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ORIGINAL ARTICLE

Investigation on the Formation of L-lysine Based Ternary Deep Eutectic Solvents and Their Properties

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DES is normally made up of two or more components, all of which are linked together by H-bonds. Abbott and colleagues were the ones who first proposed the concept of DES. As a mixture of two or more components forming an eutectic, the melting point of this eutectic mixture is lower than the individual components of that mixture. The usage of a totally enormous within the freezing point, as well as the capacity to exist in liquid state temperatures is below 150oC. DES, as a new type of green solvent, has certain - reputed properties, such as “high viscosity, high thermal stability and low vapor pressure”. L-lysine-glucose-malonic acid, L-lysine-fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ are three types of ternary deep eutectic solvents (TDESs) that we created in this study. They exist as a clear liquid for more than two weeks at room temperature. Its physical properties, such as “conductivity, density, viscosity pH and thermal properties as the thermal decomposition temperature” of these TDES were studied. The FTIR Spectra of those TDESs have been analyzed to apprehend the interaction of H bonds and three components.

Key words: Deep eutectic solvent, L-Lysine, Glucose, Fructose, ZnCl2, Malonic acid, FT-IR

Ionic liquids (ILs) have sparked a surge of interest in the recent two decades, particularly in the fields of catalysts, electrochemistry process technology and analytics, biotechnology, and functional liquids. Ion solvents (ILs) are solvents made entirely of ions. IL synthesis can be divided into two categories: those made from eutectic mixes of metal halides and organic salts, and those made from discrete anions (Smith *et al.*, 2014). Because of the growing demand for organic solvents and the expensive cost of ILs (Zhang *et al.*, 2012) researchers have increasingly concentrated on ionic liquid equivalents, such as deep eutectic solvents (DESs), which were first developed by Abbot.et.al. in 2003 (Abbott *et al.*, 2003).

DESs are made up of two or more compounds that have a lower melting factor than their constituent compounds (Zhang *et al.*, 2012, Abbott *et al.*, 2003). Furthermore, combination salt and a hydrogen bond donor (HBD),Which forms DESs resulting in hydrogen bonds with salt anion (organic and inorganic) and unique forms of HBDs (Abbott *et al.*, 2004). DESs have physicochemical properties that are similar to those of traditional ILs (Abbott *et al.*, 2004a). DESs, on the other hand, have a number of advantages over conventional ILs, including ease of synthesis, cheaper manufacturing costs, low or insignificant toxicity profiles, and long - term environmental and economic benefits (Hayyan *et al.*, 2013, Hayyan *et al.*, 2015, Hayyan *et al.*, 2013a).

DESs have recently been used in a variety of applications, including the usage of ChCl- based DESs as functional derivatives for starch-based plastics (Leroy *et al.*, 2012). They have also been used as catalysts in biodiesel fuel production from low-grade palm oil (Hayyan *et al.*, 2014, Hayyan *et al.*, 2013b), as an electrolyte in electrochemical processes like deposition of specific metals in electroplating of metals (Abbott *et al.*, 2008, Abbott *et al.*, 2007), and as visible co-solvents in enzyme-catalyzed epoxide hydrolysis (Lindberg *et al.*, 2010). Deep eutectic solvents (DESs) are now widely recognized as new appealing and environmentally friendly alternatives to ionic liquids (ILs) and extensive research into DESs has been conducted in the recent year.

The possibility of forming ternary deep eutectic solvents (TDES) has recently been investigated with the goal of improving their properties for their intended applications. Dai et.al reported that TDES could be made by combining various plant abundant primary metabolites (i.e., sugars, alcohols, amino acids, organic acids, and choline derivatives) in various ratios, and coined the term “natural deep eutectic solvents” (NADES), which was then used to study biomolecule solubilization in NADES Liu *et al.*, (2008) successfully synthesized a series of TDES and estabilished their physical properties utilizing imidazolium halides, zinc halides and amides. The physical and chemical characteristics of TDES including ChCl, urea, and nickel chloride and hexahydrate were reported by Wang et. al. (Wang *et al.*, 2014). Amino acids are one of the alternative components that have been employed before (Song *et al.*, 2012, Portugal *et al.*, 2019, Majchrowicz, & Brilman, 2012, Sistla, & Khanna, 2015) among the third components used for DES production.

A common amino acid, L-arginine (0.05,0.10,0.15, and 0.20 mol) was mixed to (Choline chloride + urea) to generate ternary deep eutectic solvents, according to Chemat *et.al*. The physical parameters of density, viscosity (298.15-353.15) K, and refractive index (298.15-333.15) K were measured as well as the thermal properties of melting point, glass transition temperature, thermal decomposition temperature, and molar heat capacity. The addition of L-arginine to eutectic solvents improves their thermal stability (Chemat *et al.*, 2016).

To extract proteins, Hongmei Zhang et.al. compared ternary and binary deep eutectic solvents (DESs) with aqueous two-phase systems (ATPSs). Four binary DESs and four ternary DESs were created, each containing a hydrogen bond acceptor (tetramethylammonium chloride, TMAC) and hydrogen bond donors. Binary DESs were more susceptible to estabilishing a two-phase splitt, according to the phase diagrams of the examined DESs. Following that, their ability to extract four different compounds was assessed. The systems based on ternary DESs were shown to have potential in the field of extraction. TMAC-urea (TMAC-U) and TMAC-glycerol-urea (TMAC-G-U)

DESs with ATPS were studied for five influence factors, including the amount of DES, salt concentration, and BSA mass (Zhang *et al.*, 2016).

Andrea Skulcova et.al was reported, the physical properties and thermal behaviour of innovative ternary green solvents (TGESs) in a nitrogen atmosphere. Physical parameters like as density and viscosity are critical for any solvent. Thermal stability is a critical quality for future TGES applications. Since it determines the thermal limits of their actual use. Choline chloride, proline, betaine, alanine, glycerol, propanediol, ethyleneglycol, urea, malonic acid, malic acid, lactic acid, and citric acid are among the three elements that make up TGESs. In the temperature range of 25-400^{0}C, their thermal stability was thoroughly investigated. Finally, the mass drop of the examined TGESs was used to analyse various temperature features. The outcomes of this study add to our understanding of innovative green solvents (Škulcová *et al.*, 2019).

Deep eutectic solvents (DESs) were studied as suitable medium for enzymatic hydrolysis by Rashid Shahdiah et.al. (2021). By mixing aqueous glycerol with ternary ammonium and phosphonium -based DES in various molar ratios, a series of ternary ammonium and phosphonium -based DESs were created (85 percent). At temperatures ranging from 298.15 K to 363.15 K, physicochemical characteristics such as surface tension, conductivity, and viscosity were measured. Temperature variations have a significant impact on the eutectic points. Choline chloride:glycerol:water (ratio: 1:2.55:2.28) and metyitriphenylphosphonium bromide:glycerol:water (ratio:1:4.25:3.75) have eutectic points of 213.4 K and 255.8 K, respectively (Rashid *et al.*, 2021).

MATERIALS AND METHODS

Preparation of TDESs:

L-lysine, glucose and malonic acid are dissolved in water in a 1:1:1 molar ratio until the solution is transparent. The ensuing liquid was maintained at room temperature for fifteen days in a dessicator containing anhydrous $CaCl_2$. Similarly, “other TDESs” are prepared. Since turbidity was not observed during this observation period, the thermal and physical properties of TDES were examined.

Characterization of TDESs:

TDES conductivity was studied using the SYSTRONICS304 Conductivity Meter at room temperature. The density of TDES was studied at room temperature using a standard Pycnometer. The pH values of these TDESs were studied using an ELICO digital pH meter and studied using “LI120” using synthetic CL-51B electrodes. For these three TDESs, fluctuations of conductivity, density and pH with temperature were also studied. The FTIR spectrum was obtained using a Perklin Elmer version 10.03.09 to analyze the interaction of binding to hydrogen.

Thermogravimetric analyzer (Perklin-Elmer/pyris) was used to regulate the thermal decomposition temperature of L-lysine-glucose-malonic acid, L-lysine-fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ TDESs. The Sample is heated at a rate of 10^{o}C min^{-1} within the temperature range of 30^{0}C to 500^{0}C in a crucible beneathneath a nitrogen atmosphere (flow rate 20 ml…min^{-1}).

RESULTS AND DISCUSSION

The Conductivity Measurements of TDESs:

In familiar, the conductivity of TDESs increases as temperature increases. In this study, TDESs conductivity values the temperature of 300-350K. The consequences indicated that L-lysine-fructose-malonic acid has the maximum conductivity between the TDESs, i.e., 10.9 mScm^{-1} at 300 K and 15.3 mScm^{-1} at 350 K. It was found that the conductivity of the TDESs L-lysine -glucose-malonic acid, L-lysine-fructose- malonic acid, L-lysine -fructose -$ZnCl_2$ were7.4, 10.9, and 2.42 mScm^{-1}at 300 K respectively. The conductivity is directly proportional to the temperature, as shown in Fig.1.

Density Measurements of TDESs:

Density measurement is required for many fluidity and mass transfer accounts and chemical process arrangement projects. In this study, the densities of L-lysine-glucose-malonic acid, L-lysine-fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ were found to be 1.221, 1.312 and 1.391g. cm^{-3} respectively (Zhang *et al.*, 2012, Wasserscheid, & Welton, 2003, Naser *et al.*, 2013, Harris, 2009).

Viscosity Measurements of TDESs:

Viscosity is a necessary attribute feature that must be considered, particularly when designing equipment and calculating float (Harris, 2009) (table 1).

The pH:

At a temperature of 300K, the pH values of L-lysine-glucose-malonic acid, L-Lysine- fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ TDESs were 1.80, 2.12 and 2.42 respectively. The change in pH with temperature is shown in Fig.2. With increasing temperature, the pH values in L-Lysine-glucose- malonic acid and L-lysine-fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ increases slightly (Fig.2). The pH values of TDESs 300K to 350K (Zhang *et al.*, 2012, Skulcova *et al.*, 2018, Stuart, 2004).

Thermal Decomposition Temperature:

The changes in the thermal decomposition temperature of these TDESs were studied, and the weight of TDESs changed as the temperature increased (Fig.3). L-lysine based deep eutectic solvents L -lysine-glucose-malonic acid and an L -lysine - fructose - $ZnCl_2$ were found to be stable up to 140^{o}C, while the TDES of L-lysine-fructose-malonic acid was found to be stable till about 500^{o}C.

Fourier transform infrared spectrum analysis:

Fourier transform IR Spectrum of DES of L-lysine-glucose-malonic acid

At 3000-3459.63 cm^{-1}, the spectra of L -lysine-glucose-malonic acid appears to have a wide peak at 3000-3459.63 cm^{-1}. Carboxylic acid's O-H is usually observed about 3400 cm^{-1}. Stretching of the N-H molecule due to primary or secondary amines is expected to be 3300-3500 cm^{-1}. Because of hydrogen bond formation (AlOmar *et al.*, 2016, Ramesh *et al.*, 2019) of such organizations of L-lysine and malonic acid there is an extended top at 3000-3459.63 cm^{-1}. Around 1728.63 cm^{-1}, the CO stretching of malonic acid carboxylic acid and an L-lysine can be discovered. Malonic acid and an L-lysine CH_2 deformations were found at 1430 cm^{-1}. The height at 1622.83 cm^{-1} changed into because of the out C = N stretching of an L-lysine. The medium height at 912.58 cm^{-1} because of a C-N stretching of an L - lysine.

Fourier Transform IR Spectrum of DES of L-lysine-fructose-malonic acid

The spectrum of L-lysine-fructose-malonic acid appears to have a wide peak at 3000-3446.48 cm^{-1}. Carboxylic acid's O-H stretch is usually discovered about 3400 cm^{-1}. Because of the quantity of primary or secondary amines, N-H stretching is expected to be 3300-3500 cm^{-1}. The wide peak at 3000-3446.48 cm^{-1} is due to the estabilishment of hydrogen bonds between the L-lysine and malonic acid groups (AlOmar *et al.*, 2016, Ramesh *et al.*, 2019). Around 1725.50 cm^{-1}, the CO stretching of carboxylic acid of malonic acid and an L-lysine CH_2 deformations were found at 1440cm^{-1}. The peak at 1632.48 cm^{-1} turned into because of the out C = N stretching of an L-lysine. Because of C-N, the stretch of L-lysine medium top measures 819 cm^{-1}.

Fourier Transform IR Spectrum of L-lysine - fructose -$ZnCl_2$

There appears to be a large height at 3000-3476.10 cm^{-1} in spectrum of an L-lysine- fructose - $ZnCl_2$ TDES spectra. Carboxylic acids - OH stretching is usually measured at 3400 cm^{-1}. Generally the -OH stretching of carboxylic acids are observed at 3400 cm^{-1}. The N-H stretching is estimated to be 3300-3500 cm^{-1} due to both primary and secondary amines. The wide height at 3000-3476.10 cm^{-1} due to the creation of hydrogen bonds between Zinc chloride and L-lysine groups (AlOmar *et al.*, 2016, Ramesh *et al.*, 2019). - OH, stretch observed in TDES is 1460.91 cm^{-1} (Ramesh *et al.*, 2019, Pavia *et al.*, 2014). Due to the formation of hydrogen bonds between the fructose and L-lysine, a broad peak appears here at 3448.19 cm^{-1}. The CO stretch of L-lysine- fructose and carboxylic acid was observed near 1732.5 cm^{-1}. The deformation of CH_2 from fructose and L-Lysine is noted at 1507.58 cm^{-1}. The out C=N stretch of L-lysine was responsible for the peak at 1635.03 cm^{-1}. They claim that height of 1179.98 cm^{-1} is due to a C-N stretch of L-Lysine (Škulcová *et al.*, 2019) (Fig.6).

Table 1: Temparature value

DES	Viscosity	Temperature
L-lysine - glucose - malonic acid	540mPa s	300K
L-lysine - fructose - malonic acid	427.5mPa s	300K
L-lysine - fructose - $ZnCl_2$	507.5mPa s	300K

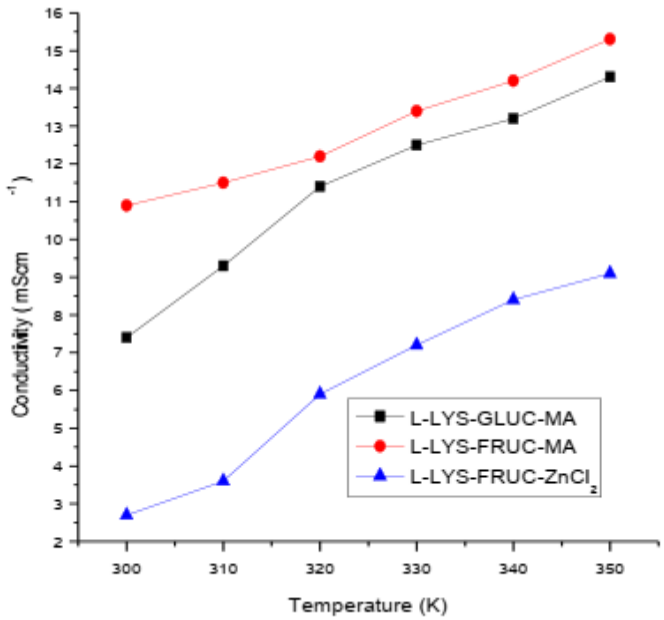

Figure 1: Conductivities for all TDESs.

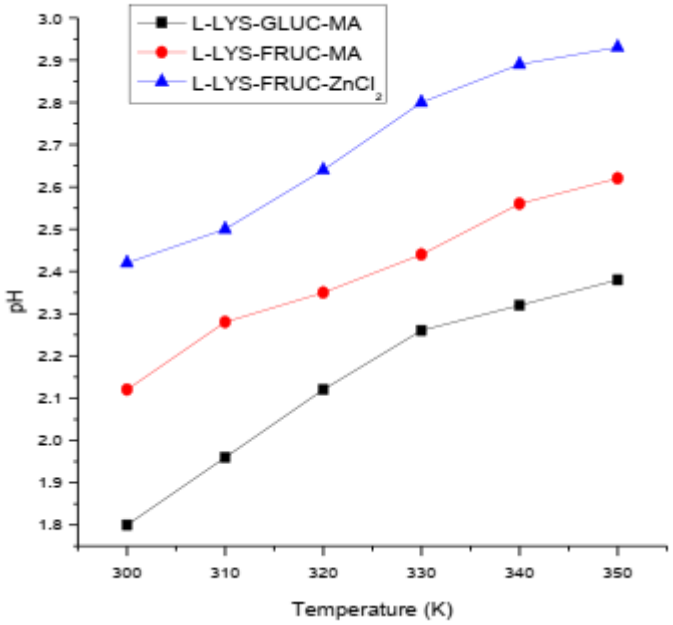

Figure 2: pH for all TDESs.

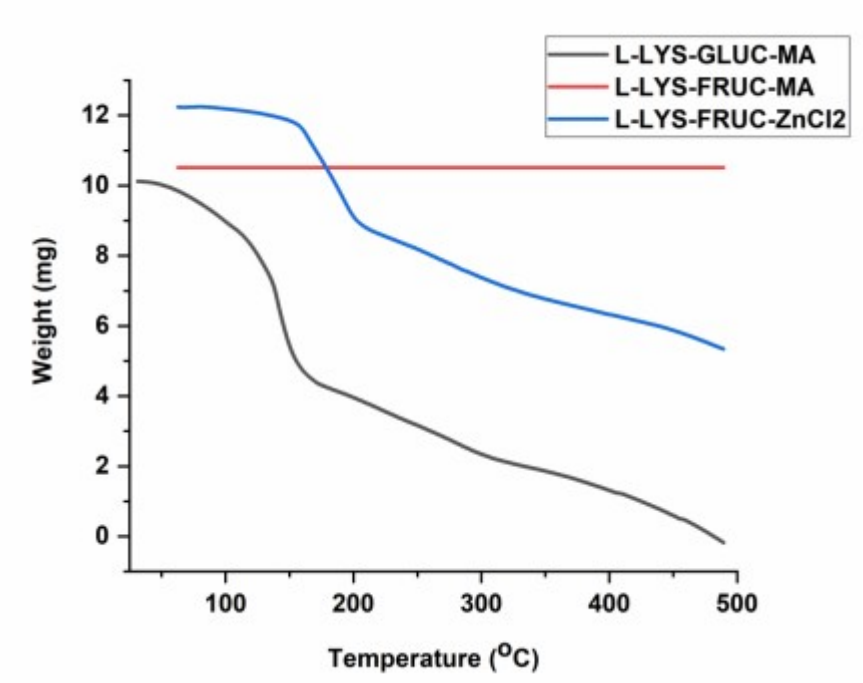

Figure 3: The Thermal decomposition Curve of all TDESs.

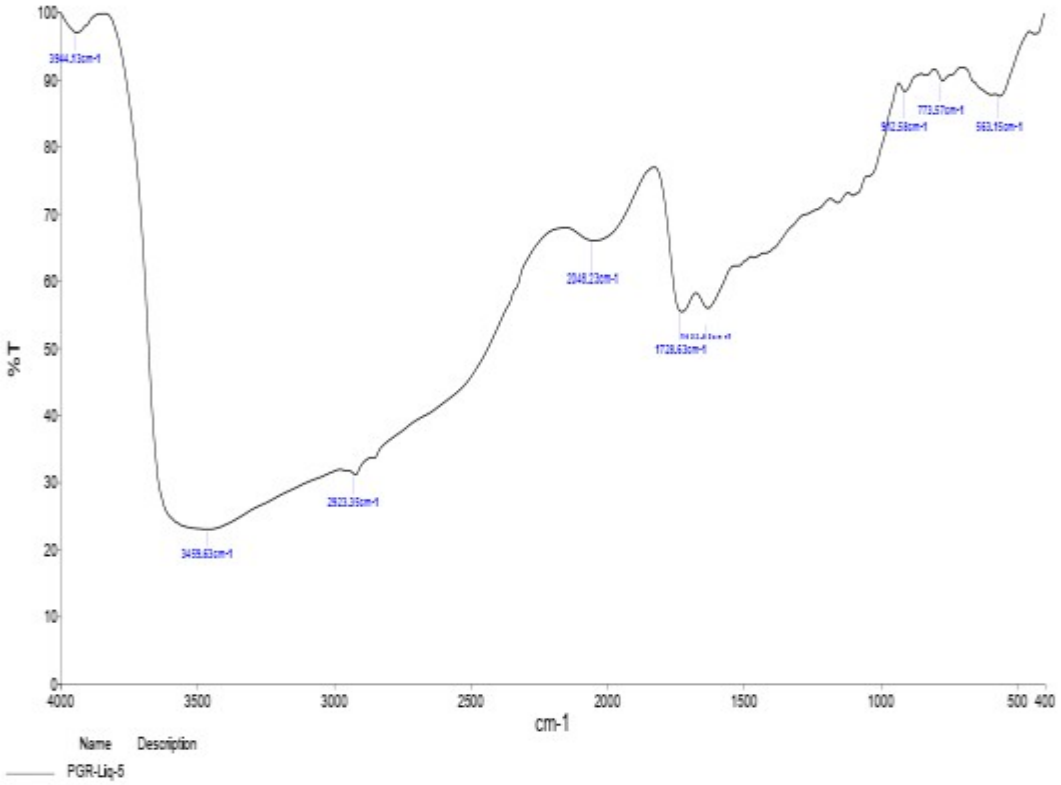

Figure 4: Fourier Transform IR Spectrum of TDESs of L -lysine -glucose-malonic acid

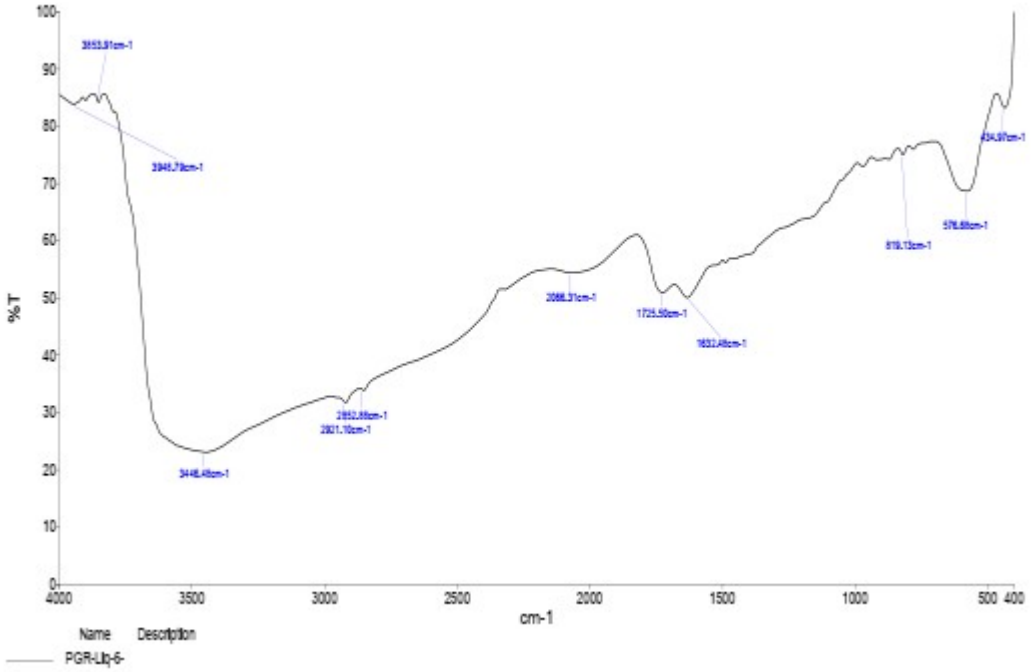

Figure 5: Fourier Transform IR Spectrum of TDESs of L-Lysine -fructose-malonic acid

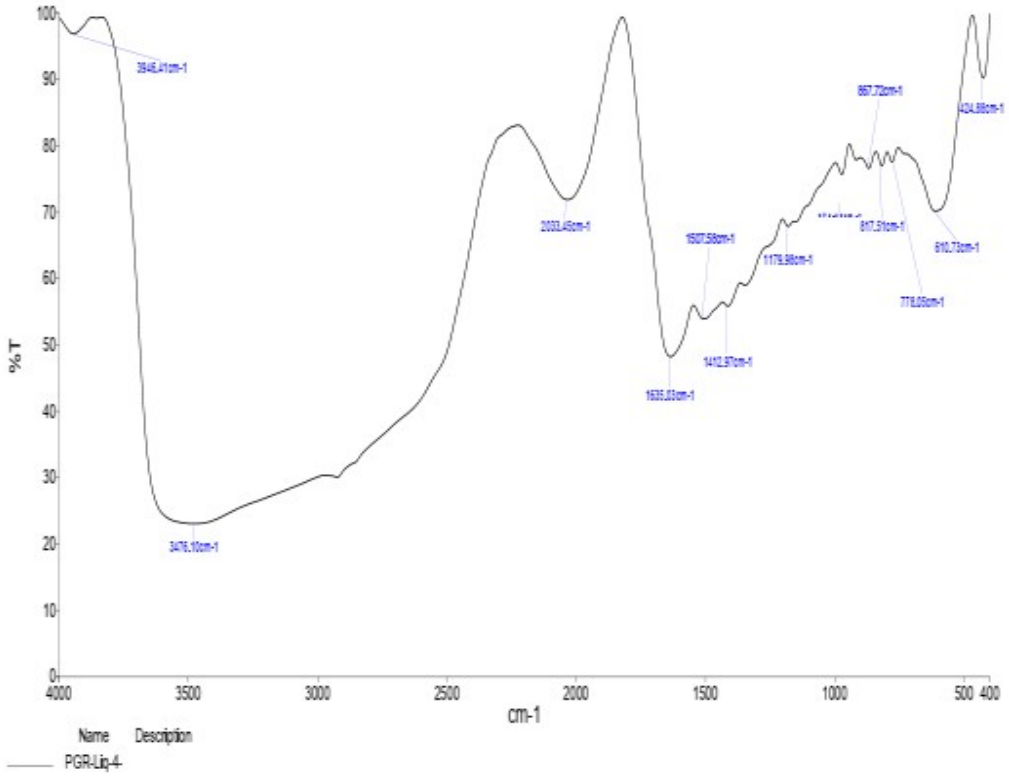

Figure 6: Fourier Transform IR Spectrum of TDES of L -lysine - fructose - $ZnCl_2$

CONCLUSION

In this work, 3 different TDESs L-lysine -glucose-malonic acid, L-lysine-fructose-malonic acid and L-lysine-fructose-$ZnCl_2$ were prepared a 1:1:1 mole ratio of three additives containing the least quantity of water. They have been around for more than 15 days as a clean liquid existed at room temperature. Their “bodily

houses" which includes conductivity, density, viscosity, pH, and the thermal decomposition temperatures have been measured of those TDESs. The FTIR Spectra of these TDESs are bought to understand the interaction of the H bond duration of TDESs formation. The extensive peaks found within side in the 3000 - 3400 cm^{-1} region of 3 types of TDESs offer enough for hydrogen bonding.

CONFLICTS OF INTEREST

The authors declare that they have no potential conflicts of interest.

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