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Ionic liquids analogues based on potassium carbonate

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ABSTRACT

Ionic liquids analogues (ILA) are emerging as a new class of green solvents with the favorable properties of low cost, low volatility, biodegradability and suitability for many industrial applications. In an attempt to synthesize a novel ILA, potassium carbonate was successfully used as a salt with either glycerol or ethylene glycol as hydrogen bond donors (HBD). The physical properties of this ILA were measured at different temperatures (293.15–353.15 K) and salt:HBD molar ratios (K_2CO_3:glycerol = 1:1 to 1:6 and K_2CO_3:ethylene glycol = 1:3 to 1:8). The properties measured included freezing point, density, viscosity, surface tension, refractive index, conductivity and pH. This type of ILA exhibited similar physico-chemical properties to other solvents reported in literature. The values of these properties indicated that the prepared ILA have great potential for possible industrial applications.

1. Introduction

Room temperature ionic liquids (ILs) are gaining increasing interest by both scientific and industrial communities. These are relatively new class of solvents which are poised to solve both the economic and environmental challenges.

Individual physical and chemical properties of ILs can vary over a broad range. However, the attracting room temperature properties of these liquids make them suitable for many industrial applications. Due to their ionic nature and large molar mass, ILs attain low vapor pressures [1,2]. The low volatility allows greener synthesis with reduced environmental impacts, in contrast to volatile organic solvents [3]. Their low molar densities make their physico-chemical properties especially sensitive to impurities or additives. In addition ILs have wide liquid temperature range, high selectivity and solubility for many organic or inorganic compounds, and less toxicity [4–6]. ILs are immiscible with many organic solvents; moreover, the solvation properties of ILs can be tuned for a specific application by varying the anion–cation combinations [7].

Such liquids have a great potential for capturing different gases with minimal solvent loss in the gas stream due to their high selectivity. CO_2 capture is one related application that has shown great achievements with superior uptake compared to conventional absorbents [8].

A major obstacle that stems against the wide spread use of ILs in the industry is their high synthesis costs compared to conventional solvents. A green alternative for traditional ILs would be composed of biodegradable constituents and exhibit high thermal and chemical stabilities. Deep eutectic solvents are one of such alternatives. These are simple mixtures of salts with hydrogen bond donor compounds such as alcohols, acids, halides, amines and sugars. Deep eutectic solvents (DESs) are regarded as ionic liquids analogues (ILA) because they share many of their intrinsic favorable properties such as their bio-degradability, non-flammability due to their low or none measurable vapor pressure and low toxicity [1,2,9]. Moreover, the fact that they are synthesized at conditions close to room conditions reduces their cost and makes them readily available for probable industrial scales.

DESs have been considered in many industrial applications. In metal deposition, DESs were applied as media and electrolytes for plating of metals [10,11]. Additionally, they have been utilized in the electropolishing of stainless steel. A DES composed of choline chloride and ethylene glycol was used for such purpose. This application showed superior performance over commercial alternatives [9]. Other applications involve its use as extraction medium for glycerol from biodiesel product mixtures [7]. This was followed by the successful application of DESs for the removal of residual palm oil-based biodiesel catalyst [12]. Recently, it was reported that these liquids can be utilized as template-delivery agents in a controlled manner for the synthesis of materials [13].

Conventionally, DESs have been synthesized from ammonium and phosphonium based salts such as: 2-hydroxyethyl-trimethylammonium chloride, trimethylphenylammonium chloride, tetra-butylammonium fluoride, tetraethylammonium chloride, triethylammonium chloride, benzyltrimethylammonium chloride, bis(trifluoromethane sulfone) imide, (lithium bis(perfluoroethysulfone) imide methyltriphenylphosphonium bromide, and benzyltriphenylphosphonium chloride. These salts

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were combined in different molar ratios with varieties of hydrogen bond donors such as: alcohols, carboxylic acids, esters, ethers, amides, and hydrated metal salts of chlorides, nitrates and acetates [14].

In the previous DES synthesis attempts, the used salts were basically quaternary ammonium or phosphonium salts with the exception of metal halides based DES reported later [15]. However, no attempt was made to use alkali metals-based salts as an ingredient for DES synthesis.

The 2:1 molar ratio of urea–choline chloride DES showed a cocrystal with a melting point of 298.15 K. Existence of such cocrystal necessitates the extension of the definition of DES beyond the conventional eutectic phenomenon. This suggests that new DES systems may exist without having clear freezing point and consequently no eutectic composition. This may be due to the lack of nucleation. Recently, low transition temperature mixtures (LTTMs) consisting of choline chloride and lactic acid [16] as well as with malonic acid [17] were reported. These particular systems did not show freezing point in all possible synthesis ratios. The higher concentrations of hydrogen bond donors, in this case, decreased the strength of the hydrogen bonding interactions.

Potassium carbonate (K_2CO_3) known as pearl ash is a white salt having a melting point of 1164.15 K. It is highly soluble in water (112 g/100 mL at 293.15 K) forming a strong alkaline solution. It can be made as the product of potassium hydroxide's absorbent reaction with carbon dioxide. It is deliquescent, often appearing a damp or wet solid. This salt is used as an intermediate in many industrial applications. It is used to soften hard water in the desalination industry. Moreover, it is used to make a safer electrolyte for oxy-hydrogen production by mixing with distilled water rather than using the common electrolyte based on potassium hydroxide. In its aqueous form, potassium carbonate is utilized for the removal of carbon dioxide from the ammonia production synthesis gas in the fertilizers industry. Additionally, aqueous potassium carbonate is also used as a fire suppressant in extinguishing deep fat fryers and various other B class related fires, and in condensed aerosol fire suppression although as the by-product of potassium nitrate. Moreover, it can also be used to pre-dry some ketones, alcohols, and amines prior to distillation [18].

Due to its low heat capacity, K_2CO_3 solutions are also used as promoters for primary or secondary amines for CO_2 capture. It was also used in combinations with the diamine piperazine for enhancing CO_2 absorption. In this case potassium carbonate in solution provides an additional sink for "storage" of the absorbed CO_2 [19].

Glycerol (1,2,3-propanetriol) is a non-toxic, colorless, odorless, viscous liquid with a sweet taste, derived from both natural and petrochemical feedstocks. The name glycerol is derived from the Greek word for sweet (glykys), and the terms glycerin, glycerine, and glycerol tend to be used interchangeably in the literature [20]. In its pure form, glycerol has 1.261 specific gravity, 1500 cP viscosity, 64 dyne/cm surface tension (all at 293.15 K) and a freezing point of 291.35 K. Glycerol is the main co-product of the vegetable oil industry [21] and generated as a byproduct from the biodiesel industry. It has been recently proposed as a valuable green solvent [22]. The three hydroxyl groups of glycerol are responsible for its solubility in water and its hygroscopic nature. Glycerol has numerous commercial applications and uses that include pharmaceutical, cosmetic, food industry, and the alkyl resin industry. The primary function of glycerol in many cases is as a humectant, a substance for retaining moisture and in turn giving softness [20]. In deep eutectic solvents, glycerol has been successfully used as a hydrogen bond donor with choline chloride to form DES by several research groups [23,24]. With the rapid emergence of vegetable oils for non-food applications, and biodiesel production, availability of glycerol has dramatically increased while its price continuously decreased to 0.50 €/kg (for pharmaceutical grade (99.9%) in 2010, and 0.15 €/kg for the technical grade (80%)) thus now making glycerol an attractive new class of green solvent [22].

Ethylene glycol, is the simplest glycol which has molecular formula $HOCH_2CH_2OH$. It is colorless, oily liquid possessing a sweet taste and mild odor. The toxicity of ethylene glycol is regarded as mild [25]. Ethylene glycol has been utilized as a hydrogen bond donor in combination with many quaternary ammonium and phosphonium salts to synthesis DESs. Examples of such salts are: choline chloride [14], methyltriphenylphosphonium bromide and benzyltriphenylphosphonium chloride [5]. These DESs have been used in variety of applications including: CO_2 capture [16], electrodeposition of metals [26], as an electrolyte for redox flow batteries [27] and many others.

It is worth mentioning that combination of liquid solvent such as ethylene glycol and a solid salt like K_2CO_3 was used as separating agents for extractive distillation for producing high purity products. This has the benefits of extractive capacity of the solvent in addition to the solid salt high separation ability [28,29].

In this study, the synthesis of a novel eutectic mixture consisting of potassium carbonate combined with either glycerol or ethylene glycol was investigated. The important physical properties density, viscosity, surface tension, refractive index, conductivity and pH were investigated as function of temperature and salt/HBD ratio. The rationale of studying such systems arises from the need of developing a green solvent that can be utilized economically for possible applications including but not limited to gas absorption, liquid–liquid extraction and catalysis. To explore the possibility of such applications, the physical properties of such new classes of DESs need to be evaluated and predicted.

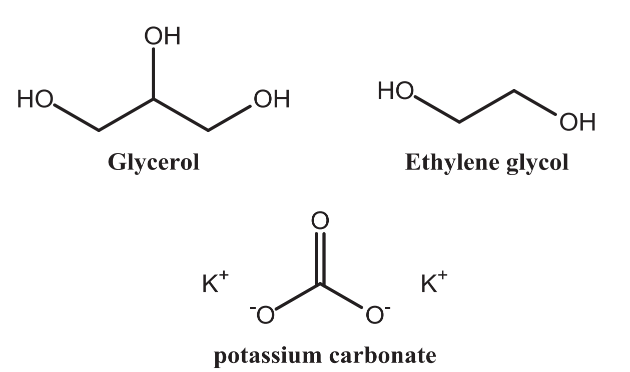
2. Experimental methodology

2.1. Chemicals used

Potassium carbonate, ethylene glycol and glycerol (>98%), were supplied by Merck Chemicals (Darmstadt, Germany). Prior to use, these chemicals were treated by drying in a vacuum oven to assure a low moisture content of below 200 ppm. The chemical structure of the used chemical ingredients are shown in Scheme 1.

2.2. Preparation of potassium carbonate based DES

DESs samples synthesized in different molar ratios of potassium carbonate to glycerol or ethylene glycol as hydrogen bond donors are shown in Table 1. An incubator shaker (Brunswick Scientific Model INNOVA 40R) was used to mix the salt and the hydrogen bond donor. Each DES mixture was mixed at 400 rpm and 353.15 K for 2 h until a homogenous transparent colorless liquid was formed. DES samples were synthesized at atmospheric pressure and under tight control of moisture content.



Scheme 1. Chemical structure of the DES components.