

Eutectic System Based on Urea and Potassium Sodium Tartrate

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ABSTRACT

Deep eutectic solvents (DESs) are considered as better alternative solvents in chemical and physical processes. The binary mixture of urea and potassium sodium tartrate is explored in this study. A eutectic system is determined at composition made up of 33% potassium sodium tartrate and 67% urea (1:2 molar ratio). This eutectic system has a freezing point of 19.83 ± 0.76 °C, density of 1.1971 ± 0.0003 g mL⁻¹, and viscosity of 34.4226 ± 0.0665 cP. The most stable conformation for the adduct of urea and potassium sodium tartrate with water molecules was determined through density functional calculations. The gas phase total energy for the adduct was determined as -5576863 kJ mol⁻¹. Electrostatic interactions between the cations and the carboxylate sites are present, H-bonding between protons of urea and the hydroxyl oxygen of the tartrate, and intramolecular H-bonding between the hydroxyl and carboxylate sites of tartrate are accounted for in the structure. The total energy associated with nonbonding interactions is computed as -826 kJ mol⁻¹, which suggests that these interactions stabilize the formation of the DES system of potassium sodium tartrate and urea.

Keywords: *deep eutectic solvent; hydrogen bonding; urea-tartrate adduct; DFT calculations*

INTRODUCTION

In common physical and chemical process, solvent is used as common medium for reacting species, separating components of mixtures, purifying via extraction, and washing of substances. Unfortunately, most available solvents have the drawbacks of being harmful and toxic. Typical organic solvents are volatile, flammable, explosive, and have low biodegradability. With the increasing consciousness about green chemistry, more environmentally benign and less hazardous chemicals and methodologies are targeted (Clarke *et al.*, 2018).

In the recent years, ionic liquids, low melting mixtures, and deep eutectic systems are being developed as solvent alternatives. Ionic liquids (ILs) are mixtures of organic salts, commonly made up of organic cation and organic or inorganic anion

(Zhang *et al.*, 2006). Most cases are made up of asymmetrically substituted organic cation, such as ammonium or phosphonium, and halogen-based anions. Although ionic liquids have many advantageous properties over common organic solvents such as low volatility and high recyclability, most ILs have high toxicity.

Low melting mixtures (LMMs) and deep eutectic solvents (DESs) are mixtures of two components, one is considered as hydrogen bond donor (HBD) and the other as hydrogen bond acceptor (HBA) (Zhang *et al.*, 2012; Liu *et al.*, 2015; Khandelwal *et al.*, 2016). DESs are generally classified as type I, II, III, and IV, depending on the types of molecules used as components. These solvents have the advantages of ease of preparation, low to negligible vapor pressure, wide liquid range, and good solvation properties. These solvents are considered

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to be a greener alternative over ionic liquids since the components are generally more biocompatible. Most DESs being reported in the literature are based on urea, glycerol, or sugar. The most commonly used DES choline chloride: urea (1:2) has been applied to various applications including metal extraction, CO₂ sequestration, and catalysis medium.

Here, we report the preparation of a low melting binary mixture of urea and potassium sodium tartrate. These chemicals have no or low toxicity, are readily available being biorenewable, and cheap. The low melting binary mixture of these two components may be a suitable alternative for solvents at ambient temperatures.

EXPERIMENTAL

Materials. Urea and potassium sodium L-(+)-tartrate tetrahydrate (KNa tartrate) were obtained from Ajax Finechem at 99.00 % purity and were used as received without further purification. The properties of these two components are summarized in Table 1.

Table 1. Properties of Components Used in This Work (Lide, 2005).

Compound	Molecular Formula	Molar Mass, g mol ⁻¹	Melting Point, °C
Urea	CH ₄ N ₂ O	60.06	133.3
NaK Tartrate	NaKC ₄ H ₄ O ₆ • 4H ₂ O	282.22	70.0

Methodology. Binary Solid-Liquid Phase Diagram. The cooling curves for the mixtures were measured with a fabricated apparatus consisted of a 20-mL test tube with rubber stopper fitted with a stirrer and thermometer, and immersed in Dewar flask filled with crushed ice (Gallus *et al.*, 2001). With constant amount of urea (2.00 g, 0.0333 mol), binary mixtures of urea and KNa tartrate were prepared by varying the amount of KNa tartrate to arrive at mole ratios of urea with KNa tartrate as follows $\chi_{\text{urea}} = 0.25, 0.33, 0.50, 0.55, 0.60, 0.67, 0.70, 0.75$. The compounds were ground using a mortar and pestle until the mixture liquefied or until a smooth paste was formed. These liquefied mixtures were sonicated for 15 min and heated at 80-100 °C until homogeneity. The liquefied mixture was placed in the cooling curve apparatus and the temperature of cooling was recorded every 10s until temperature reached 10 °C below the measured detected arrest temperature. Break and arrest temperatures were determined from the cooling curves (temperature versus time) (Williams and Collins, 1994; Deacutis

et al., 1997). Each measurement was done in triplicate and standard deviation was reported.

Density and Viscosity Measurements. The KNa tartrate: urea (1:2) solvent was prepared as described above, and stored in silica desiccator for overnight prior to measurements. The density of KNa tartrate: urea (1:2) system was determined at 28 °C using the pycnometer method (Garland *et al.*, 2009), by comparing the mass ratios between the DES and the calibration liquid (water), using the formula:

$$\rho_{\text{subs}} = \frac{m_{\text{pyc+subs}} - m_{\text{pyc}}}{m_{\text{pyc+water}} - m_{\text{pyc}}} \times \rho_{\text{water at RT}}$$

Each measurement was done in triplicate and standard deviation was reported.

The kinematic viscosity of the synthesized KNa tartrate: urea (1:2) system was determined using a Cannon-Fenske viscometer through the capillary flow method (Garland *et al.*, 2009). Capillary dimensions (A and B) were determined prior to analysis, using different calibrating liquids – water, ethyl acetate, acetone, through the Hagen-Poiseuille equation:

$$\eta = A\mu t - \frac{B\mu}{t}, \text{ where } A = \frac{\pi r^4 g h}{8Vl} \text{ and } B = \frac{V}{8\pi l}$$

The viscosity was then determined by measuring the flowtime of the solution in the calibrated Cannon-Fenske viscometer at 28 °C. Each measurement was done in triplicate and standard deviation was reported.

Density Functional Theory (DFT) Studies. All programs used were open software accessed on 07 June 2018 through the websites: GAMESS - <http://www.msg.ameslab.gov/gamesl/>, Avogadro - <https://avogadro.cc>, and MacMolPlt - <https://brettbode.github.io/wxmacmolplt/>.

Structures were constructed using the Avogadro software (Hanwell *et al.*, 2012). The most probable conformation in the gas phase of components in the DES system was constructed from geometry-optimized urea, KNa tartrate, and water molecules through the GAMESS program (Schmidt *et al.*, 1993) using the B3LYP hybrid functional with 6-31G(d) basis set. Visualization of the hydrogen bonding interactions was done using the MacMolPlt program (Bode and Gordon, 1998). All calculations were done in the gas phase and at 298.15 K. The total energy associated with the nonbonding interactions in the DES systems (ΔE_{NB}) was calculated using the equation:

$$\Delta E_{\text{NB}} = \Delta E_{\text{DES}} - \Delta E_{\text{KNaTartrate}} - 2 \times \Delta E_{\text{urea}} - 4 \times \Delta E_{\text{H}_2\text{O}}$$

where ΔE_{DES} , $\Delta E_{KNaTartrate}$, ΔE_{urea} , ΔE_{H_2O} are the total energies of the urea: KNa tartrate (1:2) system, KNa tartrate, urea, and water, respectively (Hao, 2006).

RESULTS AND DISCUSSIONS

The binary mixtures of urea and KNa tartrate were prepared via grinding, sonication and heating. Grinding is necessary to prevent decomposition of the individual components, forming a paste. After sonication and heating, we achieved homogenous, transparent binary systems; but only the binary mixture of mole fraction $\chi_{urea} = 0.67$ remained in clear liquid form after cooling to room temperature (~ 30 °C), while the rest have solidified.

The solid-liquid phase diagram for the binary mixtures of KNa tartrate: urea is shown in Figure 1. The eutectic composition occurs at the molar ratio of 1:2 for KNa tartrate: urea ($\chi_{urea} = 0.67$), with a freezing point of 19.83 ± 0.76 °C, Table 2. This temperature is significantly lower than freezing points of the pure components, allowing for an ambient temperature solvent mixture. The freezing temperature of the eutectic solvent is comparable to that of choline chloride: urea (1:2) system (at 12 °C), but lower than that of for choline chloride: L-(+)-tartaric acid (at 47 °C) (Abbott *et al.*, 2003; Shahbaz *et al.*, 2010; Hayyan *et al.*, 2010; Maugeri and Dominguez de Maria, 2012). A related DES was used by Gore *et al.* (2011) made from L-(+)-tartaric acid: dimethylurea (30:70). Although the physical properties of this DES were not determined at that time, this DES was prepared as melt at 70 °C and was used a medium for catalysis at that temperature (Gore *et al.*, 2011; Krishnakumar *et al.*, 2014). Generally, DESs which are liquid at room temperature, thus have freezing point lower than 50 °C, are promising solvents for many applications (Khandelwal *et al.*, 2016).

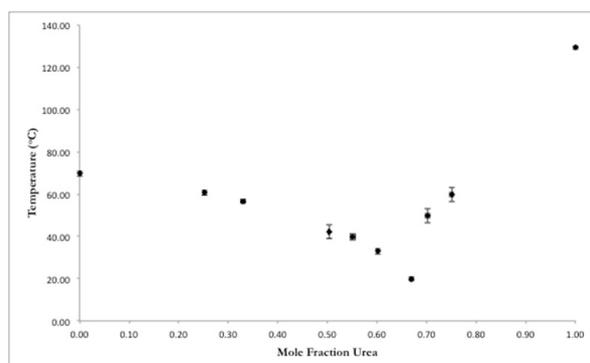


Figure 1. Freezing Point for the Binary Mixture of Urea and KNa tartrate as a Function of Composition.

The density and viscosity of the KNa tartrate: urea (1:2) eutectic system are determined as 1.1971 ± 0.0003 g cm⁻³ and 34.4226 ± 0.0665 cP at 28 °C,

respectively (Table 2). As with most DESs prepared, the eutectic system KNa tartrate: urea (1:2) is denser than water at the same temperature (Zhang *et al.*, 2012). This KNa tartrate: urea (1:2) system is less dense than the choline chloride: urea and ZnCl₂: urea systems, but falls within similar density range with the choline chloride: polyol systems (glycerol and ethylene glycol) (Abbott *et al.*, 2003; Abbott *et al.*, 2011; Craveiro *et al.*, 2016; Abbott and Barron *et al.*, 2007; Abbott *et al.*, 2006; D'Agostino *et al.*, 2011; Abbott and Harris *et al.*, 2007; Shahbaz *et al.*, 2012). The eutectic system KNa tartrate: urea (1:2) is relatively more viscous than common molecular solvents (Zhang *et al.*, 2012). It is less viscous than choline chloride: urea, choline chloride: glycerol, and ZnCl₂: urea systems, but comparable to the choline chloride: ethylene glycol system (Abbott *et al.*, 2003; Abbott *et al.*, 2011; Abbott and Barron *et al.*, 2007; D'Agostino *et al.*, 2011; Abbott and Harris *et al.*, 2007). This low viscosity type of DES is desirable for applications as medium in chemical and physical processes (Zhang *et al.*, 2012).

To gain further insights into the network of interactions between urea and KNa tartrate in the adduct, we performed DFT calculations using the B3LYP method (Hao, 2006; Zhang *et al.*, 2014; Zhu *et al.*, 2016; Palomba *et al.*, 2018). We have included the cations, Na⁺ and K⁺, as well as four water molecules in the structure optimization. The most stable gas configuration of the KNa tartrate: urea (1:2) adduct is shown in Figure 2. As shown, the cations are closer to the carboxylate sites, through electrostatic interaction. Each cation has a water molecule that surrounds it. These water molecules form hydrogen bonds with the carboxylate (O12-H17, O5-H15). The oxygens of one carboxylate moiety are also intramolecularly H-bonded to the hydroxyls (O5-H8, O11-H10). The urea molecules form hydrogen bonds with the oxygen of the hydroxyl groups of the tartrate. Interestingly, the structure shows that the one urea molecule forms only one H-bond end (O6-H36), whereas two hydrogens of the second urea molecule form H-bonds to the same oxygen site (O9-H27, O9-H38). Because of this, the former is shorter (1.890 Å) than the latter (2.020 & 2.103 Å) or with the mean experimental N-H...O hydrogen bonds (1.921(4) Å) (Taylor *et al.*, 1984). The remaining water molecules are both H-bonded intermolecularly to the second urea molecule though carbonyl O of urea, O25-H18, and protonic hydrogen, O23-H39. These water molecules seem to lock this weakly H-bonded urea to the tartrate better by acting as the mediating species, one water molecule is bonded to both the protonic hydrogen of urea and the oxygen of the carboxylate group of the tartrate. This water molecule is also H-bonded to the other water molecule that is bonded to the carbonyl

Table 2. Main Physical Properties of Water, Common Organic Solvents, and DESs.

Solvent (mol ratio)	Freezing point T_p , °C	Density ρ , g mL ⁻¹ (Temp)	Viscosity η , cP (Temp)	Literature
Water	0	0.997 (25 °C)	0.835052 (28 °C)	(Lide, 2005; Dortmund Data Bank, accessed June 21, 2018)
Ethyl acetate	- 83.8	0.9003 (20 °C)	0.416921 (28 °C)	(Lide, 2005; Dortmund Data Bank, accessed June 21, 2018)
Acetone	- 94.7	0.7845 (25 °C)	0.300479 (28 °C)	(Lide, 2005; Dortmund Data Bank, accessed June 21, 2018)
Choline Chloride: Urea (1: 2)	12	1.25 (25 °C)	750 (25 °C)	(Abbott <i>et al.</i> , 2003; Abbott <i>et al.</i> , 2006; D'Agostino <i>et al.</i> , 2011)
Choline Chloride: Glycerol (1: 2)	- 40	1.18 (25 °C)	376 (25 °C)	(Hayyan <i>et al.</i> , 2010; Abbott <i>et al.</i> , 2011; Abbott and Harris <i>et al.</i> , 2007)
Choline Chloride: Ethylene Glycol (1: 2)	- 66	1.12 (25 °C)	37 (25 °C)	(Shahbaz <i>et al.</i> , 2012; D'Agostino <i>et al.</i> , 2011; Abbott and Harris <i>et al.</i> , 2007; Shahbaz <i>et al.</i> , 2012)
Choline Chloride: L-(+)-Tartaric Acid (1: 0.5)	47	1.26 (23 °C)	-	(Craveiro <i>et al.</i> , 2016; Maugeri and Dominguez de Maria, 2012)
ZnCl ₂ : Urea (1: 3.5)	9	1.63 (25 °C)	11340 (25 °C)	(Abbott and Barron <i>et al.</i> , 2007; Abbott and Harris <i>et al.</i> , 2007)
KNa Tartrate: Urea (1: 2)	19.83 ± 0.76	1.1971 ± 0.0003 (28 °C)	34.4226 ± 0.0665 (28 °C)	This work

group of urea. Moreover, the computed total energy of the DES system is lower in comparison to the sum of the total energies of individual equilibrium geometries of urea, KNa tartrate, and water. With a ΔE_{NB} value of -826 kJ mol⁻¹ (Table 3), this network of non-covalent interactions contributes to the stability of the DES formation.

Table 3. Comparison of the Calculated Total Energies for the KNa tartrate:urea (1:2) DES with the Individual Components, using the B3LYP Functional with 6-31G(d) Basis Set.

Substance	Total Energy, kJ mol ⁻¹
KNa tartrate: urea: H ₂ O (1:2:4)	- 5576863
KNa tartrate	- 3591820
Urea	- 591095
Water	- 200512
ΔE_{NB}	- 826

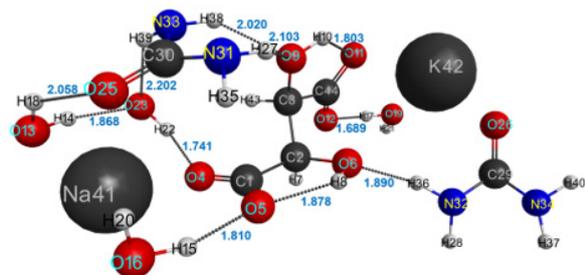


Figure 2. Optimized Structure for Adduct of KNa tartrate:urea (1:2), with 4 Water Molecules, Dashed Lines Represent the H-bonding Interactions, Lengths in Å, using the B3LYP functional with 6-31G(d) basis set.

CONCLUSIONS

Deep eutectic solvents make use of cheap, biodegradable components with little to zero toxicity, allowing these systems to be better alternatives to ionic liquids and other organic solvents in common applications. The variety of possible DES components permits modification of the physical properties of the eutectic system fit for its desired purpose. Production of DES usually involves the use of simple methods like heating and grinding, and proceeds with 100% atom economy, which makes it highly applicable for large-scale production. In this study, we have synthesized a eutectic system based on KNa tartrate: urea (1:2) through grinding, sonication, and heating to minimize decomposition. From the phase diagram, we have determined that the eutectic temperature is at 19.83 ± 0.76 °C, comparable to choline chloride: urea (1:2). The eutectic system is denser than water and has low viscosity. We also explored looking into the interactions present in KNa tartrate: urea (1:2) adduct through DFT calculations. We found that significant intermolecular H-bonding interactions occur between urea hydrogens and hydroxyl oxygens of tartrate. There are also intramolecular H-bonding between the carboxylate oxygens and the hydroxyl protons. Electrostatic interactions between Na⁺ and K⁺ ions and carboxylate site also exist. With a negative computed gas phase ΔE_{NB} , these noncovalent interactions account for the stability of the KNa tartrate: urea (1:2) system.

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