

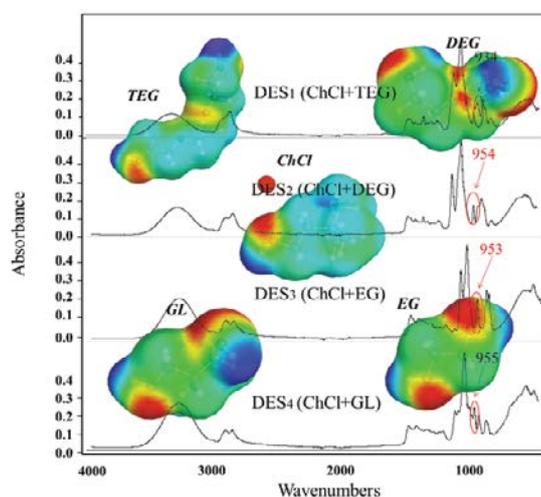
Novel Contribution to the Chemical Structure of Choline Chloride Based Deep Eutectic Solvents

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Abstract

In recent years, green alternative solvents named Deep Eutectic Solvents (DESs) attracted the interest of researchers in the field of green chemistry due to their significant properties. The investigation of functional groups forming DESs helps to deeply understand their nanostructures. In this article, Fourier transform infrared spectroscopy (FT-IR) analysis was conducted for ammonium based DESs to highlight their chemical structure. The functional groups of the prepared DESs were quite similar to their hydrogen bond donors (HBDs) with new peak represents the ammonium identity of the DESs. The findings of this study were compared with previous research for phosphonium based DESs. It was reported that phosphonium based DES forms more peaks compared to ammonium based DES. This investigation is considered as a novel work that has been done for the first time on functional groups of choline chloride (CHCl) based DESs except for DES₁ (triethylene glycol (TEG):CHCl) which was investigated previously.



Keywords: Deep eutectic solvents; Ionic liquid; Green chemistry; Ammonium salts; Fourier transform infrared spectroscopy; Structural

Introduction

At the beginning of this century, new generation of solvents, named Deep Eutectic Solvents (DES) has been reported [1]. DES is defined as a mixture of hydrogen bond donor (HBD) with hydrogen bond acceptor (HBA) which produces liquids. Abbott's fundamental work inspired other researchers to exploit the unusual properties of this system [2]. The physicochemical properties of DESs resemble those of ionic liquids [2].

DESs are not volatile organic solvents and not flammable, they are even more attractive since some of them have been proven to be biodegradable and compatible with enzymes further increasing their interest. Synthesis of DESs is 100% atom economic, easy to handle and no purification is required, thus making their large-scale use feasible [1,3]. DESs can be a good low-cost alternative to room-temperature ionic liquids (RTILs) in many applications, such as medium for the deposition of Zn, Cr, Sn, Cu and Ag metals in the electro- and electroless plating of metals [4], pharmaceuticals, purification of biodiesel, nanotechnology, enhancing oil recovery, CO₂ capture, drug

solubilization and several other technological implementations [5-12]. This article investigates the functional groups of four ammonium based DESs. The mixture of CHCl as hydrogen bond acceptor with triethyleneglycol (TEG), diethyleneglycol (EG), ethyleneglycol (EG) and glycerol (GL) forms DES₁, DES₂, DES₃, DES₄; respectively. The operational conditions of DESs combination were atmospheric pressure at 80°C and 1:3 molar ratios. FT-IR analysis was conducted for the four DESs in order to highlight the chemical structures of the formed DESs. This work was compared with previous work for phosphonium based DESs.

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Material and Method

Chemicals

CHCl (98% purity) was obtained from Sigma Aldrich (Selangor, Malaysia). TEG (99% purity) was obtained from Merck Chemicals (Darmstadt, Germany). DEG, EG, and GL (99.5% purity) were obtained from R&M Chemicals Ltd. (Essex, UK). Table 1 demonstrates the salt, HBD, abbreviations, molar ratio and symbols of the used DESs. The chemicals were kept in controlled area to avoid moisture and impurities.

DESs synthesis

The four HBDs, TEG, DE, EG and GL were mixed with CHCl in an incubator shaker (Brunswick Scientific Model INNOVA 40R). For each DES at a molar ratio 1:3, the mixture was shaken at 350 rpm and 80°C for 2–3 h until the DES is formed in homogeneous phase without precipitation.

FT-IR analysis

The functional groups of the four DESs were analyzed at room temperature using Spectrum 400 FT-IR Spectrometer. FT-IR analysis was reported to contribute in highlighting the nanostructure of DESs. Therefore, humidity and impurities were avoided due to their impact on the functional groups resulted by mixing HBA with HBDs

Results and Discussion

As novel green solvents, DESs are covered in terms of properties and applications. However, their microstructure is still in need of profound investigations. Researchers around the globe devote their efforts to highlight the chemical structures these neoteric solvents. Recently, Aissaoui et al. (2015) have investigated the functional groups of phosphonium based DESs. The appearance of new peaks detecting the combination of DESs was reported [13]. In addition, García et al. (2015) have investigated the chemical structure of CHCl:Urea based DES using the density functional theory (DFT) combined with a topological analysis of the electronic density [14]. Moreover, FT-IR analysis was performed by Yue et al. (2012) to report the microscopic structure of CHCl:Urea [15].

In this study, for the four DESs, hydroxyl telescopic vibrations at 3300 cm^{-1} was revealed by the presence of O–H stretching bands between 3200 and 3500 cm^{-1} (Figure 1-4) [16-19]. This in good agreement with the results published by Aissaoui et al. (2015) for methyltriphenylphosphonium bromide (MTPB) based DESs. Where, MTPB as HBA was mixed with TEG, DEG, EG and GL; respectively [13]. The peaks illustrated in the region between 3200 and 3500 cm^{-1} can also be due to the presence of water in DESs. DESs are hydrophilic solvents and interact with water [20]. Formation of the proton transfer salts was demonstrated by the observed FT-IR spectrums. The FT-IR spectra of the formed DESs, DES₁ [12], DES₂, DES₃ and DES₄ illustrate the existence of C–H stretching bands of alkanes, CH₃ and CH₂ between 3000 and 2800 cm^{-1} [16-19]. Clearly, Figure 1-4 show very similar spectrum for the four DESs. This is due to the chemical structure

Salts	Abbreviation	HBD	Molar ratio	Symbol
Choline Chloride	ChCl	TEG	1:3	DES ₁ [12]
Choline Chloride	ChCl	DEG	1:3	DES ₂
Choline Chloride	ChCl	EG	1:3	DES ₃
Choline Chloride	ChCl	GL	1:3	DES ₄

Table 1: Composition and abbreviation of DESs used in this research.

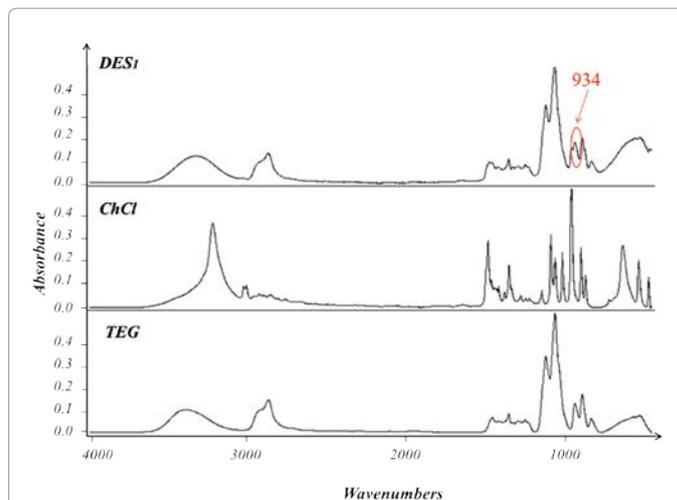


Figure 1: FT-IR spectra of the TEG, ChCl and DES₁ at room temperature in the region of 400–4000 cm^{-1} [12].

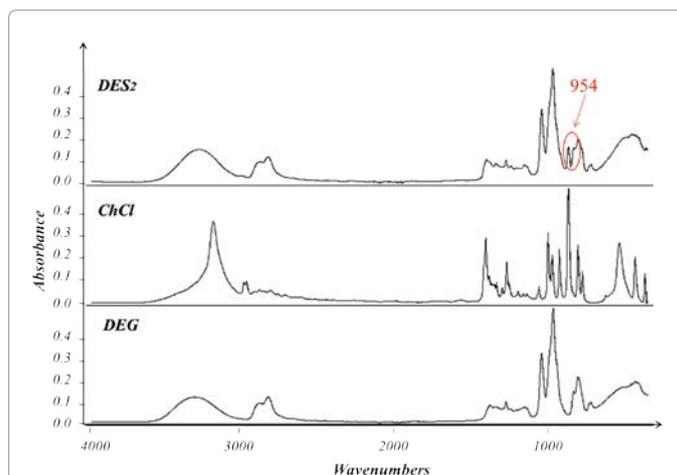


Figure 2: FT-IR spectra of the DEG, ChCl and DES₂ at room temperature in the region of 400–4000 cm^{-1} .

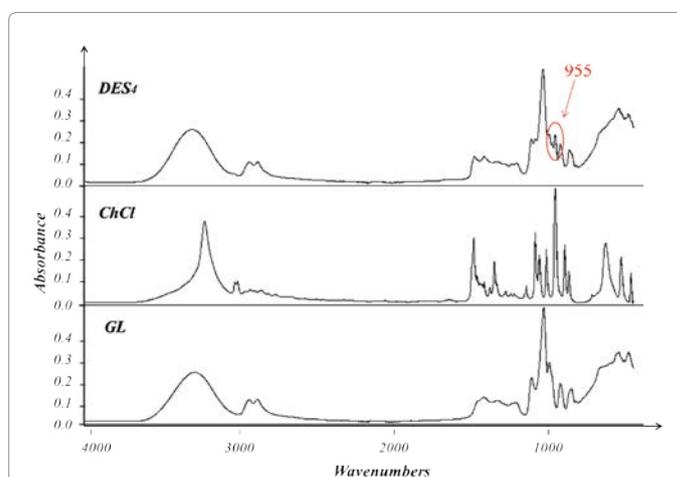


Figure 3: FT-IR spectra of the EG, ChCl and DES₃ at room temperature in the region of 400–4000 cm^{-1} .

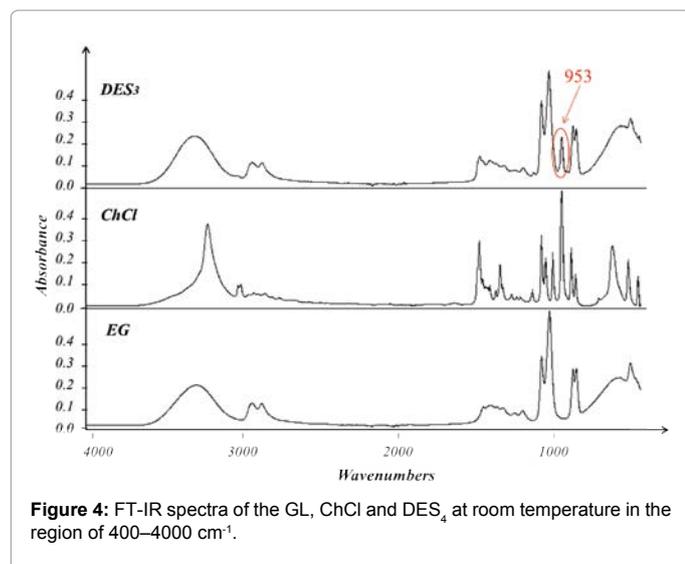


Figure 4: FT-IR spectra of the GL, ChCl and DES₄ at room temperature in the region of 400–4000 cm⁻¹.

of HBDs which are from same organic solvent family (glycols). In addition, the presence of water in all DESs gives them similar peaks in same region. Moreover, the presence of CHCl as an organic salt in all DESs can be also a good reason for the similarity of the DESs in terms of functional groups. For the four ammonium based DESs, a portion of the cloud of electrons of the oxygen atom was transferred to the hydrogen bond, reducing the force constant is the reason behind the change in vibrational state occurred. Thus, the shift of the OH stretching vibration indicated the existence of a hydrogen bond between the TEG and CHCl when the DES was formed [13]. This in agreement with the work reported by Aissaoui et al. (2015) for the DESs formed using MTPB as salt and (TEG, DEG, EG and GL) as HBDs [13]. The N–H stretching bands may be overlapped with C–H vibrational bands in the region of 3000–2800 cm⁻¹ when the frequency is lower than 3000 cm⁻¹ [16–19]. Comparing the formed DESs with their HBA, it was noticed that the stretching vibration in the region between 2500 and 3100 cm⁻¹ in CHCl disappeared after the formation of the ammonium DESs. The disappearance of stretching vibration in the region between 2500 and 3100 cm⁻¹ in CHCl was also observed in the case of MTPB as HBA [13]. The existence of water and the ammonium anion in the four DESs were observed by the two peaks in the region between 4000 and 2500 cm⁻¹.

The region of 3200 to 2400 cm⁻¹ also identifies ammonium structures [16–19]; this region presents N-H stretching at 2869 cm⁻¹ [16–19]. Additionally, ammonium-based DESs have similar peaks in the same region 600–408 cm⁻¹. The presence of the Cl in the formed DESs was also shown in all figures between 600 and 408 cm⁻¹ [17–19]. It was deduced that the DESs have similar functional groups as their HBDs except the new peak appeared in the region 935–955 cm⁻¹. The new peak refers to the ammonium structure identity of the DESs [17–19]. Therefore, it appears after the combination of HBDs as glycols with CHCl as ammonium salt.

The analysis of the functional groups using FT-IR analysis was not conducted often in previous studies for DESs except our previous published work and some other investigations [13,15]. Therefore, further investigations are highly recommended to cover the necessary work for the investigation of the chemical structures of DESs to help deeply understand the properties of DESs.

Conclusion

In this study, novel FT-IR investigation was performed by analyzing the functional groups of four ammonium DESs prepared by mixing four glycols as HBDs with CHCl as HBA. It was deduced that the functional groups of the mixed DESs behave as their HBDs. However, new peak was detected confirming the ammonium identity of the DES. This work motivates further investigations on the microstructures of DESs to highlight the molecular structures and combination mechanisms of these neoteric green solvents.

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