

Neoteric FT-IR Investigation on the Functional Groups of Phosphonium-Based Deep Eutectic Solvents

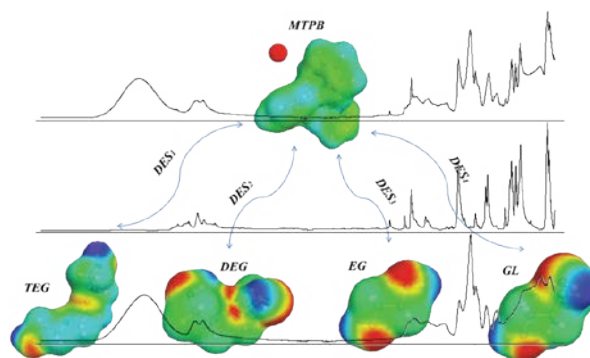
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Abstract

Deep eutectic solvents (DESs) are novel solvent media that are currently under investigation as an alternative to ionic liquids and conventional solvents. The physical properties of DESs as well as their mild environmental footprint and potentially critical industrial application necessitate understanding the interaction of functional groups on both the salt and hydrogen bond donor (HBD). In this study, four DESs were prepared by mixing triethylenglycol, diethylenglycol, ethylenglycol, and glycerol as HBDs with methyltriphenyl phosphonium bromide as a salt at a molar ratio of 1:4. Fourier transform infrared spectroscopy was conducted to highlight the chemical structure and mechanism of the combination of the four DESs. New spectra illustrating the combination of the functional groups of the HBDs and salt were observed and interpreted. This study is the first to investigate the properties of neoteric FT-IR for phosphonium-based DESs in addition to (MTPB:TEG) which was reported previously.



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

Introduction

In recent decades, deep eutectic solvents (DESs) have emerged as a novel class of ionic liquids (ILs) [1]. DESs share many characteristics with conventional ILs (e.g., no flammability and low volatility) [2]. In addition, DESs are relatively cheap to produce because they are made from inexpensive starting materials and are easy to prepare. Moreover, biodegradable and nontoxic constituents can be employed to prepare DESs [3].

DESs are a combination of two or more compounds, and the final solvent has a melting point that is lower than that of its individual components. DESs comprise mixtures of organic halide salts, such as choline chloride (CHCl), with an organic compound that acts as a hydrogen bond donor (HBD). The HBD can form a hydrogen bond with the halide ion. Examples of HBDs include amides, amines, alcohols, and carboxylic acids [4]. By convention, DESs must have a melting point equal to or less than 100°C.

Recently, Kareem et al. (2010), Luo et al. (2012), Shahbaz et al. (2011-2012) and Hayyan et al. (2013) have reported the physical properties of both phosphonium- and ammonium-based DESs and demonstrated their potential use in industrial applications [5-11]. Hayyan et al. (2013) analyzed the cytotoxicity and toxicity of phosphonium- and ammonium-based DESs [12].

In the present study, four DESs were prepared by mixing triethylenglycol (TEG), diethylenglycol (DEG), ethylenglycol (EG), and glycerol (GL) as HBDs with methyltriphenylphosphonium bromide (MTPB) as a salt at a molar ratio of 1:4. Fourier transform infrared spectroscopy (FT-IR) was performed for each DES to compare the components with their products and identify the transformation resulting from the formation of the DESs.

Materials and Method

Chemicals

MTPB (99% purity) and TEG (99% purity) were obtained from Merck Chemicals (Darmstadt, Germany). DEG, EG, and GL (99.5% purity) were obtained from R&M Chemicals Ltd. (Essex, UK). Table 1

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shows the salt, HBD, abbreviations, molar ratio, and symbols of the four DESs. The chemicals were stored in a highly controlled environment to prevent moisture and impurity contamination.

DES preparation

The DESs were prepared according to methods reported in the literature [1]. In brief, a measured amount of MTPB was mixed with one of the four HBDs (TEG, DEG, EG, and GL) at a molar ratio of 1:4 and placed in an incubator shaker (Brunswick Scientific Model Innova 40R). The mixture was shaken at 350 rpm at a temperature of 80°C for 2–3 hours until the DESs became homogeneous with no precipitation.

FT-IR analysis

A Spectrum 400 FT-IR spectrometer was employed to analyze the functional groups of the four DESs at room temperature. The four HBDs (TEG, DEG, EG, and GL) and the salt, MTPB were analyzed using FT-IR to identify the transformations resulting from the formation of the DESs.

Results and Discussion

The chemical structures and combination mechanism of the DESs are unknown and were therefore investigated in this study. It should be noted that DES₁ (MTPB:TEG) FT-IR analysis was investigated by Hayyan et al. (2015) [13] and repeated in this article for comparison. The observed FT-IR spectra revealed the formation of proton transfer salts. The presence of O–H stretching bands between 3200 and 3500 cm⁻¹ in the four spectrum figures was attributed to hydroxyl telescopic vibrations at 3300 cm⁻¹ [6,14–16]. Figure 1 reveals that a shift in the OH stretching vibration of pure ethyleneglycol occurred when the DES was formed. This in agreement with the observation reported by Hou et al. for a DES formed using levulinic acid as the HBD and tetrabutylphosphonium bromide [17]. The FT-IR spectra of the TEG in the DES indicate that the change in vibrational state occurred because a portion of the cloud of electrons of the oxygen atom was transferred to the hydrogen bond, reducing the force constant. Thus, the shift of the OH stretching vibration indicated the existence of a hydrogen bond between the TEG and TMPB when the DES was formed. The region between 3000 and 2800 cm⁻¹ shows the existence of C–H stretching bands of the alkanes CH₃ and CH₂ for the four DESs [6,14–16]. Because of the water content and organic structure of the HBDs (i.e., TEG, DEG, EG, and GL) and organic salt (i.e., MTPB), the functional groups of the four formed DESs appear to be relatively consistent. For the phosphonium-based DESs (i.e., DES₁, DES₂, DES₃, and DES₄), the P–H stretching bands may be overlapped with C–H vibrational bands in the region of 3000–2800 cm⁻¹ at frequencies lower than 3000 cm⁻¹.

Comparing Figures 1–4 shows that the stretching vibration in the region of 2000–3100 cm⁻¹ in the MTPB disappeared after the phosphonium-based DESs were formed. For the four DESs, the region of 2340–4000 cm⁻¹ contains only two peaks, proving the existence of an OH group and phosphonium cation.

The presence of Br in the formed DESs was also observed in the region of 600–408 cm⁻¹ (Figures 1–4) [14–16]. The four DESs

Salts	Abbreviation	HBD	Molar ratio	Symbol
Methyltriphenylphosphonium bromide	MTPB	TEG	1:4	DES ₁ , [13]
Methyltriphenylphosphonium bromide	MTPB	DEG	1:4	DES ₂
Methyltriphenylphosphonium bromide	MTPB	EG	1:4	DES ₃
Methyltriphenylphosphonium bromide	MTPB	GL	1:4	DES ₄

Table1: Composition and abbreviation of DESs used in this research.

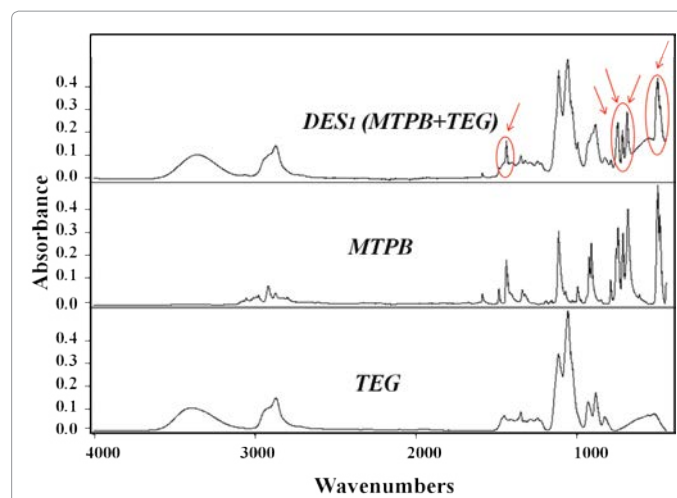


Figure 1: FT-IR spectra of the TEG, MTPB and DES₁ at room temperature in the region of 400–4000 cm⁻¹ [13].

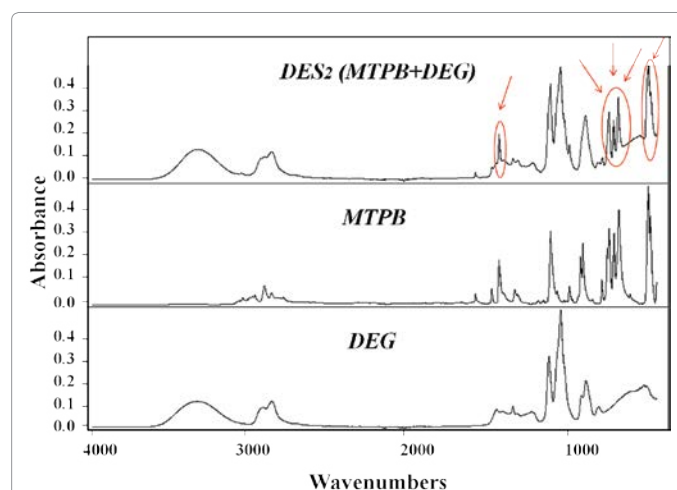


Figure 2: FT-IR spectra of the DEG, MTPB and DES₂ at room temperature in the region of 400–4000 cm⁻¹.

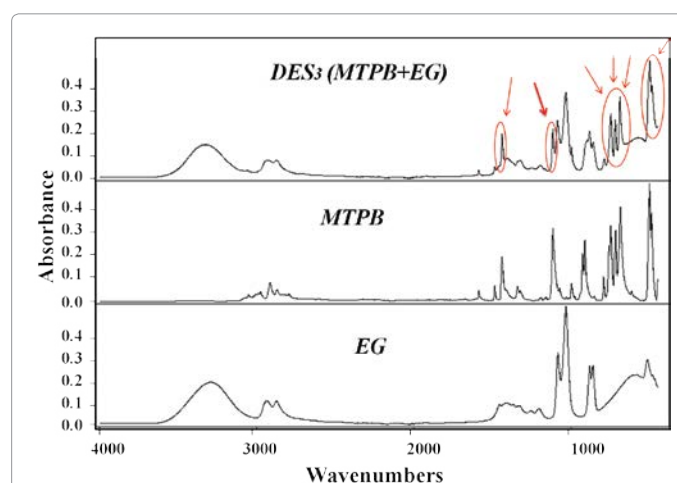


Figure 3: FT-IR spectra of the EG, MTPB and DES₃ at room temperature in the region of 400–4000 cm⁻¹.

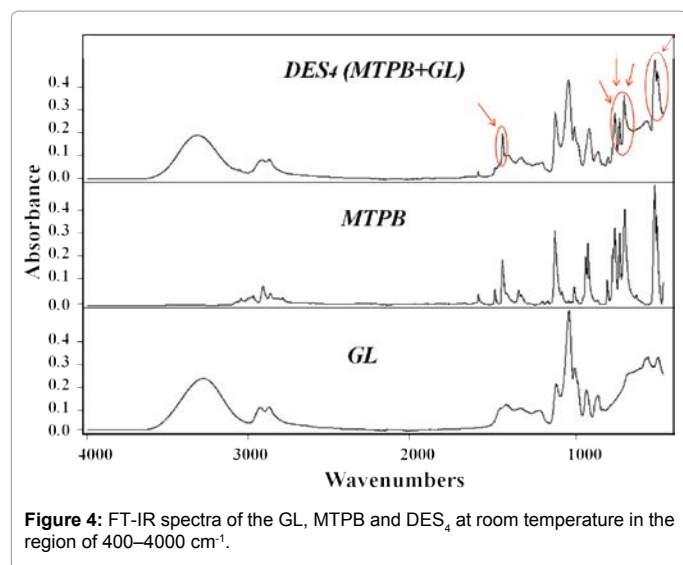


Figure 4: FT-IR spectra of the GL, MTPB and DES₄ at room temperature in the region of 400–4000 cm⁻¹.

demonstrate similar chemical compositions for DES₁, DES₂, DES₃, and DES₄ with varying levels of absorbance. In addition, a peak not present in the other three DES spectra was observed at 1119 cm⁻¹ in DES₃.

To the best of our knowledge, few studies have analyzed the functional groups of phosphonium-based DESs. Therefore, we recommend that future studies on DESs conduct further analyses.

Conclusion

In this FT-IR investigation, the functional groups of four neoteric phosphonium DESs were analyzed. The findings indicate that the functional groups of the mixed DESs behave as their HBDs, and the appearance of new peaks confirms the phosphonium identity of the DESs. The findings of this study warrant further investigation of DES green solvents to elucidate the molecular structure and combination mechanism of DESs.

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