± 0.023 |
| 50                | 1.3939 ± 0.007 | 1.3939 ± 0.007 | 1.3939 ± 0.007 |
| 70                | 1.3690 ± 0.031 | 1.3754 ± 0.030 | 1.3789 ± 0.007 |
| 90                | 1.3447 ± 0.009 | 1.3467 ± 0.004 | 1.3477 ± 0.046 |
| 95                | 1.3390 ± 0.005 | 1.3399 ± 0.011 | 1.3404 ± 0.074 |
| 100               | 1.3330 ± 0.022 | 1.3330 ± 0.022 | 1.3330 ± 0.022 |

**Conclusion**

Together these results provide important insights into thermophysical properties of both pure deep eutectic solvents, and deep eutectic solvents with different water content. In pure system, the function of temperature are dependent on the interaction between choline chloride and a hydrogen-bonding donor. Mixing DESs with water shown that the mixture are not homogeneous and water have significant effect on physical properties of DESs such as viscosity, conductivity and density.

**Acknowledgments.**

The authors would be like to thanks prof Andy Abbott and prof Karl Rider at University of Leicester/Chemistry department- Materials center to a lots of help and support during did this study. As well as, we would like to thanks ministry of higher education and scientific research and Kufa University to provide scholarship to authors.

**Reference.**

[1] Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Journal of the American Chemical Society, 2004, 126, 9142.

[2] Abbott, A. P.; Capper, G.; Davies, D. L.; McKenzie, K. J.; Obi, S. U. Journal of Chemical & Engineering Data 2006, 51, 1280.

[3] Abbott, A. P.; Al-Mursheidi, A. Y.; Alshammari, O. A.; Harris, R. C.; Kareem, J. H.; Qader, I. B.; Ryder, K. Fluid Phase Equilibria 2017, 448, 99.

[4] Duan, L.; Dou, L.-L.; Guo, L.; Li, P.; Liu, E.-H. ACS Sustainable Chemistry & Engineering 2016, 2, 2405.

[5] Abbott, A. P.; Frisch, G.; Ryde, K. S. Annual Review of Materials Research 2013, 43, 335.

[6] Smith, E. L.; Abbott, A. P.; Ryder, K. S. Chemical Reviews 2014, 14, 11060.

[7] Aparicio, S.; Atilhan, M.; Karadas, F. Industrial and Engineering Chemistry Research 2010, 49, 9580.

[8] Fannin, A. A.; Floresani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. The Journal of Physical Chemistry 1984, 88, 2614.

[9] R. B. Leron; Soriano, A. N.; M. Li Journal of the Taiwan Institute of Chemical Engineers 2012, 43, 551.

[10] Sedev, R. Current Opinion in Colloid & Interface Science 2011, 16, 310.

[11] Yu, G.; Zhao, D.; Wen, L.; Yang, S.; Chen, X. AICHE Journal 2012, 58, 2885.

[12] Stefanovic, R.; Ludwig, M.; Webber, G. B.; Atkin, R.; Page, A. J. Physical Chemistry Chemical Physics 2017, 19, 3297.

[13] Buttry, D. A.; Ward, M. D. Chemical Reviews 1992, 92, 1355.

[14] Kanazawa, K. K.; Gordon, J. G. Analytica Chimica Acta 1985, 175, 99.
[15] Yujiao, X.; Haifeng, D.; Suojiang, Z.; Xiaohua, L.; Xiaoyan, J. *Journal of Chemical & Engineering Data* **2014**, *59*, 3344.
[16] Hammond, O. S.; Bowron, D. T.; Edler, K. J. *Angewandte Chemie* **2017**.
[17] Shahi, D.; Mjalli, F. S. *Physical Chemistry Chemical Physics* **2014**, *16*, 23900.
[18] Abbott, A. P. *ChemPhysChem* **2004**, *5*, 1242.
[19] Bormashenko, E. Y. *Wetting of Real Surfaces*, De Gruyter **2013**.
[20] C. Kolbeck; J. Lehmann; K. R. J. Lovelock; T. Cremer; N. Paape, P.;
[21] 20 Wasserscheid; A. P. Fröba; Maier, F.; Steinrück, H.-P. *The Journal of Physical Chemistry B* **2010**, *114*, 17025.
[22] G. García; Aparicio, S.; Ullah, R.; Atilhan, M. *Energy & Fuels* **2015**, *29*, 2616.
[23] Q. Zhang; Vigier, K. D. O.; Royer, S.; Jerome, F. *Chemical Society Reviews* **2012**, *41*, 7108.
[24] Q. Cao; X. Lu; X. Wu; Y. Guo; Xu, L.; Fang, W. *Journal of Chemical & Engineering Data* **2015**, *60*, 455.
[25] Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. *Fluid Phase Equilibria*, 219.
[26] K. Shahbaz; F. G. Bagh; F. Mjalli; AlNashef, I.; Hashim, M. *Fluid Phase Equilibria* **2013**, *354*, 304.
[27] B. Mokhtarani; M. M. Mojtahedi; H. R. Mortaheb; M. Mafi; Yazdani, F.; F. Sadeghian *Journal of Chemical & Engineering Data* **2008**, *53*, 677.
[28] R. B. Leron; Soriano, A. N.; Li, M.-H. *Journal of the Taiwan Institute of Chemical Engineers* **2012**, *43*, 551.