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Thermal and Physical Properties of L-Lysine Based Deep Eutectic Solvents

P. G. Ramesh[1] and D.Ilangeswaran[2]

[1]Department of Chemistry, Swami Dayananda College of Arts & Science, Manjakkudi, Tiruvarur, Tamilnadu, India.

[2]Department of Chemistry, Rajah Serfoji Govt.College (Autonomous), Thanjavur, Tamilnadu, India.

Abstract

Now a day's green ionic liquid analogues is considered as deep eutectic solvents. The deep eutectic solvents is abbreviated as DESs. In the present study , a L – Lysine based DES with citric acid,tartaric acid, $MnCl_2$ and $ZnCl_2$ was synthesized at 1:1 mole ratios.The thermal properties namely thermal decomposition temperature, glass transition temperature and molar heat capacity were measured The physical properties namely conductivity, density, viscosity and pH measured and analyzed as a function of temperature.The temperature in the range 300 – 350K.The physical properties were correlated as a function of temperature to represent the present data. The revealation of FT-IR spectra show the physical and thermal property play a vital role to change its nature by forming the Hydrogen bond.

Keywords: *Deep Eutectic solvents, citric acid, tartaric acid, $MnCl_2$, $ZnCl_2$, L - Lysine, FT-IR*

1. Introduction

Deep eutectic solvents (DES) are emerging type of environmentally green solvents.As a new type of solvents, DES has an extremely large number of applications . Even though the problems associated with conventional volatile organic solvents are well studied, the usage of green and bio-degradable solvents still remains a never ending challenge [1]. In this sense, the advantages of using DESs as reaction medium is highlighted from the fact that they are bio-degradable, non-toxic, recyclable and could be easily prepared using inexpensive raw materials[2,4,6,9,14,15,17]. In recent years, low melting mixtures consisting of carbohydrates, urea,and inorganic salts have been introduced as new alternative sustainable solvent for organic transformations[8].

In the present work , it is proposed to 1:1 mole ratio of L-Lysine (citric acid,tartaric acid,$MnCl_2$ and $ZnCl_2$) based DESs and measured their thermal properties glass transition temperature,thermal decomposition tempperature and molar heat capacity as well as physical properties conductivity, density, viscosity and pH. These DESs were characterized by FT-IR Spectra to evaluate the association of L-Lysine with Citric acid, Tartaric acid, $MnCl_2$ and $ZnCl_2$ by hydrogen bond formation .

2. 2. Materials and Methods

2.1 Materials

The molecular formula, molecular weight and chemicals used in this work are listed in table.The chemicals were analytical reagent (A.R) grade are used . L-Lysine, Citric acid,Tartaric acid,and $MnCl_2$ and $ZnCl_2$ were used for the synthesis of the DESs.

Table1: Details of molecular formula and molecular weight of L-Lysine, Citric acid, Tartaric acid,$MnCl_2$ and $ZnCl_2$ used in the present work

S.No.	Component	Molecular Formula	Molecular Weight ($gmol^{-1}$)
1.	L-Lysine	$C_6H_{14}N_20_2$	146.19
2.	Citric acid	$C_6H_8O_7$	192.12
3.	Tartaric acid	$C_6H_6O_7$	150.08
4.	Manganese chloride	$MnCl_2$	125.83
5.	Zinc chloride	$ZnCl_2$	136.28

2.2 Synthesis of DESs

The mixture 1:1 mole ratio of (Citric acid, Tartaric acid, MnCl2 and $ZnCl_2$) with L-Lysine dissolved in water to a clear solution and subjected to the evaporation of excess water by gentle heating until a solution with constant weight is obtained. The resultant liquid was cooled to room temperature and kept in a dessicator for a fortnight. As there was no turbidity seen during this observation method was examined for its thermal and physical properties.

2.3 Glass transition temperature

The glass transition temperatures of L-Lysine based DESs (Citric acid- L-Lysine , Tartaric acid- L-Lysine, $Mncl_2$-L-Lysine , $ZnCl_2$-L-Lysine) mixtures were determined using a differential Scanning Calorimeter (Perklin Elmer pyris). The measurement was carried out under Nitrogen atmosphere with liquid nitrogen (room temp) cooling system .The first two samples were hermetically sealed in aluminium pans, the sample was first cooled from 500^0C to 40^0C with the heating rate of 10^0 C.

2.4 Thermal decomposition temperature

The thermal decomposition temperatures of (citric acid-L-Lysine, Tartaric acid-L-Lysine, $MnCl_2$- L-Lysine, $ZnCl_2$-Lysine) .The Samples were placed in a crucible under nitrogen atmosphere (flow rate 20 ml…min^{-1}) and heated at the temperature range from 30^0C to 500^0C (first two mixture) and 28^0C to 600^0C (third and fourth mixture) with the heating rate of 100^0C min $^{-1}$.

2.5 Molar heat capacity

The molar heat capacities of(citric acid- L-Lysine , Tartaric acid - L – Lysine , $MnCl_2$ -L-Lysine and $ZnCl_2$ L-Lysine) mixture were using determined using differential scanning calorimeter.The sample mass in the range of 40 to 70 mg was prepared and kept it .

2.6 Characterization of DESs

The conductivity of the DESs was measured using Systronics Conductivity Meter 304 at room temperature . The density of the DES was measured at room temperature using a standard Pycno meter . The pHof these four DESs were measured using digital pH meter of ELICO make model no LI120 using the combined electrode CL-51B.The variation of conductivity, density and P^H with temperature were also measured for these four DESs. The FTIR of the DESs were measured using a Perklin Elmer version 10.03.09.

3. RESULTS AND DISCUSSION

In the present work deep eutectic solvents of (Citric acid, Tartaric acid, $MnCl_2$, $ZnCl_2$) with amino acid L-Lysine were prepared to form BDES. The effect of L-Lysine on (citric acid, tartaric acid, $MnCl_2$, $ZnCl_2$) mixtures on the thermal properties namely glass transition temperature, thermal decomposition temperature and molar heat capacity and the physical properties namely conductivity, density and pH . The physical properties were correlated as a function of temperature to represent the present data[7]. These deep eutectic solvents were characterized by FT-IR Spectra to evaluate the association of L-Lysine with Citric acid, Tartaric acid, $MnCl_2$ and $ZnCl_2$ by hydrogen bond formation .

3.1 Thermal Decomposition temperature

The thermal decomposition temperature is able to study the thermal stability rampe temperature analysis [13] . The thermal stability of the DES have been schematically represented and obviously shown the function of temperature Vs weight in figure 1.

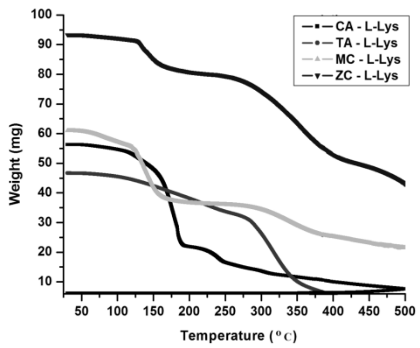

Fig.1The thermal decomposition temperatures of all DESs.

3.2 Molar heat capacity

The molar heat capacities of DESs (citrc acid-Glycine,malonic acid-Glycine) and (Ethylene Glycol-Tartaric acid) were measured temperature range from 30^oC to 130^oC.

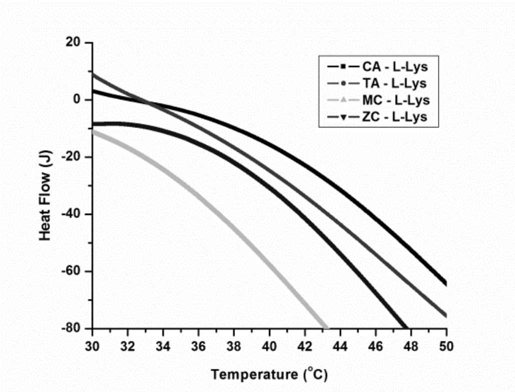

Fig.2 DSC Curve for all DESs.

3.3 Conductivity

The electrical conductivites of the DESs citric acid-L-Lysine,tartaric acid-L-Lysine, $MnCl_2$-L-Lysine and $ZnCl_2$-L-Lysine was found to be 1.24,2.00,3.1 and 3.99 $mScm^{-1}$ at room temperature [1,7,13,16]. It seems from the graph that the conductivity is proportional to the temperature as plotted . In these four DESs the Hydrogen bond formation formed [12]. As the temperature increased the conductivity increased significantly.The data showed a clear trend of increased conductivity of the DESs is shown in figure 3.

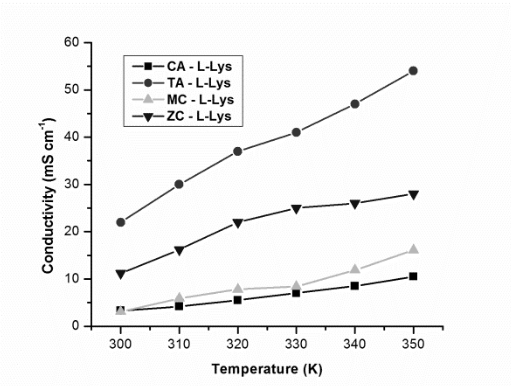

Fig.3 Conductivity for DESs as a Function of Temperature.

3.4 Density

The mass transfer Calculations and design chemical processes on fluid Mechanics density is a most important factor [7, 16]. The densities Measurement are calculated .The densities of these samples have been measured as

DESs	Density
Citricacid-L-Lysine	1.388 gcm^{-3}
tartaricacid-L-Lysine	1.249 g cm^{-3}
$MnCl_2$-L-Lysine	1.361 g cm^{-3}
$ZnCl_2$-L-Lysine	1.328 g cm^{-3}.

3.5 Viscosity

In a hydrodynamic processess, the viscosity is a key factor behind all applications of ionic liquids[12]. The transport phenomena in pure molten salts and ionic liquids are more is the aqueous solutions.

DESs	Viscosity
Citricacid-L-Lysine	529mPa s at 298.9K
Tartaricacid-L-Lysine	3879.9mPa s, 2343.1 mPa s, 2343.1 at 298.9
$KMnCl_2$-L-Lysine	1625.97mPa s at 299.2K
$ZnCl_2$-L-Lysine	8757.4mPa s at 299.2K

3.6 The pH

The pH is an important physical property and it has essential impact on chemical reactions. The pH is important for DESs applications in catalysis and biochemical reactions [3,5,10] .The pH Measurement are calculated. The pH of these DESs have been measured as citric acid - L-Lysine, tartaric acid - L-Lysine, $MnCl_2$ - L-Lysine and $ZnCl_2$ - L-Lysine 1.24, 2.00,3.32 and 3.99 at the temperature of 300K. The pH in Citric acid-L-Lysine and $ZnCl_2$ –L-Lysine slightly increased with increasing temperature. The two DESs Tartaric acid - L-Lysine and $MnCl_2$- L-Lysine showed decreased pH with increasing temperature. The pH values of DES based on all DESs appear to be stable within the temperature range 300K to 350K. As the temperature increases the pH values of this DES increased. This may be due to weakening of hydrogen bonding between Citric acid-L-Lysine and $ZnCl_2$ – L- Lysine at higher temperatures which in turn responsible for the free liberation of free amino acid. The variation of pH as a function of temperature plot was denoted in figure4.

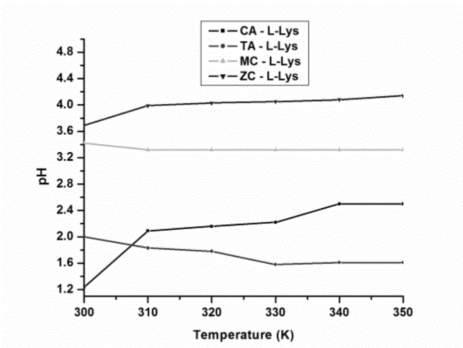

Fig. 4 pH for all DESs as a function of temperature.

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3.7 FTIR Spectrum of DESs

FTIR Spectrum of Citric acid-L-Lysine

The Fourier transformation infrared spectrum of DES of citric acid -L-Lysine is shown in figure 5 . In the FTIR spectrum of DES of citric acid - L-Lysine , there seems to be a broad speak at 3935.33-3448.19 cm^{-1}. Generally the O-H stretching of carboxylic acids are observed at 3400 cm^{-1}. The N-H stretching due to either primary or secondary amines are expected at 3300 to 3500 cm^{-1}. Here the broad peak at 3935.33- 3448.19 cm^{-1} due to the hydrogen bond formation of these groups of citric acid and L-Lysine. The C = O stretching of carboxylic acid of citric acid and L-Lysine are observed around 1732.5 $cm^{-1.}$ The CH_2 deformations of citric acid and L-Lysine were noticed at 1414.45 cm^{-1}. The peak at 1631.81 cm^{-1} was due to the out C = N stretching of L-Lysine. The medium peak at 1119.26 cm^{-1} was due to C – N stretching of L-Lysine .

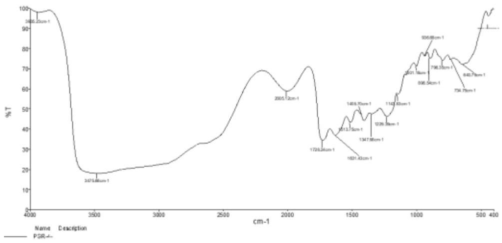

Fig .5 FTIR Spectrum of DES of Citric acid - L-Lysine

FTIR Spectrum of tartaric acid –L-Lysine

The Fourier transformation infrared spectrum of DES of tartaric acid -L-Lysine is shown in figure 6. In the FTIR spectrum of DES of tartaric acid - L-Lysine , there seems to be a broad peak at 3950-3454.82cm^{-1}. Generally the O-H stretching of carboxylic acids are observed at 3400 $cm^{-1.}$ The N-H stretching due to either primary or secondary amines are expected at 3300 to 3500 cm-1. Here the broad peak at 3950-3454.82 cm^{-1} due to the hydrogen bond formation of these groups of Tartaric acid and L-Lysine .The C = O stretching of carboxylic acid of tartaric acid and L-Lysine are observed around 1735.31 cm^{-1}. The CH_2 deformations of Tartaric acid and L-Lysine were noticed at 1519.33. cm-1 . The peak at 1631.45 cm^{-1} was due to the out C = N sterching of L-Lysine.The medium peak at 1298.06-1134.59 cm^{-1} was due to C – N strecting of L-Lysine .

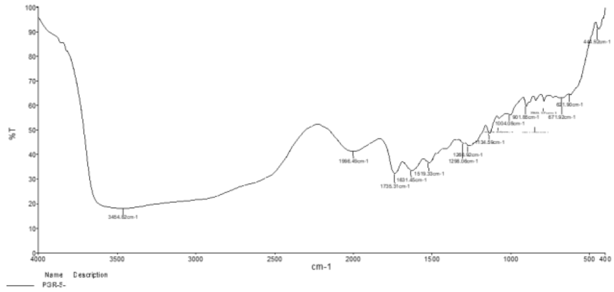

Fig .6 FTIR Spectrum of DES of tartaric acid - L-Lysine

FTIR Spectrum of $MnCl_2$ - L-Lysine

The Fourier transformation infrared spectrum of DES of $MnCl_2$ - L-Lysine , there seems to be a broad peak at 4000-3419.65 cm^{-1} is shown in figure 7 . Generally the O-H stretching of carboxylic acids are observed at 3400 cm^{-1}. The N-H stretching due to either primary or secondary amines are expected at 3300-3500 cm^{-1} . Here the broad peak at 4000-3419.65 cm^{-1} due to the hydrogen bond formation of these groups of Manganese chloride and L-Lysine. The CH_2 deformations of MnCl2 $_{and}$ L-Lysine were noticed at 1502.32 cm^{-1}. The peak at 1631.45 cm^{-1} was due to the out C = N stretching of L-Lysine. The medium peak at 1350.13-1138.96 cm^{-1} was due to C – N stretching of L- Lysine.

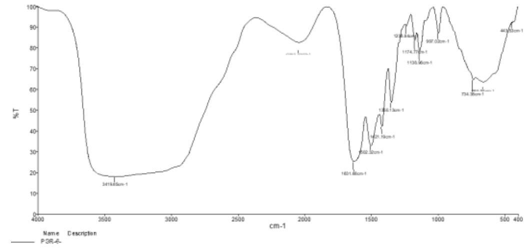

Fig .7 FTIR Spectrum of DES of $MnCl_2$ - L-Lysine

FTIR Spectrum of $ZnCl_2$ - L-Lysine

The Fourier transformation infrared spectrum of DES of $ZnCl_{2\,+}$ L-Lysine, there seems to be a broad peak at 4000-3501.22 cm^{-1} is shown in figure 8. Generally the O-H stretching of carboxylic acids are observed at 3400 cm^{-1}. The N-H stretching due to either primary or secondary amines are expected at 3300-3500 cm^{-1} . Here the broad peak at 4000-3419.65 cm-1 due to the hydrogen bond formation of these groups of Zinc chloride and L-Lysine. The CH_2 deformations of $ZnCl_2$ and L-Lysine were noticed at 1502.32 cm^{-1} . The peak at 1631.45 cm^{-1} was due to the out C = N stretching of L-Lysine .The medium peak at 1350.13-1138.96 cm^{-1} was due to C – N stretching of L-Lysine .

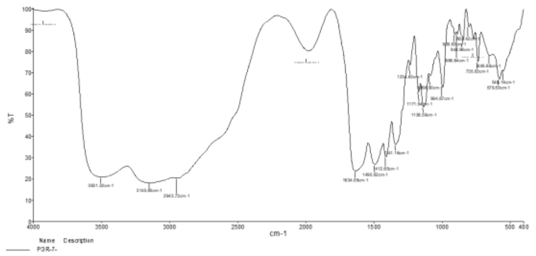

Fig. 8 FTIR Spectrum of DES of $ZnCl_2$ - L-Lysine

4. Conclusions

Binary DESs of L-Lysine with 1:1 mole ratio of citric acid,tartaric acid, $MnCl_2$ and $ZnCl_2$ have made varying 1:1 mole ratios as expected and observed that the thermal decomposition temperatures,glass transition temperatures and molar heat capacities augments with increasing molar ratio. Densities,viscosities,conductivities and pH values portend the effect of the temperature.The present study might be more useful towards the potential application and industrial applications.

In this work L – Lysine has been used to prepare DESs with Citric acid, Tartaric acid, $MnCl_2$ and $ZnCl_2$. The physical properties conductivity, density, vicosity and pH were reported as function of temperature . The thermal properties namely thermal decomposition temperature and glass transition temperature were measured for the DESs.

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