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# Acoustic, volumetric, transport, optical and rheological properties of Benzyltripropylammonium based Deep Eutectic Solvents

Anusha Basaiahgari [1], Somenath Panda [1], Ramesh L. Gardas*

*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

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ABSTRACT

The present study is focused on synthesis and physicochemical properties of a new class of Deep Eutectic Solvents (DESs) based on Benzyltripropylammonium chloride as hydrogen bond acceptor (HBA) and different hydrogen bond donors (HBD) like phenol, ethylene glycol, glycerol and lactic acid. Several physicochemical properties such as, density, speed of sound, conductivity and refractive index of these four DESs have been measured in the temperature range of 293.15–343.15 K and used to calculate various derived thermodynamic properties. Further, rheological measurements have been carried out to understand the viscosity and flow behavior of these DESs and also the influence of different hydrogen bonding environment on the nature of DESs. The temperature dependent density and viscosity values have been fitted using second order polynomial and well-known Vogel-Tammann-Fulcher (VTF) equations, respectively The experimental results implies that both the type of HBD and temperature has significant influence on the physicochemical characteristics of the synthesized DES.



## 1. Introduction

Solvents play an essential role in the field of Green Chemistry, when they satisfy certain important criteria like non-toxicity, biodegradability, easy availability, recyclability, low-cost etc. The growing concern of global warming and industrial pollution has motivated the research community to explore such solvents to minimize the impact on the environment. In recent years, a new class of solvents, known as Deep Eutectic Solvents (DESs) have gained significant interest as possible green solvents due to their non-toxic and bio-degradable nature. They are usually obtained by mixing of two or three components resulting in a product whose melting point is lower than the either of its individual constituents. The decrease in melting point of the mixture relative to the melting points of the individual components is caused by the charge delocalization through hydrogen bonding between hydrogen bond acceptor (HBA) (e.g. halide ion) and hydrogen bond donor (HBD) moiety [1].

Typically, most of the DESs are formed by molecules like quaternary ammonium salts as HBA, and poly amides, poly alcohols, poly carboxylic acids etc. as HBD [1,2]. The first report on DESs was given by Abbott et al. [3] in 2001 using quaternary ammonium salts. The starting components of DESs are capable of self-association through hydrogen bonding, which generally characterized by large depression in freezing point and subsequently termed as eutectic mixture [4,5] and they exist as liquids at temperatures below 150 °C. DESs show properties relevant to room temperature molten salts i.e., ionic liquids(ILs), like task specificity, low vapor pressure and tunable physicochemical properties and thus raised interest among researchers to explore various types of DESs with respect to their properties and applications. However, significance of DESs lies in the fact that they promise to overcome some problems posed by ILs in terms of cost and environmental concerns [5]. The preparation of DESs is cost effective and relatively simple. The purity of DESs mostly depends upon purity of used starting components. As a result, it is easy to maintain their purity and thus, post synthesis purification is not necessary.

DESs have been used for various applications in the fields of organic transformations [6,7], electro chemical processes [8,9], $CO_2$ gas absorption [10], bio diesel purification [11] etc. Recently, Smith et al. showed that how the interest in DESs has grown significantly in terms of their applications in various fields since their first description [1]. However, in order to use the DESs at industrial scale or for process design, it is of prime importance to have accurate and reliable knowledge of physicochemical properties of DESs.

* Corresponding author.
*E-mail address:* gardas@iitm.ac.in (R.L. Gardas).
*URL:* http://www.iitm.ac.in/info/fac/gardas
[1] A.B. and S.P. have contributed equally to this work.

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Considering the progress of development in this research field and their potential applications, the available data is however, insufficient. In addition, though there are models available for prediction of thermophysical properties of ILs, predictive models for DESs are relatively scarce [12]. Hence, formulating DESs with new combinations of salts and HBDs and studying their thermophysical properties is important for enhancing the accuracy of predictive modeling and also to improve the scope of applications.

In this context, we have prepared four DESs based on Benzyltripropylammonium Chloride as HBA and different HBDs like ethylene glycol, lactic acid, glycerol and phenol. Different combinations of these Salt and HBDs leading to the formation of DESs have been studied. A systematic study of various thermo physical properties as a function of temperature has been performed for these synthesized DESs. One of studied properties include density which is the basic and precisely measurable physical property that defines the nature of substance as well as helps in the optimization of process and product design. Further acoustic behavior of DESs has also been studied as function of temperature in the range of 293.15–343.15 K. In addition, the rheological behavior of DESs has also been analyzed by studying the viscosity and flow behavior. The rheological measurements help us to gain idea about different intermolecular interactions in these DESs. It is important to analyze the behavior of viscosity since it is an important property that determines the applicability of DESs in industrial fields in terms of usage, storage and transport. Furthermore, transport properties like conductivity and optical property like refractive index have also been measured. Some other important thermophysical parameters have been derived from the prior experimental values.

## 2. Experimental section

### 2.1. Chemicals and synthesis of DESs

The source, purity and freezing points of the salt and HBDs used in this experiment are summarized in Table S1 and their structures are given in Fig. 1. All initial components except lactic acid were kept in vacuum and dried for 48 h prior to synthesis. We have closely followed the methods of synthesis reported earlier [13]. A closed double-walled beaker with temperature control and magnetic stirrer was used to mix a predetermined ratio of the salt and hydrogen-bond donor. All mixing procedure was done at atmospheric pressure. The temperature was gradually increased to 70 °C and then maintained to be constant. The mix was stirred for a minimum of 3 h and in some cases; the temperature was increased up to 100 °C. Most of the DESs formed as a homogenous colorless liquid, except for the phenol based one, which showed light orange color. Upon cooling to room temperature, some DESs turned as semi-solid, and small precipitate was found in some cases. The precipitate was filtered and all DESs were kept under vacuum for another 24 h to reduce the water content. Various mole ratios tried for the formation of DESs are given in Table S2. Synthesized DESs were stored in tightly sealed vials and were kept in desiccator over silica gel, in order to avoid contact with air, moisture and contaminants.

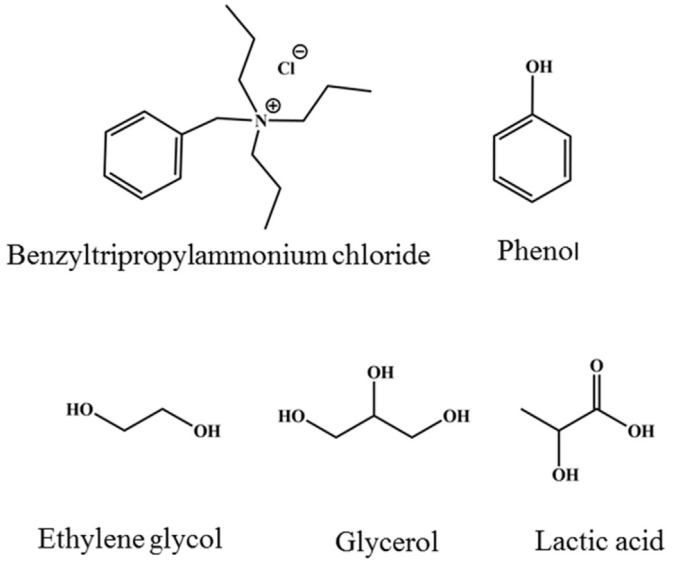


**Fig. 1.** Structures of salt and hydrogen bond donors.

### 2.2. Measurement techniques

The density and speed of sound of DESs were simultaneously measured with an Anton Paar DSA 5000M instrument at atmospheric pressure and with precise temperature control. The instrument uses U-shaped vibrating glass tube and a sound velocity cell both placed in a metallic block for density and sound velocity measurements, respectively. The instrument can measure density in the range of 0–3 g $cm^{-3}$ and speed of sound in the range of 1000–2000 m $s^{-1}$. Density and speed of sound data were measured in the range of 293.15 K to 343.15 K with 5 K increment. All values reported are the average of three measurements and the associated standard uncertainties are presented along with data tables. The temperature of the metallic block is precisely controlled by Peltier device with an accuracy of ±0.01 K. Prior to experiments, the internal calibration of the instrument was carried out by using Millipore quality water and dry air and calibration was confirmed by using a reference ionic liquid, namely, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [$C_6$Mim][$Tf_2$N] [14].

Viscosity measurements were performed using Anton Paar Lovis 2000 ME attached to the DSA 5000M master instrument. It uses the rolling ball in a capillary method and can measure viscosities in the range of (0.3–10,000) mPa.s. Temperature is kept constant through a built-in Peltier device with an accuracy of 0.02 K.

The Rheological studies were performed on an Anton Paar MCR 102 (Modular Compact Rheometer), with a CP 40 Cone and Plate measuring geometry. The cone inclination was 1° and the gap between the cone and plate was kept at 0.1 mm. About 0.5 mL of the DES sample was placed on the lower base, and the cone geometry was lowered to the truncation gap and allowed to equilibrate for 2 min. The temperature of the lower plate was controlled by P-PTD 200/AIR Peltier temperature device. Steady shear measurements were performed at 25 °C in (0.1–1000 $s^{-1}$) shear rate.

The electrical conductivity of the DESs was measured by a Eutech (PC 700) instrument consisting a built-in temperature sensor and an electrode with a cell constant of K = 1. The instrument can measure the conductivity in the range of 0.0 μS to 200 mS. The conductivity cell was calibrated with an aqueous solution of 0.01 N KCl. The temperature of the conductivity probe inserted into the sample was kept constant with the help of a custom made double layered glass jacket setup connected with Julabo constant temperature bath with an accuracy of ±0.03 K. Nitrogen atmosphere was also maintained through the glass jacket set up.

The refractive index measurements were performed with Anton Paar Abbemat 500 refractometer at a wavelength of 589 nm at atmospheric pressure. Prior to measurements, the sample holder was thoroughly cleaned and the instrument was calibrated with Millipore quality freshly degassed water. The sample was kept on the top of the measuring prism and irradiated at different angles by