

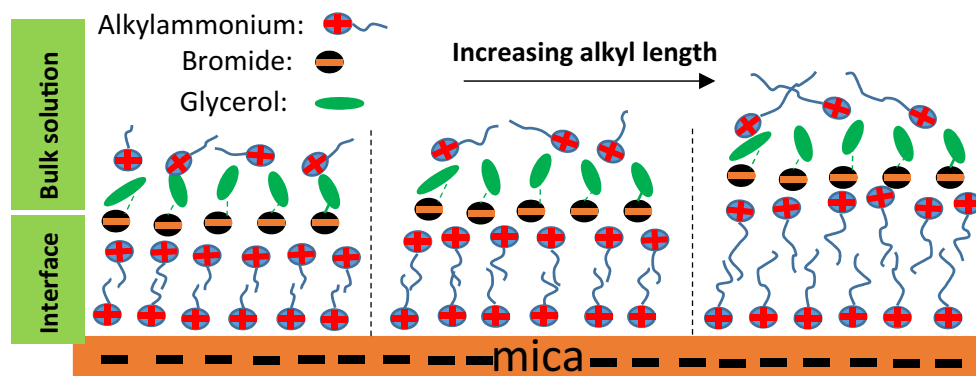
Regular Article

Effect of cation alkyl chain length on surface forces and physical properties in deep eutectic solvents

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GRAPHICAL ABSTRACT

Increasing the alkyl length changes the nanostructure of DESs.



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ABSTRACT

Deep eutectic solvents (DESs) have been prepared from mixtures of alkyl ammonium bromide salts (ethylammonium bromide, propylammonium bromide and butylammonium bromide) and glycerol at a 1: 2 M ratio. These DESs reveal the effect of cation alkyl chain length on interfacial structure at mica (a model anionic) surface. As the cation chain length is increased it becomes more amphiphilic and solvophobic, leading to stronger association of alkyl chains, as revealed by atomic force microscope force curve measurements. The effect of increasing cation alkyl chain length on phase transition and thermal decomposition temperatures, density, refractive index, viscosity, ionic and thermal conductivity and air liquid surface tension are also probed. Combined, these studies reveal the length of the cation alkyl chain weakly affects composition dependent properties (e.g. density, refractive index, thermal conduction, etc.) but has a stronger effect where intermolecular (ionic) forces play a role, such as on viscosity, and on surface tension and interfacial structure. To the authors knowledge, this is the first report of amphiphilic nanostructure in DESs and the first systematic study of the effect of cation alkyl chain length on physical properties.

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1. Introduction

A deep eutectic solvent (DES) is a liquid formed when a high melting point salt is mixed with an appropriate molecular hydrogen bond donor (HBD) [1]. The parent salt in many DESs

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includes a quaternary ammonium. Reline, the archetypical DES, is formed from choline chloride (ChCl, mp = 301 °C) and urea (mp = 133 °C) at a 1:2 salt:HBD molar ratio. At this composition, the mixture has a reported freezing point of 12 °C [2]. Molecular dynamics simulations have been used to show that the vast reduction in melting point of the DES compared to the parent salt and HBD is due to Cl⁻ ions hydrogen bonding with urea to form a “complexed” anionic species in which the charge of the Cl⁻ is delocalised [3].

DESs are related to ionic liquids (ILs), which are pure salts that are liquid at temperatures below 100 °C [4]. In ILs, low melting points are achieved by making at least one of the ions large and asymmetric, which increases the distance between charge centres and frustrates lattice packing. The key distinction between ILs and DESs is that reduced melting points in DESs are achieved via the added HBD, rather than changing the structure of the ions. Many DESs share a range of favourable physicochemical properties with ILs: low vapour pressure, relatively wide liquid range and electrochemical windows, and nonflammability [5]. Like ILs, the solvent properties of DESs can be tailored via the careful selection of salt, and changing the HBD provides an additional tuning mechanism. While the ion concentration in a DES is lower than corresponding ILs due to the HBD, DESs have several advantages: they can be formed from low cost starting materials, are easy to prepare [2], and can more easily be prepared from biodegradable [6], biocompatible [7] and low-toxicity constituents [8].

The uses of DESs for a variety of applications have recently been reviewed [1,9,10]. DES applications are currently dominated by ChCl-based systems, although some other types of DESs including alkylammonium halide systems have gained some attention [11,12]. DESs have been used as solvents for nanomaterial synthesis [13–15], as media for surfactant self-assembly [16–18], lubrication [19], and as extraction solvents [20]. DESs have also attracted considerable interest as electrolytes, especially for electrosynthesis [21–24].

We recently described the nanostructure of ChCl-based DESs with three HBDs (urea, ethylene glycol and glycerol) at the graphite electrode interface for potentials between -1 V to +1 V, using a combination of atomic force microscope (AFM) force curves and simulations [25]. This work, together with other studies of ChCl:ethylene glycol on glassy carbon [26] and ChCl:urea on Hg [27], are important steps towards understanding the complexities of DES structures at electrified surfaces. The structure of solid – DES interfaces are also important for lubrication, adhesion and colloidal stability [28,29]. It has been reported that the length of alkyl chain of imidazolium based ILs could greatly affect the surface charge properties of charged particles, [30–32] therefore, changing the colloidal stability.

The physicochemical properties of many DESs have been well documented in reviews [1,10]. The HBD type strongly affects DES properties, e.g. the melting point of ChCl-ethylene glycol is -66 °C [33] while that of ChCl-dimethyl urea is 149 °C [2]. The anion can also be used to modulate DES properties. For example, the melting point of 1:2 choline[X]:urea decreases in the order F⁻ > NO₃⁻ > Cl⁻ > BF₄⁻ [10], attributed to decreasing electrostatic attractions between the ions. As a result of the near-ubiquity of the choline cation, the effect of the cation structure on the physical properties of DESs has been less well studied.

In this article we describe solid – liquid interfacial structure of DESs formed from mixtures of alkylammonium bromide salts and glycerol. Force curve measurements reveal solvophobic association of alkyl chains and liquid nanostructure increases with chain length. The effect of increased nanostructure is then probed for a variety of physical properties. Alkylammonium bromide/glycerol DESs are selected for study because they are easily available with

different cation chain lengths and because the DESs are liquid at room temperature, but critically because we have previously studied ionic liquids with the same cations in terms of bulk properties [34], bulk nanostructure [35,36], and interfacial nanostructure [37], which provides a framework for interpreting the data obtained in this study. While these DESs are unlikely to be used in, for example, electrochemical applications due to the ammonium protons, the results obtained provide key fundamental insights.

In this paper we provide the first systematic investigation of the effect of cation alkyl chain length (C₂ to C₄) on DES properties including glass transition temperature, melting point, density, viscosity, ionic conductivity and thermal conductivity. AFM force curves are used to examine the structure of these DESs near mica surfaces; mica is a well-defined model anionic substrate [38,39]. In addition to probing the interfacial structure, these force curves can be used to make some inferences about the heretofore unreported bulk structure.

2. Materials and methods

2.1. Materials

Alkylamines (ethylamine (66–72% in H₂O), propylamine (99%) and butylamine (99.5%)) were purchased from Sigma Aldrich. Concentrated hydrobromic acid (HBr) (48% in H₂O) was purchased from Fluka. Glycerol (99.5%) was purchased from Thermal Fisher. All materials were used without further purification.

2.2. General sample preparation

Alkylammonium bromide salts were prepared via a 1:1 M acid-base reaction in an ice-chilled environment. Concentrated hydrobromic acid (HBr) was slowly added to a diluted, aqueous solution of alkylamine (~40%) and then stirred for several hours. The majority of water was removed using a rotational evaporator at 50 °C to yield a colourless solid. The alkylammonium bromide salts (ethylammonium bromide (EABr), propylammonium bromide (PABr), or butylammonium bromide (BABr)) were further dried in an oven at 110 °C for at least 2 h. The melting points of these salts were determined by differential scanning calorimetry (DSC) at a heating rate of 5 °C min⁻¹ under nitrogen gas flow.

DESs were prepared by mixing the alkylammonium salts and glycerol at a 1:2 salt: HBD molar ratio in a sealed glass vial at 70 °C until a homogeneous clear solution was formed. The water contents were always below 1 wt% for the investigated DESs determined by Karl Fischer titration (Metrohm 870 KF Titrino Plus). Care was taken when handling the DESs due to their hygroscopic nature and for each measurement fresh sample was used. The purity of each DES was examined using ¹H NMR-Spectroscopy (c.f. Supplementary Material, Fig. S1). Melting point as a function of composition for three DESs was probed using DSC (Supplementary Material Fig. S2). All samples were glassy, and the melting point is determined from the endotherm in DSC traces. The eutectic points is ~1:2 for BABr – glycerol, between 1:2 and 1:2.5 for PABr – glycerol, and ~1:1.25 for EABr – glycerol. For ease of comparison, all subsequent studies are conducted at 1:2 salt: glycerol.

2.3. Density

A standard pycnometer was used to determine densities at room temperature (22 ± 1 °C). The volume of the flask was calibrated with Milli-Q™ water before every measurement.

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