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سەرۆکایەتی ئەنجومەنی وەزیران
وەزارەتی خوێندنی بالا و توێژینه‌وه‌ی زانستی
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ب/ هه‌سه‌نگاندنی توێژینه‌وه‌کان سه‌باره‌ت به‌ به‌زرکردنە‌وه‌ی پلەی زانستی
بە‌زرکردنە‌وه‌ی پلەی زانستی له (مامۆستای یارده‌ده‌ر) بۆ () (مامۆستا)

بە‌رپێژ /

دواى رێزوسلاو....

له‌به‌ر ناوبانگی كه‌سایه‌تی زانستی به‌رپێژتان لیژنه‌كه‌مان به‌ خوشحالی یه‌وه جه‌نابتانی ده‌ستنیشان کردووه بۆ هه‌سه‌نگاندنی ئەم
توێژینه‌وانه‌ی لای خوارموه، و داواکارین له‌به‌رپێژتان له‌ماوه‌ی یه‌ك مانگدا وه‌لامان بده‌یته‌وه‌ له‌ به‌رواری وەرگرتنی نووسراومان .
له‌گه‌ل رێژدا.....

ناونیشانی توێژینه‌وه‌کان:

- 1- Improvement of chemical, thermal, and mechanical properties of Polypropylene (PP) - Cellulose microcrystalline composites (CMC).
- 2- Research Article Physical, Thermal and Structural Properties of 1 Choline Chloride: 2 Urea Based Ionic Liquids

هاوینج:

١/ فۆرمی هه‌سه‌نگاندنی توێژینه‌وه‌.

٢/ وینه‌ی هه‌ر توێژیته‌وه‌یه‌کی لای سه‌رموه‌.

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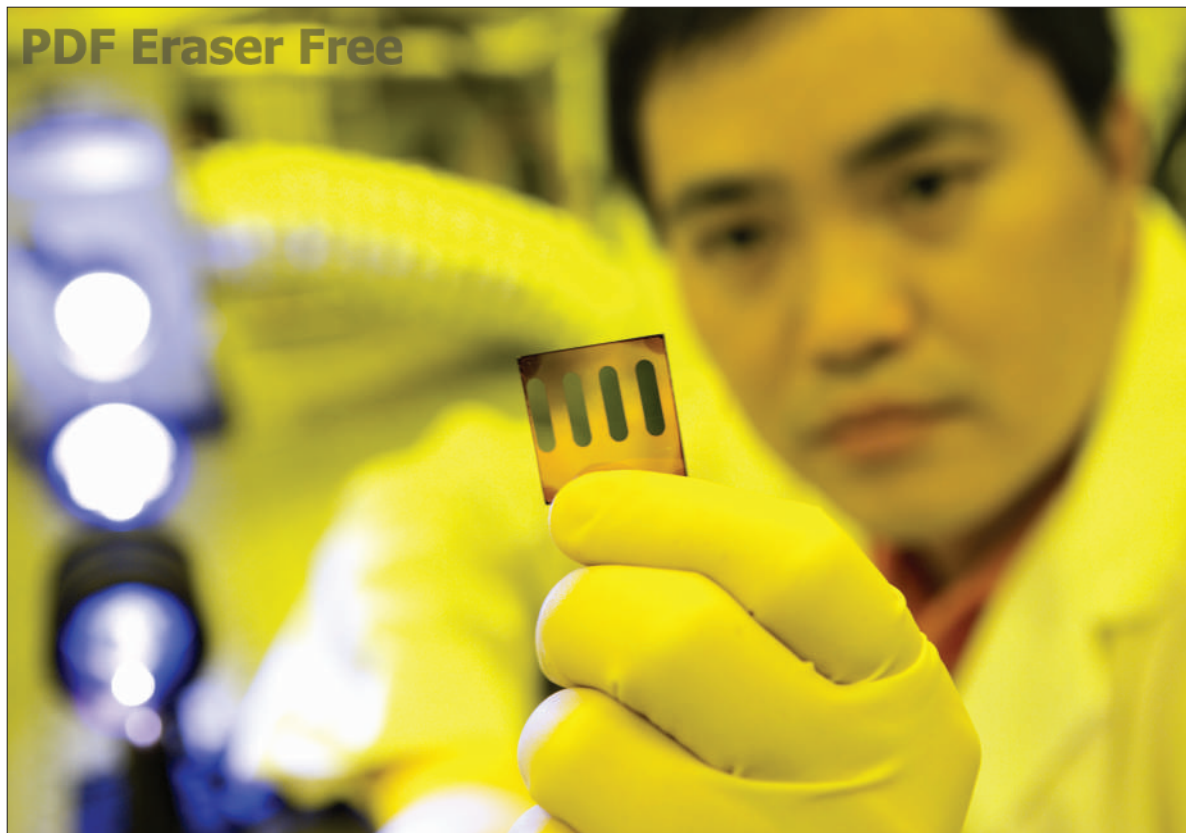
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Research Article

Physical, Thermal and Structural Properties of 1 Choline Chloride: 2 Urea Based Ionic Liquids

Abstract

Background and Objective: Deep eutectic solvents are, extensively, recognized as novel as well as green alternative solvents to the conventional ionic liquid owing to their low cost and tolerance to moisture. This study was conducted to analyze the physical, thermal and structural properties of 1 choline chloride: 2 urea based ionic liquids. **Materials and Methods:** Firstly, the physical properties, in terms of viscosity, conductivity and density as a function of temperature are investigated intensively. Later, the microscopic structure of 1 choline chloride:2 urea 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. **Results:** Walden distribution indicated that the synthesized ionic liquid in this investigation is categorized as a poor ionic liquid. The investigated ionic liquid is, relatively, thermally stable and the melting point of this ionic liquid initiated at around 17°C and finalized at around 25°C. The construction of choline chloride is remained during the formation of the ionic liquid. **Conclusion:** Generally, the obtained data and inspections are in an excellent agreement with the previous studies.

Key words: Deep eutectic solvents, ionic liquids, choline chloride, urea, physical properties

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

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 uninterrupted making. Consequently, it is extremely preferred to invent solvents that are green naturally and besides, that are economically in expensive. 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 science¹. 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 solution². Certainly, in their essential investigation countless thrilling innovations, have been described and shortened^{1,3,4}. 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 development⁵. 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 (Fig. 1).

DESs, in general, can be made through a definite molar ratio of quaternary ammonium salts, hydrogen-bond acceptors and hydrogen-bond donors⁶. The term eutectic originates from a Greek expression that means "simply melted" and specifies the temperature where the stages all together crystallize from molten solution⁷. 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 classes⁸. The 1st DES was proposed by Abbott *et al.*⁹: the eutectic amalgamation of ChCl and urea (Fig. 2).

Figure 2 explains the chemical construction and charge density of ChCl, urea and the shaped DES. Obviously, an interaction among the hydrogen atom attached with the oxygen atom of ChCl cation was heading for the oxygen atom

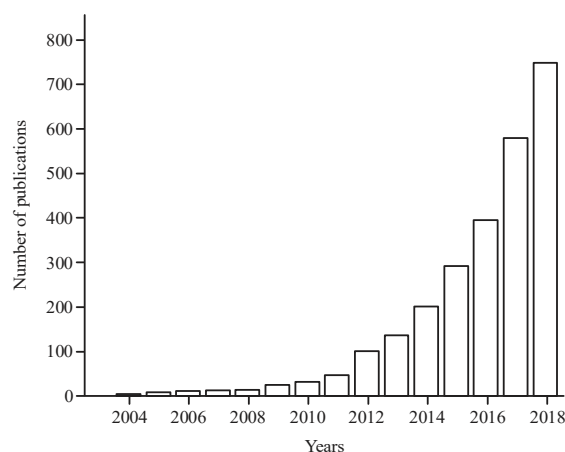


Fig. 1: Number of publications according to the web of knowledge search for the expression "DES" in 10 March, 2019

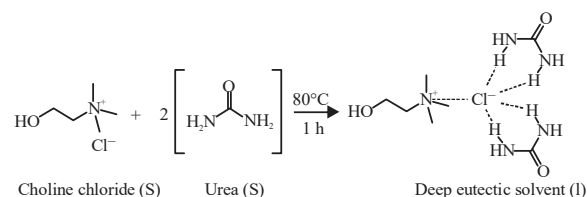


Fig. 2: Synthesis of 1 ChCl:2 urea DES

of urea. This is a novel interaction that might happen throughout the DES amalgamation. It ought to be renowned that the Abbott *et al.*⁹ and Perkins *et al.*¹⁰ 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 Reline¹¹ 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. Previously, it was stated that DESs are commonly divided into four groups¹². 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 viscosities¹³. In addition, the construction of the anion has a great impact on the viscosity and typically beyond the configuration of the cation¹⁴. 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 accumulation¹⁵. Hence, fewer ionic-interaction and further delocalized charge causes greater conductivity, thus, more ionic-conductivity standards will be predictable for the stronger Bronsted acids¹⁶. 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.

DES possesses many applications in different area, therefore there is a need to understand the physical properties, namely phase behavior, viscosity, conductivity and density. Then through the Walden rule, which is of the correspondent molar conductivity alongside with the logarithm of the fluidity, one can investigate the ionicity of the utilized DES. Therefore, one of the objectives here is to comprehend more explicitly what is signposted by such a high degree of conformity with the Walden rule. The microscopic structure of the DES can be investigated by means of FTIR spectroscopy. Differential scanning calorimetry (DSC) which is one of the supreme effective thermal analysis techniques to determine the energy absorbed or released by a sample as it is heated or cooled utilized to study the thermal stability, melting temperature and in do/exothermic reactions. The aim of this study was to analyze the 1 choline chloride:2 urea on physical, thermal and structural basis and their properties.

MATERIALS AND METHODS

Study area: The preparation of the ionic liquids in this investigation was carried out at department of Chemistry, College of Education, University of Garmian, Sulaimani, Iraq. While the characterizations were carried out at Scientific Research Centre, Soran University, Erbil, Iraq, from January, 2019 until October, 2019.

Ionic liquid preparation: Choline chloride ($(\text{CH}_3)_3\text{N}(\text{Cl})\text{CH}_2\text{CH}_2\text{OH}$, Sigma Aldrich, $\geq 99\%$) and urea (Sigma Aldrich, $>99\%$) were utilized as received. The DES was made by mixing 1 mole of ChCl with 2 moles of urea together and heating, with stirring, at 80°C up to a homogeneous colorless liquid had made as explained in Fig. 3.



Fig. 3: Graphical representation of formation DES from 1 ChCl and 2 urea

Ionic liquid characterization: In this study the kinematic-viscosity and electrical conductivity of the 1 ChCl:2 urea system was cautiously recorded from $25\text{--}80^\circ\text{C}$ at the atmospheric pressure. The viscosity and conductivity recording were taken after 5 min at every single temperature to offer an acceptable temperature counterbalance. For measuring the viscosity of the ionic liquid the authors utilized the Ubbelohde viscometer through the constants 0.099, 0.300 in HERZOG Triplex-Verizon 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.

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°C then heated from -150°C to $+130^\circ\text{C}$ at a rate of $10^\circ\text{C min}^{-1}$ afterwards cooling to -150°C and lastly heated back to 130°C with the similar heating speed. The thermo graphical representation displayed a distinctive sharp endothermic peak equivalent to the melting point of the configurations. FTIR analysis was made utilizing a Perkin Elmer FTIR spectrophotometer with a resolve of 4 cm^{-1} .

RESULTS AND DISCUSSION

Physical properties: From the data obtained in this study, it can be noted that, the 1 ChCl:2 urea 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 temperature dependence of viscosity of ionic liquids obey the Arrhenius equation¹⁷ or Vogel equation¹⁷ and the identical can be utilized for 1 ChCl:2 urea system.

Figure 4 shows the linear relationship among conductivity and the reciprocal of viscosity of the 1 ChCl:2 urea system. As anticipated, the conductivity of the ionic liquid increased with the increasing fluidity, i.e., the reciprocal of viscosity. Moreover, this trend has been found in other ionic liquid systems¹⁸. The higher viscosity of the 1 ChCl:2 urea system is due to the creation of strong hydrogen bonds comparing to the other ionic liquids or even high-temperature molten-salts¹⁹.

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. Walden rule is more applicable to be utilized for molten-salts and ionic liquids²⁰. In this study the Walden rule has been used (Fig. 5) to identify the position of the 1 ChCl:2 urea ionic liquid among the other types of liquids. Although ionic liquids are liquids consist of entirely of ions, not all of the existing ions seem to be contribute in conduction procedures. There is plentiful curiosity in counting and highlighting the degree of ionicity²¹. The reason behind using Walden rule is because it is a good indicator in order to differentiate between the non, poor, good and super ionic liquids²². Also, Walden rule is an estimated and enthusiastically available method to guesstimating ionicity.

From Fig. 5 that the solid prototypical, blue, line relates to a diluted aqueous 0.01M KCl solution wherein the system is recognized to be completely distanced and to possess ions of equivalent mobility and offer a suitable standardization point²³. According to Walden distribution the synthesized ionic liquid in this investigation is categorized as a poor ionic liquid. This was expected since 1 ChCl:2 urea ionic liquid possess high viscosity due to the hydrogen bonding. Apart from a few exceptions²⁴, most ionic liquids locate underneath the KCl line. This can be transcend through adding a suitable

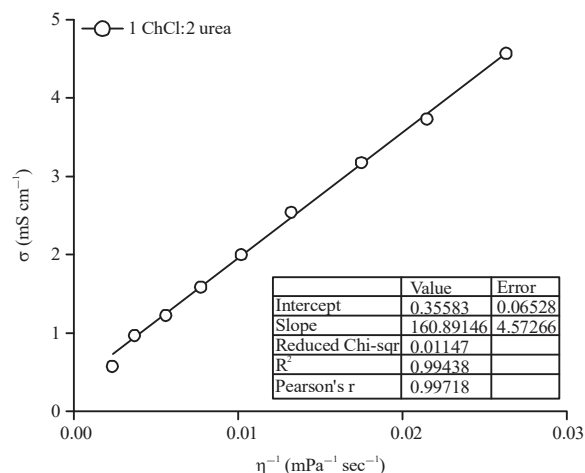


Fig. 4: Conductivity vs. the inverse of viscosity (fluidity) of the 1 ChCl:2 urea system

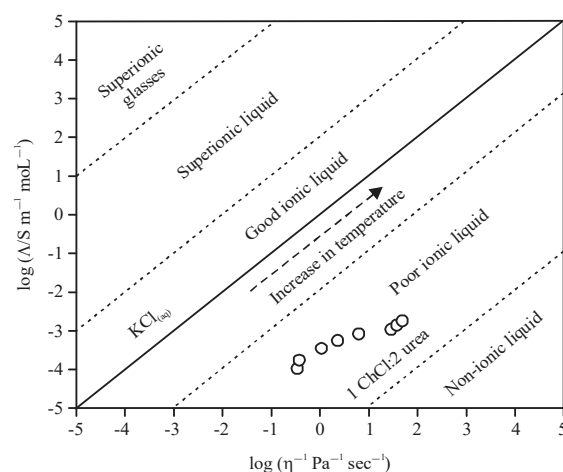


Fig. 5: Walden plot of log of molar conductivity alongside with log of fluidity for 1 ChCl:2 urea system

amount of water to this ionic liquid²⁵, so that we can move 1 ChCl:2 urea from poor ionic liquid to good ionic liquids. Some of the ionic liquids investigated previously display ionicity values nearby the good ionic liquids²¹, this is considered in the way that the ion associations have analogous influence on both the diffusion and conduction motions.

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 Fig. 6, the melting temperatures are ~302 and ~134°C for choline chloride and urea, respectively. These outcomes are in an excellent covenant with Morrison *et al.*²⁶. While, in a eutectic system, chemical compounds usually in solid phase

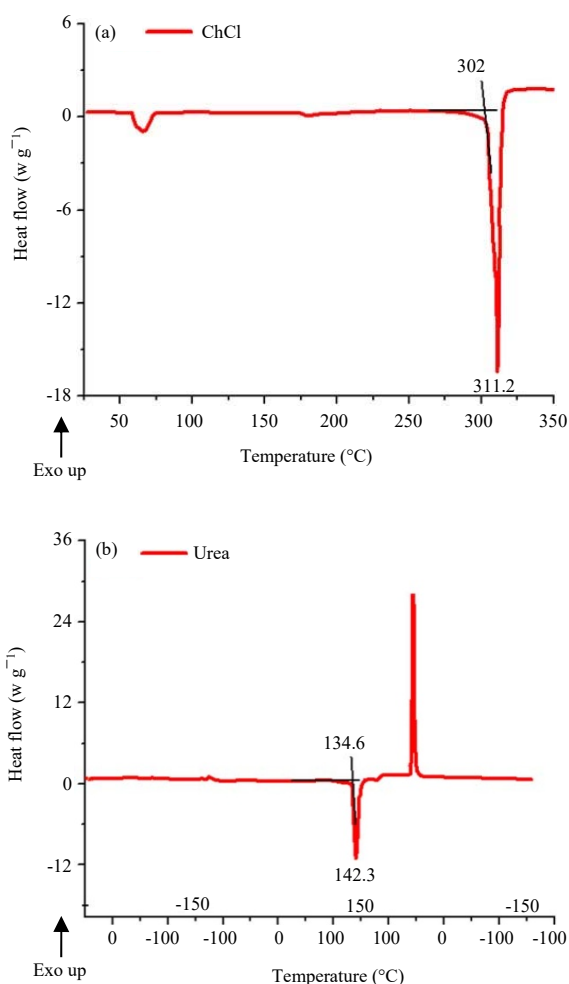


Fig.6(a-b): DSC curve for melting point measurement (a) ChCl and (b) Urea

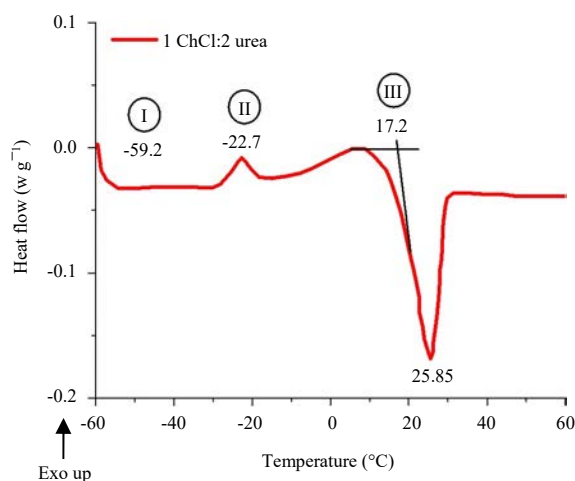


Fig. 7: DSC thermogram curve of 1 ChCl:2 urea mixture

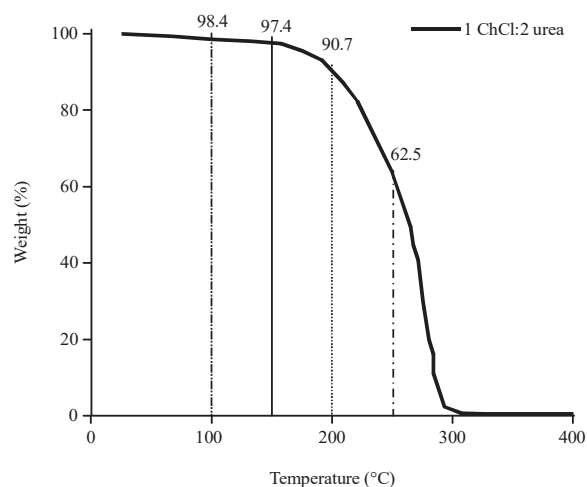


Fig. 8: Thermogravimetric analysis of 1 ChCl:2 urea ionic liquid system

are melted at a lower temperature than the melting temperature of any individual compounds to form eutectic solvent.

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 1 ChCl:2 urea 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 Fig. 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, 1 ChCl:2 urea. Within heating the ionic liquid from 60°C, an exothermic peak with an inception temperature of ~27°C was detected (Fig. 7). This was subsequent via an endothermic peak with an inception temperature of ~17.2°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 broader²⁷. Additionally, there are many hydrogen bonds among molecules in 1 ChCl:2 urea ionic liquid, which might lead to the wide range melting temperature.

Figure 8 shows the thermo-gravimetric analysis curve performed on the 1 ChCl:2 urea system. On this curve, it is possible to observe two zones, one where the temperature is $T < 150^\circ\text{C}$ and the other is $T > 150^\circ\text{C}$. 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

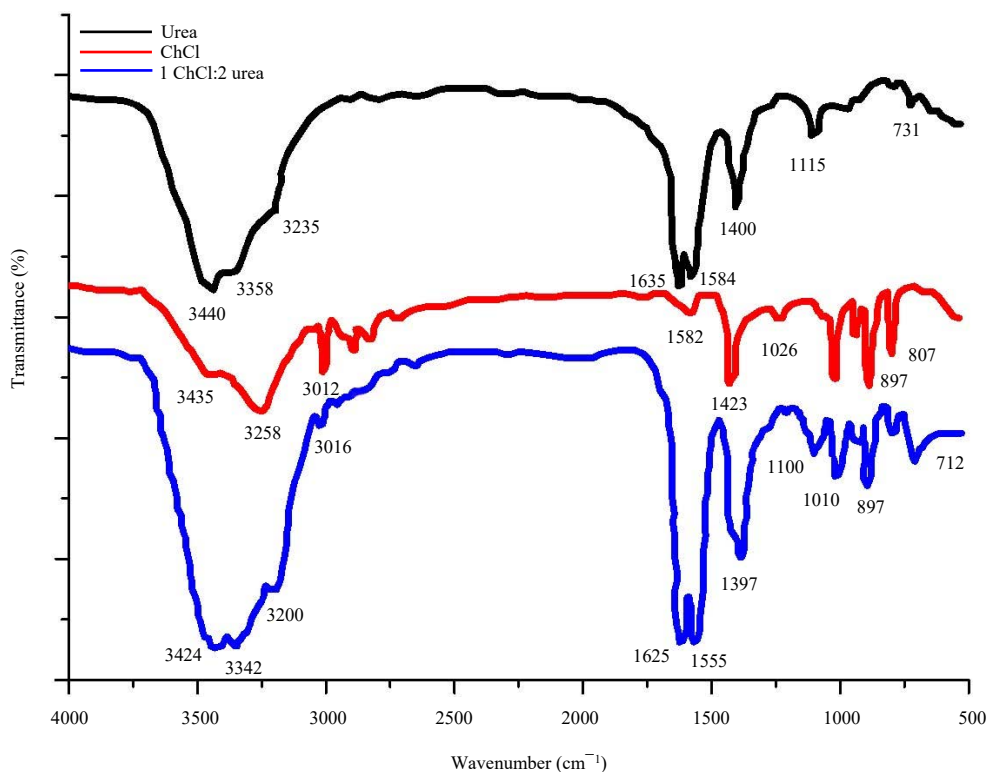


Fig. 9: FTIR spectrum of urea, ChCl and 1 ChCl:2 urea system

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 1 ChCl:2 urea 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 Ren *et al.*²⁸. It can be noted from Fig. 8 that the system lost nearly 10 and 38 w% at 200 and 250°C correspondingly. In fact, the stability of this type of ionic liquid is quit acceptable, because most of the applications of it can be done below this range^{12,29-31}.

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 1 ChCl:2 urea ionic liquid system. Figure 9 illustrates the FTIR spectra of urea, ChCl and 1 ChCl:2 urea system. It can be seen that, approximately, the typical spectrum of the 1 ChCl:2 urea ionic liquid system is an overlay of those of urea and choline chloride. Moreover, the absorption bands at 3440, 3358 and 3235 cm⁻¹ in urea and 3435, 3258 and 3012 cm⁻¹ in ChCl changed to broader band

in 1 ChCl:2 urea ionic liquid system. This is, perhaps, caused by the construction of additional hydrogen bonds among urea choline chloride³². Besides, the bands related to choline chloride, seemed in spectrum of 1 ChCl:2 urea system. This can be an indicator to reveal that the construction of ChCl was not destroyed in the 1 ChCl:2 urea ionic liquid system³³. The extra hydrogen bonds possibly occur as, O-H...N-H, O-H...O and O-H...OH as shown in Fig. 9.

The present study is proposed to add different explanation in terms of physical, structure and thermal properties in details. Since for any novel ionic liquids it is essential to characterize the physical, structure and thermal properties, to found their importance in commercial applications. From the thermal properties point of view one can set the optimum operation conditions. Whereas, the physical properties such as density, viscosity and conductivity could offer vital evidence on the pureness of samples and the molecular interaction in the liquid. Up to now, thermal and physical properties of 1 ChCl:2 urea have not yet been comprehensively studied. In similar study, Morrison *et al.*²⁶ described the thermal properties ChCl base ionic liquid systems and then examined whether theses ionic liquids can be utilized to improve solubility of poorly water soluble mixtures³⁴.

CONCLUSION

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 1 ChCl:2 urea ionic liquid. This ionic liquid has revealed superiority above ionic liquids that can be synthesized easily, cheap, biodegradable, 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, 1 ChCl:2 urea 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 this ionic liquid. The microscopic structure of 1 ChCl:2 urea system through FTIR spectroscopy shows the possibility of formation of supplementary hydrogen bonding among urea and choline chloride. Also, the structure of choline chlorides dominant during the interaction with urea to form the 1 ChCl:2 urea 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°C which is relatively quite stable system, since most of the applications can be run below this temperature. This attempt aimed to extend the thermal and physical properties of 1 ChCl:2 urea because it has not yet been comprehensively studied.

SIGNIFICANT STATEMENT

This study provide an easily synthesized, cheap, biodegradable and less toxic ionic liquids which is not dangerous for the surroundings in comparison with greatest number of other ionic liquids. This study will help the researcher to understand the physical properties, with regard to viscosity, conductivity and density as a function of temperature. Thus, encouraging the researchers to do extra research to increase the ionicity of this ionic liquid is essential since this ionic liquid is considered a poor ionic liquid due to the low conductivity and high viscosity.

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