



## Study of thermodynamic properties of choline chloride urea in aqueous media at different temperatures

S. S. Nandre<sup>a</sup>, U. G. Deshpande\*<sup>b</sup> and S. R. Patil<sup>c</sup>

<sup>a</sup>Late Annasaheb R. D. Deore Arts & Sci. College, Mhasadi, Tal.-Sakri, Dist. Dhule(MS)

<sup>b</sup>Pratap College, Amalner, Dist.-Jalgaon (MS) India

<sup>c</sup>A. S. C. College, Chopda, Dist.-Jalgaon (MS) India

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### ABSTRACT

The densities and viscosities of binary mixtures of Choline chloride urea in aqueous media have measured at 298.15, 303.15, 308.15 and 313.15 K temperature. Eutectic mixtures of urea and arrange of quaternary ammonium salts are liquid at ambient temperatures and have interesting solvent properties. The data have been used to calculate the excess volumes deviation in viscosities. The outcome data have been analyzed in terms of molecular interactions existing between the components of the mixtures.

**Keywords:** Choline chloride urea, molecular interaction, Excess molar volume.

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### INTRODUCTION

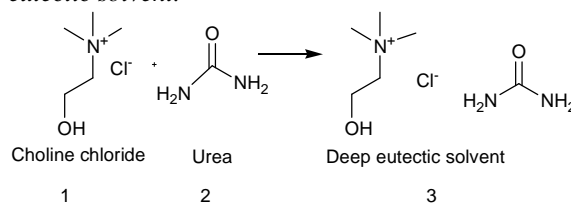
The salts that melt below 100°C are described with the term ionic liquids. On the other hand the term room temperature ionic liquids are used for ILs melts whose melting points below room temperature. Whereas, the term room-temperature ionic liquids (RTILs) is usually reserved for ILs melts with melting points below room temperature. ILs that consists of only cations and anions are electrolytes forming liquids. ILs has the properties like low vapour pressure, non-volatile, miscible with certain organic solvents or water and good solubility of organic and inorganic materials, highly polar, chemically inert. Ionic liquids are reusable and can be structured, non-inflammable and thermally stable[1-3].

These deep eutectic mixtures have been used as solvents in biologic transformation such as hydrolase catalyzed biotransformation [4] and extraction of glycerol from biodiesel into a eutectic-based solvent [5]. Deep eutectic solvents are used as electrolytes for dye-sensitized solar cells [6]. The ability of deep eutectic mixtures to serve as solvents, however, has not been adequately explored in the field of synthetic organic chemistry field. Deep eutectic mixtures of urea and a range of quaternary ammonium salts are liquid at ambient temperatures and have interesting solvent properties. These mixtures were initially used for biologic conversion because of their biodegradable properties. Deep eutectic solvents composed solely of biomaterials, in particular choline cations combined with propionate, hydrogen succinate, and hydrogen maleate, are ionic liquids with strong hydrogen bonding characteristics at room temperature [7].

### EXPERIMENTAL SECTION

Choline chloride and urea used of A.R. grade with purity > 99% Make S.D. fine chem. Industries, Mumbai. A deep eutectic solvent was prepared by a previously reported simple method [8] with 100% atom economy. Choline chloride (1 mole) was reacted with urea (2 moles) at 80°C. The resulting molten salt was used directly in reactions without purification. This method produced no byproducts; therefore there was no loss during isolation of the solvent.

Scheme 1: Preparation of deep eutectic solvent.



We synthesized a deep eutectic solvent composed wholly of biomaterials referred to as "Bio-ILs" or "Deep Eutectic Mixture". Abbott *et al* [9]. published a series of studies on the low melting point of deep eutectic liquid systems based on choline chloride ([Ch] [Cl]). These studies suggest that choline cations can substitute for synthetic cations. Choline is a naturally occurring biocompatible compound that is not hazardous if it is released back to nature as choline or its deep eutectic mixture [10]. Urea is a compound present in all animals. Because choline chloride and urea are both inexpensive, processes that use this deep eutectic solvent are economically viable. This freshly prepared DES is mixed in distilled water with different concentration. The mixtures of the desired composition were prepared by weighting on a HR-120 (A & D Japan) electronic balance with a precision of  $\pm 0.0001$  g. all mixed solvents were prepared by molality.

The densities of pure liquids and binary mixtures were measured by using  $15\text{cm}^3$  double arm pycnometer as describe earlier, [11-13] the Pycnometer was calibrated by using conductivity water with  $0.9970\text{ g/cm}^3$  as its density at 298.15 K. The pycnometer filled with air bubble free experimental liquid was kept in transparent walled water bath for 10-15 min. to attain thermal equilibrium. The position of liquid levels in the two arms was recorded.

The dynamic viscosities were measured using an Ubbelohde suspended level viscometer, calibrated with conductivity water. An electronic digital stopwatch with readability of  $\pm 0.01$  sec. was used for the flow time measurement, at least three repetitions of each data reproducible to  $\pm 0.05$  sec. were obtained and the result was averaged. Since all flow times were greater than 200 sec. and capillary radius (0.5 mm) was far less than its length (50 to 60 mm.). The kinetic energy and corrections respectively were found to be negligible. The uncertainties in dynamic viscosities are of the order  $\pm 0.003$  m Pa s.

### THEORY AND CALCULATIONS

Excess molar volume  $V^E$  was calculated from the density measurement by the relationships as follows:—

$$V^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho} - (x_1 V_1 + x_2 V_2) \quad \text{-----(1)}$$

Dynamic viscosities ( $\eta$ ) of Choline chloride urea and water mixtures at different temperatures were calculated by the measuring density and flow time of the mixture (Table 1 and Table 2).

The viscosity deviation was calculated by

$$\Delta\eta = \eta - \{x_1 \eta_1 + x_2 \eta_2\} \quad \text{----- (2)}$$

The activation parameters  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  were determined using Eyring and John's equation-

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) \quad \text{----- (3)}$$

Where  $\eta$  - is viscosity of mixture,  $h$ ,  $N$  and  $V$  are Planck's constant, Avogadro's number and molar volume respectively.

**Table 1-Values of density,viscosity and excess properties of binary mixtures of Choline chloride urea(1) and water (2) at 298.15 and 303.15K**

Temp (K)	X <sub>1</sub>	ρ (gm/cm <sup>3</sup> )	η (mPaS)	V <sup>E</sup> (m <sup>3</sup> mol <sup>-1</sup> )	Δη (mPaS)
298.15	0.0002	1.01568	0.05167	-0.331	-99.6941
	0.0010	1.01683	0.05067	-0.3538	-162.923
	0.0019	1.01344	0.04833	-0.2965	-234.177
	0.0089	1.02092	0.04008	-0.4579	-787.378
3.3.15	0.0002	1.01484	0.04636	-0.3417	-85.426
	0.0010	1.01599	0.04683	-0.3646	-125.315
	0.0019	1.01272	0.04544	-0.3093	-170.382
	0.0089	1.02024	0.04042	-0.4717	-520.323

**Table 2-Values of density,viscosity and excess properties of binary mixtures of Choline chloride urea(1) and water (2) at 308.15 and 313.15 K**

Temp (K)	X <sub>1</sub>	ρ (gm/cm <sup>3</sup> )	η (mPaS)	V <sup>E</sup> (m <sup>3</sup> mol <sup>-1</sup> )	Δη (mPaS)
308.15	0.0002	1.0134	0.04252	-0.3456	-74.5909
	0.0010	1.01427	0.04348	-0.3635	-104.838
	0.0019	1.0111	0.04159	-0.3097	-139.163
	0.0089	1.01907	0.03733	-0.4805	-405.09
313.15	0.0002	1.01181	0.04033	-0.356	-65.9605
	0.0010	1.01287	0.04058	-0.3774	-83.483
	0.0019	1.00937	0.04008	-0.3176	-103.274
	0.0089	1.01711	0.03473	-0.4847	-257.350

**Table 3- Thermodynamic Activation Parameters for Choline chloride urea + Water system**

X <sub>1</sub>	ΔH <sup>#</sup> x 10 <sup>-3</sup> (J mol <sup>-1</sup> )	ΔS <sup>#</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	ΔG <sup>#</sup> x 10 <sup>-3</sup> (J mol <sup>-1</sup> )			
			298.15K	303.15K	308.15K	313.05K
0.0002	12.70983	-2.48454	13.45059	13.46301	13.50544	13.51786
0.0010	11.29228	-7.22162	13.44541	13.48152	13.49763	13.55374
0.0019	9.89143	-11.629	13.35861	13.41676	13.47490	13.53305
0.0089	7.679981	-18.2065	13.10824	13.19927	13.29030	13.38133

## RESULTS AND DISCUSSION

The experimental values of density, viscosity, excess volume and viscosity deviation are presented in Table 1 and Table 2. The experimental data of density of choline chloride urea and water systems over the temperature range T= (298.15 to 313.15) K are shown in figure 1. A very good linear correlation is observed for all systems between density and temperature this linear behavior with temperature being also reported by other authors for pure ionic liquids [14-15]. The sign and magnitude of V<sup>E</sup> gives a good estimate to the strength of unlike molecular interactions in the solution phase. Positive V<sup>E</sup> indicates the weak interactions, whereas, large negative values of V<sup>E</sup> are found, when these interactions are strong. In the present investigation, the values of excess molar volumes are found to be negative indicating strong hydrogen bonding interaction for the entire mole fraction of choline chloride urea and water.

The dynamic viscosities, η, of choline chloride urea and water systems as function of temperature are presented in figure 2. The viscosities of ionic liquids are strongly dependent upon temperature and exhibits classical Arrhenius behavior in the studied temperature range.

The negative Δη may be attributing to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the molecules. Increase of temperature disturb hereto and homo association of the molecules which increases fluidity of the liquid. Values of Δη are more at higher temperature provide additional evidence for the existence of interactions of weak magnitude like dipole-induced dipole type between components of liquid mixtures as shown in Fig. 3.

The magnitude of Δη, the sign and extent of deviation of this property from ideality depends on the strength of interaction between unlike molecules. The excess viscosity gives the strength of the molecular interaction between interacting molecules; the large negative values of excess viscosity for all the systems can be attributed to the presence of the dispersion, induction and dipolar forces between the components.

The observed values of ΔH<sup>\*</sup> and ΔG<sup>\*</sup> for the binary mixture are positive as shown in Table 3. The ΔG<sup>\*</sup> and ΔH<sup>\*</sup>

values are steadily decreases with increase in concentration of DES choline chloride urea.

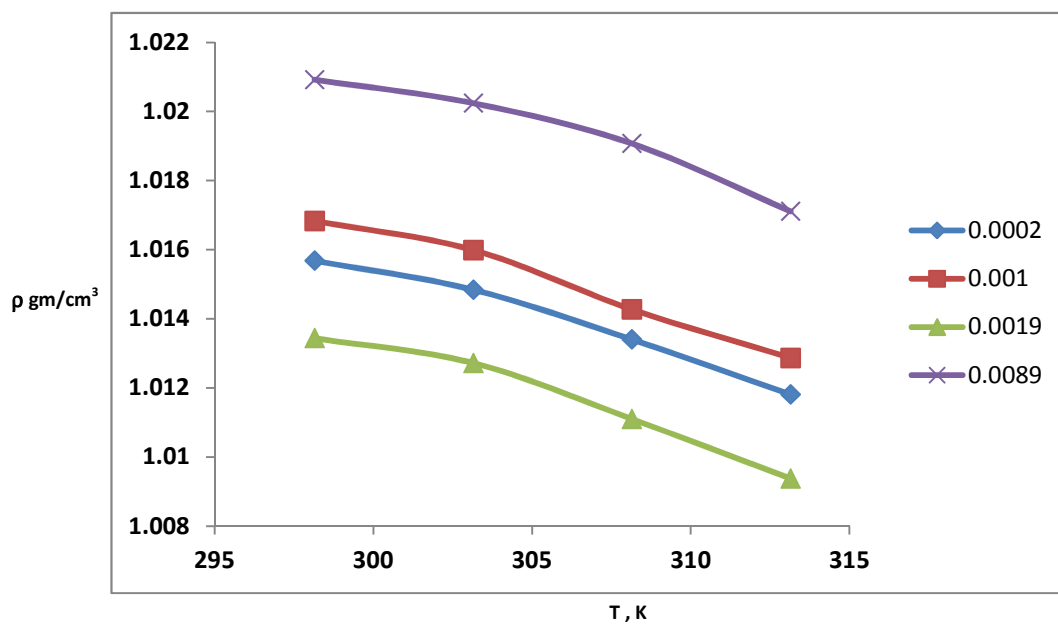


Fig.1: The variation of density with temperature for different concentration of Choline Chloride Urea and water

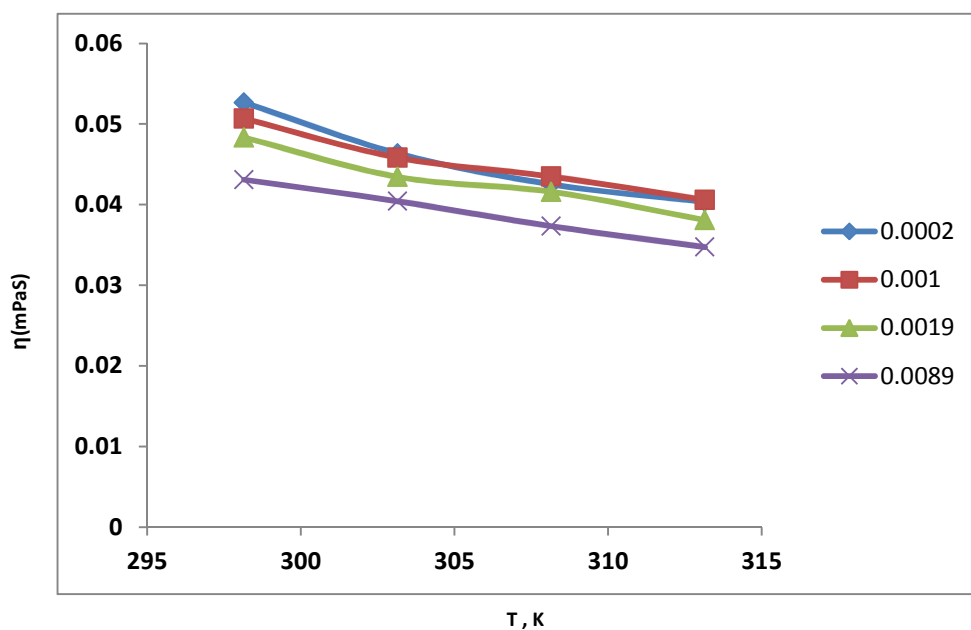


Fig.2: The variation of viscosity with temperature for different concentration of Choline Chloride Urea and water

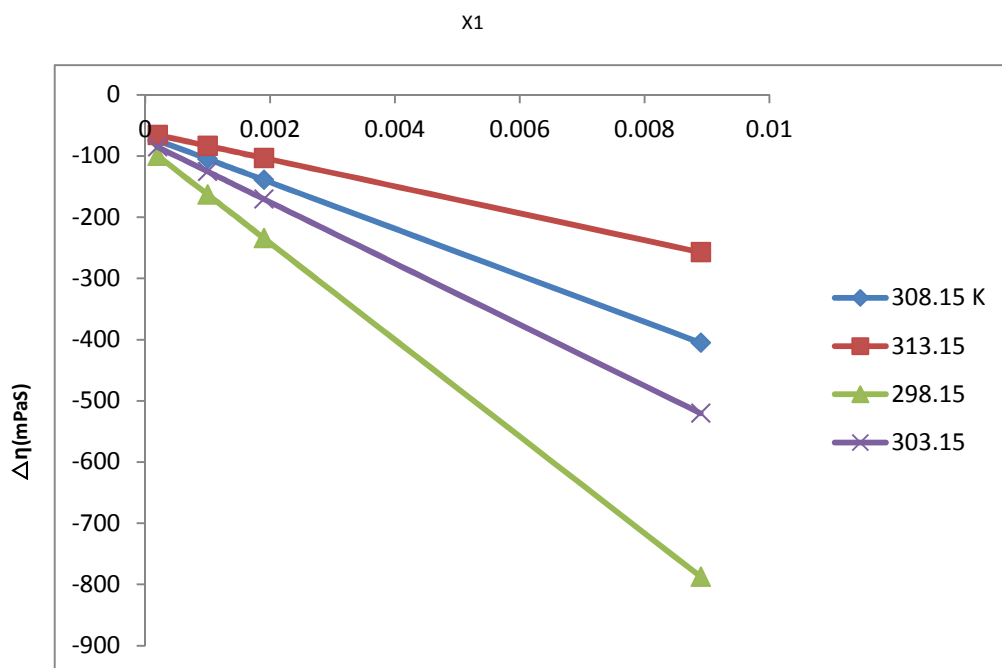


Fig.3: Experimental viscosity deviation  $\Delta\eta$  for different concentration of Choline Chloride Urea and water at 308.15 and 313.15 K

### CONCLUSION

This paper reports experimental data for density, and viscosity at 298.15 to 313.15 K for binary mixture of choline chloride urea and water from these data, several thermodynamics excess functions have been calculated and studied to explain the intermolecular interactions between mixing components. Large negative deviations are observed for both the investigated binary systems. This reveals that the existence of molecular interactions in the binary mixtures. The present investigation shows that greater molecular interaction exists in of choline chloride urea and water which may be due to hydrogen bond formation and weak molecular interaction that exists in the binary mixtures[16-17]. Which may be due to the interaction tends to be weaker with rise in temperature which may be due to weak intermolecular forces and thermal dispersion forces.

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