

Physical, thermal and structural properties of 1ChCl: 2 Urea based ionic liquids

Ashna F. ARKAWAZI^(a), Azeez Abdullah BARZINJY^{(b) (c)*}, Samir Mustafa HAMAD^{(d) (e)}

^(a)Department of Chemistry, College of Education, University of Garmian, Sulaimani, Iraq

^(b)Department of Physics, College of Education, Salahaddin University-Erbil, Erbil, Iraq

^(c)Department of Physics Education, Faculty of Education, Tishk International University, Erbil, Iraq

^(d)Scientific Research Centre, Delzyan Campus, Soran University, Soran 44008, Erbil, Iraq

^(e)Computer Department, Cihan University-Erbil, Erbil, Iraq

Abstract

Fourth generation of ionic liquids, relatively cheaper and environmental friendly, is called deep eutectic solvents (DESs). Generally, at present time are extensively recognized as novel remarkable as well as green alternative solvents to the conventional ionic liquids owing to their low cost and tolerance to moisture. DESs first came to the public vision in 2001, since then, researches and applications of deep eutectic solvents can cover, almost, all of the fields of science. In this study the physical, thermal and structural properties of 1ChCl: 2Urea based ionic liquids is reported. Firstly, the physical properties, in terms of viscosity, conductivity and density as a function of temperature are investigated intensively. Later, the microscopic structure of 1ChCl: 2Urea is studied by means of FTIR spectroscopy. Finally, the thermal properties, in terms of melting temperature and thermal stability, are also reported in this investigation. Overall, the obtained data and inspections are in an excellent agreement with the previous studies.

* Corresponding author:

azeez.azeez@su.edu.krd

Received 17 Aug 2019,

Revised 11 Feb 2021,

Accepted 13 Feb 2021.

Keywords: deep eutectic solvents; ionic liquids; choline chloride; urea; 1ChCl:2Urea; physical properties.

1. Introduction

Human beings are captivating countless hard-work, comprising water purification with a lesser amount of energy, manufacturing high power batteries using a reduced amount of heavy metal ions, producing electricity with a smaller amount of carbon releases, and growing the energy competence of all classes of electrical devices[1-4]. Nearly, in all projects, materials science acting an essential role through providing clarifications to scheme, manufacture, and assess the practical materials that are the main modules in an arrangement [5, 6].It can be understood that, solvent is one of the most important element in any chemical procedure. In this common sense, conventional organic solvents are typically the furthestmost expensive and ecologically intimidating in chemical industry. Therefore, at temperatures upper than the boiling-point of the solvent, reactions need to be performed in vacuum-packed apparatuses under high-pressure, which is unsafe and not easy for an interrupted making. Consequently, it is extremely preferred to invent solvents that are green naturally and besides, that are economically inexpensive. Moreover, novel solvents with exceptional physical and chemical characteristics can deliver an opportunity to produce purposeful materials that cannot be achieved differently. Investigation into ionic liquids was anticipated to expose novel cutting edge in materials science[7]. Ionic liquids are, basically, liquids that are consist of completely of ions. Accordingly, molten NaCl is an ionic liquid: contrarily, a solution of NaCl in water is an ionic solution[8].Certainly, in their essential investigation countless thrilling innovations, have been described and shortened [7, 9, 10]. Nevertheless, it is quite interesting to impulse ionic liquids into comprehensive requests as a result of their extraordinary cost, complex synthesis process and sensitivity to air and moisture. A current novel type of ionic liquid equivalents, named deep eutectic solvents(DESs), possess numerous analogous features and properties with ionic liquids, but they are considerably inexpensive and stable in air, and therefore more capable than ionic liquids for industrial development [11].The concept of DES, in general, is still in its early period in comparison with ionic liquids; nevertheless, the growing number of annual publications makes the area very encouraging (Figure 1).

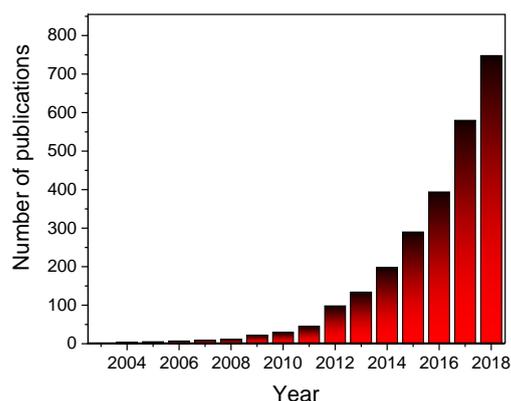


Figure 1: Number of publications according to the web of knowledge search for the expression “DES” in 10 March 2019.

DESs, in general, can be made through a definite molar ratio of quaternary ammonium salts, hydrogen bond accepters, and hydrogen-bond donors[12]. The term eutectic originates from a Greek expression that means “simply melted” and specifies the temperature where the stages all together crystallize from molten solution[13]. DESs consist of an extensive range of liquids nearly to the eutectic configuration of the combinations; contrarily to ionic liquids, which are made mainly of one kind of discrete anion and cation, they can comprise a range of anionic and cationic classes[14]. The 1st DES was proposed by Abbott et al.[15]: the eutectic amalgamation of ChCl and urea (Figure 2).

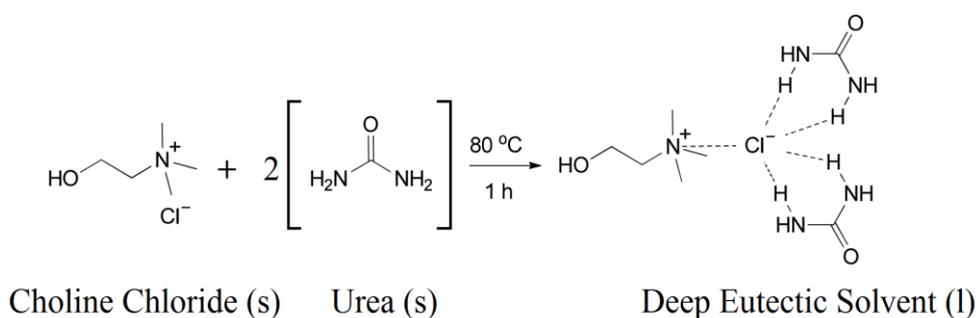


Figure 2: Synthesis of 1ChCl:2urea DES

Figure 2 explains the chemical construction and charge density of ChCl, urea and the shapedDES. Obviously, an interaction among the hydrogen atom attached with the oxygen atom of ChCl cation was heading for the oxygen atom of urea. This is a novel interaction that might happen throughout the DES amalgamation. It ought to be renowned that the Abbott group [15] and Perkins et al. [16] described the contact between the Cl⁻ anion of ChCl and the hydrogen atom of urea. These hydrogen bond connections are the key intention for the important reduction of the melting point of DESs. This DES is at the present time recognized under the commercial name Reline [17] and is profitably accessible. Nevertheless, it is basically arranged by putting the solid components at the suitable molar percentage. Also, ChCl-based DESs were less toxic than phosphonium-based DESs. One of the crucial dissimilarities among DESs and ionic liquids is that ionic liquids are entirely composed of ions, whereas DESs comprise both ionic and neutral types. As the leading article that presented a choline chloride: urea sort DES, the previous period of time has perceived remarkable developments in this domain. We, previously, stated that DESs are commonly divided into four groups [18]. The ChCl/urea DES is among type 3 DESs. It can be agreed that, viscosity is a vital characteristic of ionic liquids for various requests. Usually, materials with more van der Waals connection and hydrogen bonding possess greater viscosities [19]. In addition, the construction of the anion has a great impact on the viscosity and typically beyond the configuration of the cation [20]. On the other hand, the ionic-conductivity, which relies upon the existing charge-carriers and their mobility, relies upon viscosity, changes with the molecular-weight, and dimension of the ions. The conductivity of ionic liquids, in general, is restricted typically through their ion-mobility subsequent from accumulation [21]. Hence, fewer ionic-interaction and further delocalized charge causes greater conductivity; thus, more ionic-conductivity standards will be predictable for the stronger Bronsted acids [22]. Also, ionic-conductivity reduces whenever the size of the cation increase, i.e. they system possess is less mobility. The correlation among viscosity and conductivity is recognized; the higher the viscosity, the inferior the conductivity. Therefore, the electrical conductivity upsurges with cumulating the temperature. In this investigation the authors prepared the mixtures of choline chloride with urea (Type 3 DESs). Physical properties, namely phase behaviour, viscosity, conductivity and density have been investigated. FTIR spectroscopy has been used to analyse the structure of the investigated ionic liquid. Thermal stability and melting temperature also investigated in this study.

2. Materials and methods

Choline chloride ((CH₃)₃N(Cl)CH₂CH₂OH, Sigma Aldrich, ≥ 99%), and urea (Sigma Aldrich, >99%) were utilized as received. The DES was made by mixing ChCl-Urea together and heating, with stirring, at 80 oC up to a homogeneous colorless liquid had made (Figure 3).



Figure 3: Graphical representation of formation DES from 1 ChCl and 2 Urea

In this study the kinematic-viscosity and electrical conductivity of the 1ChCl: 2Urea system was cautiously recorded from 25 °C to 80 °C at the atmospheric pressure. The viscosity and conductivity recording were taken after 5 minutes at every single temperature to offer an acceptable temperature counterbalance. Melting points were measured by means of Mettler-Toledo-DSC1 differential scanning calorimeter (DSC). The calibration was accomplished under nitrogen-atmosphere through liquid-nitrogen cooling arrangement. A few droplet of the ionic liquid were sealed in an airtight manner in copper pans, the samples were first cooled from room temperature up to $-150\text{ }^{\circ}\text{C}$ then heated from $-150\text{ }^{\circ}\text{C}$ to $+130\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ afterwards cooling to $-150\text{ }^{\circ}\text{C}$, and lastly heated back to $130\text{ }^{\circ}\text{C}$ with the similar heating speed. The thermo graphical representation displayed a distinctive sharp endothermic peak equivalent to the melting point of the configurations. For measuring the viscosity of the ionic liquid the authors utilized the Ubbelohde viscometer through the constants 0.099, 0.300 in HERZOG Triplex-Veriom at thermostats. Jenway 4510 conductivity meter (cell constant = 1.01 cm^{-1}) has been utilized for the conductivity measurements as a function of temperature. A handy densitometer (Densito 30P, Mettler Toledo) was utilized to figure out the temperature dependent density of the ionic liquid. FTIR analysis was made utilizing a Perkin Elmer FTIR spectrophotometer with a resolve of 4 cm^{-1} .

3. Results and Discussions

3.1. Physical Properties

The temperature dependence of viscosity of ionic liquids obey the Arrhenius equation [23] or Vogel equation [23] and the identical can be utilized for 1ChCl: 2Urea system. From the data obtained in this study, it can be noted that, the 1ChCl: 2Urea ionic liquid system possesses larger viscosity at low temperature ranges, which falls speedily throughout heating as a result of the larger mobility of ingredients. The higher viscosity of the 1ChCl: 2Urea system is due to the creation of strong hydrogen bonds comparing to the other ionic liquids or even high-temperature molten-salts [24]. Figure 4 shows the linear relationship among conductivity and the reciprocal of viscosity of the 1ChCl: 2Urea system. As anticipated, the conductivity of the ionic liquid increased with the increasing of fluidity, i.e. the reciprocal of viscosity. Moreover, this trend has been found in other ionic liquid systems [25].

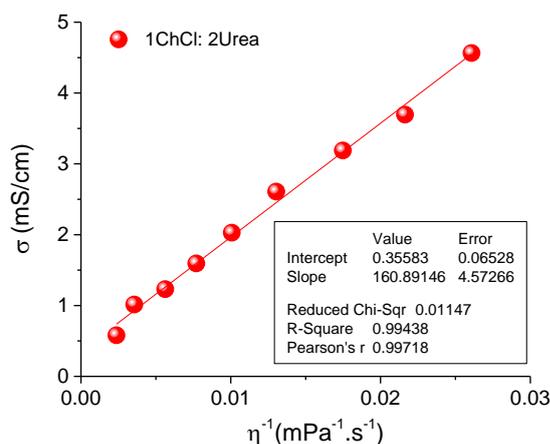


Figure 4: Conductivity vs. the inverse of viscosity (fluidity) of the 1ChCl: 2Urea system

Walden rule, which is of the correspondent molar conductivity alongside with the logarithm of the fluidity, *i.e.* reciprocal of viscosity, is a proper sign of the ionicity of the ionic liquids. The molar conductivity can be easily calculated by multiplying the molecular weight of the ionic liquid by the conductivity then dividing by the density of the ionic liquid. The reason behind using Walden rule is to differentiate between the non, poor, good, and super ionic liquids [26]. Walden rule is more applicable to be utilized for molten-salts and ionic liquids [27]. In this study the Walden rule has been used (**Figure 5**) to identify the position of the 1ChCl: 2Urea ionic liquid among the other types of ionic liquids.

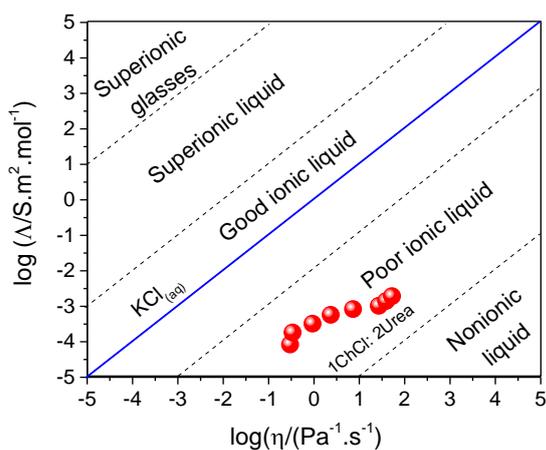


Figure 5: Walden plot of log of molar conductivity alongside with log of fluidity for 1ChCl: 2Urea system

It can be seen from **Figure 5** that the solid prototypical, blue, line relates to a diluted aqueous KCl solution wherein the system is recognized to be completely distanced and to possess ions of equivalent mobility. According to Walden distribution the synthesized ionic liquid in this investigation is categorized as a poor ionic liquid. This was expected since 1ChCl: 2 Urea ionic liquid possess high viscosity due to the hydrogen bonding. This can be transcended through adding a suitable amount of water to this ionic liquid [28], so that we can move 1ChCl: 2 Urea from poor ionic liquid to good ionic liquids.

3.2 Thermal Properties

The DSC thermal analyzes were carried out with the objective of characterizing the exothermic, endothermic and vitreous transitions of choline chloride with urea as a hydrogen bond donor species. As depicted in Figure 6, the melting temperatures are ~ 302 °C and ~ 134 °C for Choline Chloride and urea respectively. These outcomes are in an excellent covenant with Morrison et al.[29]. While, in a eutectic system, chemical compounds usually in solid phase are melted at a lower temperature than the melting temperature of any individual compounds to form eutectic solvent.

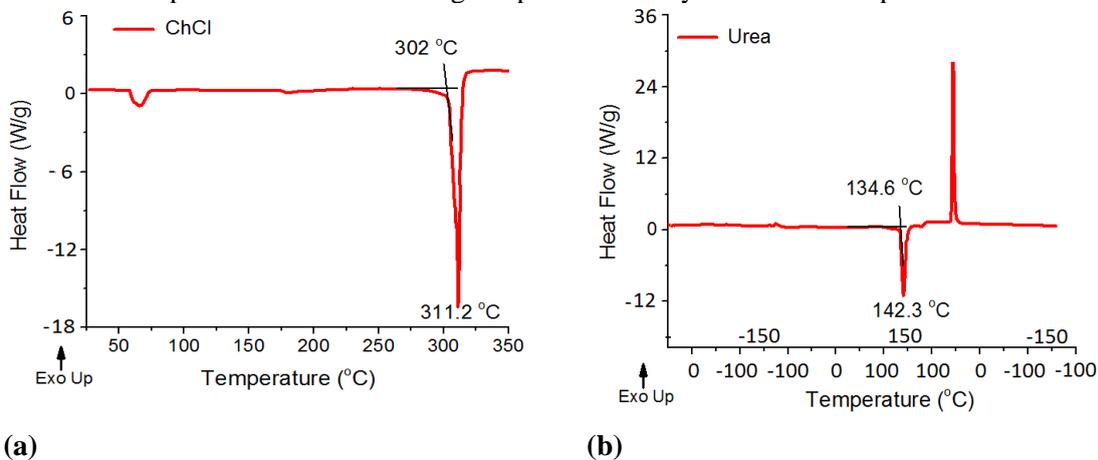


Figure 6: DSC curve for melting point measurement (a) ChCl and (b) urea

All analyzes were initially cooled to -150 °C prior to heating. The urea sample showed crystallization at ~ 38 °C during cooling and a melting at ~ 134 °C. Clearly, the 1ChCl: 2Urea DES system experiences two phase alterations from glass-transition to crystallization and from crystallization to melting throughout the DSC thermogram-process. The behavior I in **Figure 7** represent a deviation from the baseline, attributed to a glass transition (T_g). The behavior II is an exothermic peak attributed to crystallization. Finally the behavior III is an endothermic peak, which represents the melting of the compound, 1ChCl: 2Urea. Within heating the ionic liquid from 60 °C, an exothermic peak with an inception temperature of ~ 27 °C was detected (**Figure 7**). This was subsequent via an endothermic peak with an inception temperature of ~ 17 °C. The melting process initiated at around 17 °C and was finalized at around 25 °C. The wide-ranging melting temperature, *i.e.* from 17 °C to just about 26 °C, may be because of the heating rate. Whenever the heating rate is larger, the computed melting temperature range will be broader[30]. Additionally, there are many hydrogen bonds among molecules in 1ChCl:2Urea ionic liquid, which might lead to the wide range melting temperature.

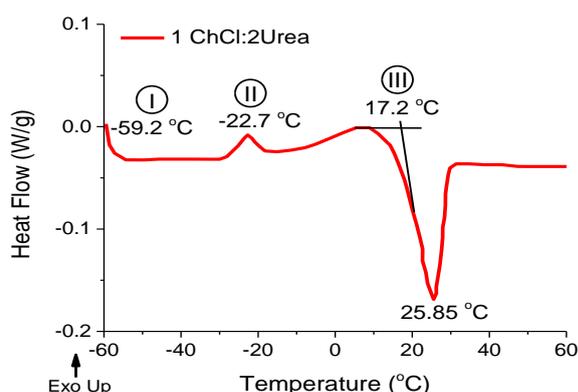


Figure 7: DSC thermogram curve of 1ChCl: 2Urea mixture

Figure 8 shows the thermo-gravimetric analysis curve performed on the 1ChCl:2Urea system. On this curve, it is possible to observe two zones, one where the temperature is $T < 150$ °C and the other is $T > 150$ °C. In the first part of the curve, the mass loss is regular, while in the second part the loss started to accelerate obviously. It is noted that the mass loss up to 150 °C is 2.6%, which might be correspond to the loss of water available in the sample. From this temperature, *i.e.* 150 °C, the second part of the curve initiated which is related to the thermal decomposition of the 1ChCl:2Urea system, specifically, the two components that form this ionic liquids, Choline chloride and Urea, are chemically unstable at this temperature range. Similar results have been found by Renet *al.* [31]. It can be noted from **Figure 8** that the system lost nearly 10 w% and 38 w% at 200 °C and 250 °C correspondingly. In fact, the stability of this type of ionic liquid is quite acceptable, because most of the applications of it can be done below this range [18, 32-34].

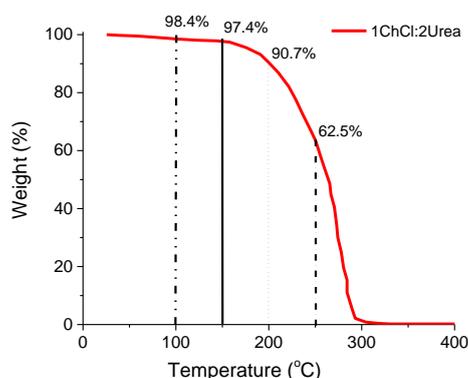


Figure 8: Thermo-graphic analysis of 1ChCl:2Urea ionic liquid system

3.3. Structural Properties

FTIR spectroscopy is utilized to investigate the interface between dissimilar groups, investigate and classify constructions. Frequency-shifts, band-widths and absorbance values of the identical chemical bond in diverse structure are all utilized to investigate the construction of the 1ChCl: 2Urea ionic liquid system. Figure 9 illustrates the FTIR spectra of Urea, ChCl and 1ChCl: 2Urea system. It can be seen that, approximately, the typical spectrum of the 1ChCl: 2Urea ionic liquid system is an overlay of those of urea and choline chloride. Moreover, the absorption bands at 3440 cm^{-1} , 3358 cm^{-1} and 3235 cm^{-1} in urea and 3435 cm^{-1} , 3258 cm^{-1} and 3012 cm^{-1} in ChCl changed to broader band in 1ChCl: 2Urea ionic liquid system. This is, perhaps, caused by the construction of additional hydrogen bonds among urea choline chloride [35]. Besides, the bands related to choline chloride, seemed in spectrum of 1ChCl: 2Urea system. This can be an indicator to reveal that the construction of ChCl was not demolished in the 1ChCl:2Urea ionic liquid system [36]. The extra hydrogen bonds possibly occur as; $O - H \dots N - H$, $O - H \dots O$ and $O - H \dots OH$ as shown in Figure 6.

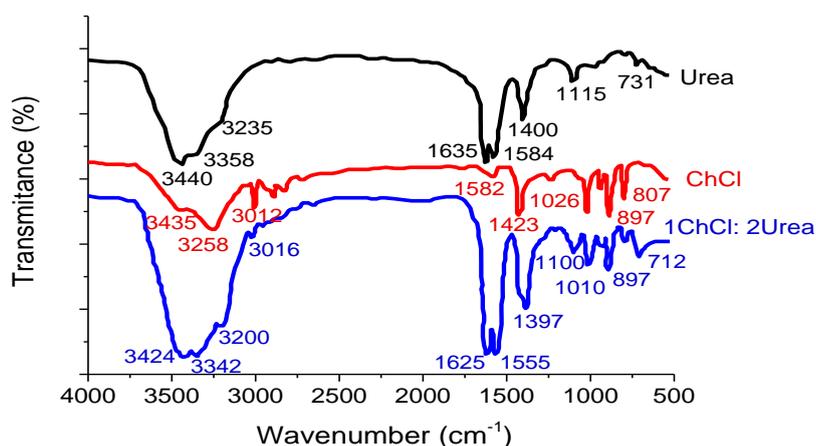


Figure 9: FTIR spectrum of urea, ChCl and 1ChCl:2Urea system

4. Conclusion

Over the past ten years, ionic liquids have sustained to be utilized considerably as a medium for preparation and countless reactions. Regardless of the important prospective of ionic liquids most of the ionic liquids are still expensive and therefore looking for low-cost ionic liquids has become a main attention of recent ionic liquids investigation. Therefore this investigation highlighted the synthesis and characterization of the 1ChCl: 2Urea ionic liquid. This ionic liquid has revealed superiority above ionic liquids that can be synthesized easily, cheap, less toxic i.e. not dangerous for the surroundings in comparison with greatest number of other ionic liquids. Overall, we believe this investigation intensively studied physical properties, with regard to viscosity; conductivity and density as a function of temperature. Accordingly, 1ChCl: 2Urea ionic liquid is considered a poor ionic liquid due to the low conductivity and high viscosity. Extra research is essential to increase the ionicity of the ionic liquid. The microscopic structure of 1ChCl: 2Urea system through FTIR spectroscopy shows the possibility of formation of supplementary hydrogen bonding among urea and choline chloride. Also, the structure of choline chloride is dominant during the interaction with urea to form the 1ChCl:2Urea ionic liquid. Finally, the thermo-gravimetric analysis curve is two forms, in the first form the mass loss is evenly, while in the second form the mass loss is not evenly. This ionic liquid lost only 10 w% at 200 oC which is relatively quite stable system, since most of the applications can be run below this temperature.

Acknowledgements- Firstly, the authors would like to direct their gratitude to the Soran research Centre, Garmian University and Tishk International University for their facility and entrance fee to obtainable implements. Please contact the corresponding author for any further assistance regarding the experimental part in this investigation. This study is partially supported by Garmian University and Tishk International University (TIU) Research Center.

References

1. Hu, J., et al., *Ion-selective electrodes with colloid-imprinted mesoporous carbon as solid contact*. Analytical chemistry, 2014. **86**(14): p. 7111-7118.
2. M. Bounagua, A. Bellaouchou, A. El Abidi, R. Ben aakame, M. Fekhaoui, *Mor. J. Chem* 8 N° 2 (2020) 359-366
3. Li, X., et al., *Nanostructured catalysts for electrochemical water splitting: current state and prospects*. Journal of Materials Chemistry A, 2016. **4**(31): p. 11973-12000.
4. A. Machrouhi, M. Farnane, A. Elhalil, M. Abdennouri, H. Tounsadi, N. Barka. *Mor. J. Chem.* 7 N°1 (2019)098-110
Mor. J. Chem. 9 N°1 (2021) 099- 108

5. Wu, S., et al., *A novel approach to fabricate carbon sphere intercalated holey graphene electrode for high energy density electrochemical capacitors*. Chemical Engineering Journal, 2017. **317**: p. 461-470.
6. Zhang, B., et al., *Mechanisms and properties of ion-transport in inorganic solid electrolytes*. Energy Storage Materials, 2018. **10**: p. 139-159.
7. Torimoto, T., et al., *New frontiers in materials science opened by ionic liquids*. Advanced Materials, 2010. **22**(11): p. 1196-1221.
8. Seddon, K.R., *Ionic liquids: a taste of the future*. Nature materials, 2003. **2**(6): p. 363.
9. MacFarlane, D.R., et al., *Ionic liquids and their solid-state analogues as materials for energy generation and storage*. Nature Reviews Materials, 2016. **1**(2): p. 15005.
10. Gebresilassie Eshetu, G., et al., *Energy storage materials synthesized from ionic liquids*. Angewandte Chemie International Edition, 2014. **53**(49): p. 13342-13359.
11. Cui, Y., et al., *Design, synthesis and properties of acidic deep eutectic solvents based on choline chloride*. Journal of Molecular Liquids, 2017. **236**: p. 338-343.
12. Zeng, Q., et al., *Deep eutectic solvents as novel extraction media for protein partitioning*. Analyst, 2014. **139**(10): p. 2565-2573.
13. Endres, F., A. Abbott, and D. MacFarlane, *Electrodeposition from ionic liquids*. 2017: John Wiley & Sons.
14. Smith, E.L., A.P. Abbott, and K.S. Ryder, *Deep eutectic solvents (DESs) and their applications*. Chemical reviews, 2014. **114**(21): p. 11060-11082.
15. Abbott, A.P., et al., *Novel solvent properties of choline chloride/urea mixtures*. Chemical Communications, 2003(1): p. 70-71.
16. Perkins, S.L., P. Painter, and C.M. Colina, *Molecular dynamic simulations and vibrational analysis of an ionic liquid analogue*. The Journal of Physical Chemistry B, 2013. **117**(35): p. 10250-10260.
17. Hammond, O.S., D.T. Bowron, and K.J. Edler, *Liquid structure of the choline chloride-urea deep eutectic solvent (reline) from neutron diffraction and atomistic modelling*. Green Chemistry, 2016. **18**(9): p. 2736-2744.
18. Abbott, A.P., et al., *Speciation, physical and electrolytic properties of eutectic mixtures based on CrCl₃·6H₂O and urea*. Physical Chemistry Chemical Physics, 2014. **16**(19): p. 9047-9055.
19. Nazari, S., et al., *Physicochemical properties of imidazo-pyridine protic ionic liquids*. Journal of Materials Chemistry A, 2013. **1**(38): p. 11570-11579.
20. Greaves, T.L., et al., *Protic ionic liquids: solvents with tunable phase behavior and physicochemical properties*. The Journal of Physical Chemistry B, 2006. **110**(45): p. 22479-22487.
21. Greaves, T.L. and C.J. Drummond, *Protic ionic liquids: properties and applications*. Chemical reviews, 2008. **108**(1): p. 206-237.
22. Lee, S.-Y., et al., *Nonhumidified intermediate temperature fuel cells using protic ionic liquids*. Journal of the American Chemical Society, 2010. **132**(28): p. 9764-9773.
23. Okoturo, O. and T. VanderNoot, *Temperature dependence of viscosity for room temperature ionic liquids*. Journal of Electroanalytical Chemistry, 2004. **568**: p. 167-181.
24. Janz, G.J., et al., *Molten salts: Volume 4, part 2, chlorides and mixtures—electrical conductance, density, viscosity, and surface tension data*. Journal of Physical and Chemical Reference Data, 1975. **4**(4): p. 871-1178.
25. Hayamizu, K., et al., *Ionic conduction and ion diffusion in binary room-temperature ionic liquids composed of [emim][BF₄] and LiBF₄*. The Journal of Physical Chemistry B, 2004. **108**(50): p. 19527-19532.
26. Constantin, V., A.K. Adya, and A.-M. Popescu, *Density, transport properties and electrochemical potential windows for the 2-hydroxy-N, N, N-trimethylethanaminium chlorides based ionic liquids at several temperatures*.

- Fluid Phase Equilibria, 2015. **395**: p. 58-66.
27. Angell, C.A., Y. Ansari, and Z. Zhao, *Ionic liquids: past, present and future*. Faraday discussions, 2012. **154**: p. 9-27.
28. Barzinjy, A. and M. Zankana, *A Novel Application of the Quartz Crystal Microbalance for Determining the Rheological Properties of the Highly Viscous Liquids*. Acta Physica Polonica A, 2016. **130**(1): p. 239-244.
29. Morrison, H.G., C.C. Sun, and S. Neervannan, *Characterization of thermal behavior of deep eutectic solvents and their potential as drug solubilization vehicles*. International journal of pharmaceutics, 2009. **378**(1-2): p. 136-139.
30. Dumas, J.P., et al., *Model for the DSC thermograms of the melting of ideal binary solutions*. Thermochimica acta, 2013. **571**: p. 64-76.
31. Ren, H., et al., *The properties of choline chloride-based deep eutectic solvents and their performance in the dissolution of cellulose*. BioResources, 2016. **11**(2): p. 5435-5451.
32. Barzinjy, A.A., S.M. Hamad, and A.F. Arkawazi, *Ionic Liquids: Sustainable Media for Nanoparticles*. Jordan Journal of Physics, 2019. **12**(1): p. 45-62.
33. Barzinjy, A.A.A., *Electrodeposition of Ni-Cr alloy from Ethaline Deep Eutectic Solvent*. ZANCO Journal of Pure and Applied Sciences, 2016. **28**(2).
34. Alrbaey, K., et al., *Electropolishing of Re-melted SLM Stainless Steel 316L Parts Using Deep Eutectic Solvents: 3 × 3 Full Factorial Design*. Journal of Materials Engineering and Performance, 2016: p. 1-11.
35. Yue, D., et al., *Structure and electrochemical behavior of ionic liquid analogue based on choline chloride and urea*. Electrochimica Acta, 2012. **65**: p. 30-36.
36. Ge, X., et al., *Deep eutectic solvents (DESS)-derived advanced functional materials for energy and environmental applications: challenges, opportunities, and future vision*. Journal of Materials Chemistry A, 2017. **5**(18): p. 8209-8229.