



Probing intermolecular interactions in a binary mixture of deep eutectic solvents with DMSO by impulsive stimulated Raman spectroscopy

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The physicochemical properties of deep eutectic solvents (DESs) can be altered in binary mixture with co-solvents like water, dimethyl sulfoxide (DMSO), etc. due to the synergistic effect of hydrogen bond donors-acceptors (HBDs- HBAs) that arises from the interactions of DESs with (organic) solvents. We investigated the intermolecular interactions of DES (1,3-Propanediol-based) of varying compositions in binary mixture with DMSO and observed the emergence of a new vibrational mode using impulsive stimulated Raman spectroscopy (ISRS). © Anita Publications. All rights reserved.

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1 Introduction

Deep eutectic solvents (DESs) are an emerging class of solvents alternative to commonly used organic solvents and ionic liquids due to their facile and low-cost preparation, high biodegradability, nonflammability, a relatively wide temperature-range of stability of the liquid phase, and low vapor pressure [1-3]. Because of their non-toxic nature, they are also termed as green ionic liquid analogues. DESs are now widely recognized as inexpensive and environmentally-benign liquid media for potential use in the broad area of research as well as can be utilized for large-scale industrial applications. Nowadays, they are used in several interesting applications, including electrodeposition, electrochemistry, inorganic synthesis, and as media for several organic processes [2,3]. In 2003, Abbott and co-workers reported synthesis of the first DES (i.e. Reline, with significant depression in freezing point, $T_m = 12$ °C), which is composed of choline chloride ($T_m \approx 302$ °C) and urea ($T_m \approx 133$ °C) in a 1:2 mole ratio [4,5]. Cholinium cation (2-hydroxyethyl)-trimethylammonium cation) is the most frequently employed quaternary ammonium cation as a hydrogen bond acceptor (HBA) for the synthesis of DESs. Choline chloride is biodegradable, non-toxic, and readily available component. The choline cation is a subclass of the vitamin B family that is thought to serve a crucial function in our daily lives by participating in numerous metabolic processes. DESs are regarded as designer solvents as their chemical properties can be tailored by appropriately combining various quaternary ammonium salts with a wide range of available hydrogen bond donors (HBD). Additionally, it has been proposed that the formation

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of hydrogen bond networks is the primary driving force behind the chemical reaction between HBD and HBA that results in the synthesis of DESs [6]. The charge delocalization between the HBD and HBA leads to a significant drop in the freezing point of DESs. Thus, the depression in freezing point of DESs depends on the strength of H-bond interactions. Other salts, for example, ammonium, imidazolium, and phosphonium-based salts were also explored but to a lesser degree in comparison with ChCl-based DESs [7,8].

To efficiently utilise DESs as a greener alternative to ionic liquids for a wide range of applications, it is essential to comprehend its specific solvent-solvent and solute-solvent interactions at the molecular level, since these interactions control the bulk physicochemical properties [9,10]. Despite various studies on these benign/non-toxic media, a lack of relevant information regarding their chemical and physical characteristics may limit their rational design and introduction to new applications. A strategy of cosolvent-modified mixtures to provide a way to tune the physicochemical properties was reported [11-13]. In this regard, the effect of water on intermolecular hydrogen bond interactions of DESs and the importance of the variable molar composition of water was studied in detail [14]. Apart from water, other organic solvents are commonly employed in binary mixtures with DESs. Dimethyl sulfoxide (DMSO), one of the most extensively utilized organic co-solvent [15,16], has recently become a prime subject of study because of its cooperative function and featuring effective intermolecular interactions within DES and as well between the DES and DMSO.

In this work, we used DMSO, a dipolar aprotic solvent as a co-solvent because of its unique properties such as high polarity, capacity to dissolve both protic and aprotic organic and inorganic compounds and existence in liquid phase across a broad temperature range [17]. We report, for the first time, the interaction of 1,3-Propanediol-based DES with DMSO in a binary mixture probed by tracking the vibrational frequencies using steady-state and time-resolved Raman spectroscopy in the ground state. Herein, by varying the molar composition of DMSO in a binary mixture with DES, we focus on examining the specific composition of DMSO for which intermolecular interactions are significantly modified.

2 Materials and methods

2.1 Materials

Choline chloride (ChCl, > 99 wt%), 1,3-Propanediol (98 wt%), and Dimethyl sulfoxide (DMSO, > 99.9 wt%) are procured from M/s Sigma-Aldrich (all materials are of spectroscopic grade) and used as such without any further purification. Choline chloride as HBA component and 1,3-Propanediol as HBD component are mixed in 1:3 molar ratio under constant stirring at 353 K until homogenous liquid is formed, reflecting the formation of DES. DESs samples with various DES/DMSO compositions are prepared in v/v. All the prepared DESs samples are tightly sealed with parafilm to protect them from moisture and air.

2.2 Methods

Steady-state Raman spectroscopy

A micro-Raman spectrometer (inVia confocal Raman microscope, Renishaw) is used to record the steady-state Raman spectra. The sample drop of ~2 μL is placed on aluminium foil and focused with an objective (N Plan EPI X50 NA0.75, Leica). An NIR (near infrared) laser of 785 nm wavelength with a 10s exposure period and 10% of its maximum intensity is used to excite the sample. Back-scattered light was collected and the Rayleigh scattered light is blocked using a 785 nm edge filter. The residual scattered light is dispersed using a 1200 lines/mm diffraction grating and detected by an air-cooled CCD (charge-coupled device) detector. The data is acquired using commercially available software (Wire 3.1, Renishaw). The baseline correction using asymmetric least square function and data smoothening with averaging over 10 adjacent points are accomplished in Origin software (Origin Lab Corp., 2018 release).

Impulsive stimulated Raman spectroscopy (ISRS)

ISRS is a time-domain approach to record vibrational fingerprints of molecules of varying complexities using broadband femtosecond pulses with a high temporal resolution. In ISRS, two temporally separated pulses, typically referred to as Raman pump pulse and probe pulse are used in which Raman pump pulse generates vibrational coherence in the ground state which is further interrogated by the probe pulse (see Fig 1(a, b)). The vibrational coherence, in result, creates a wavepacket in the ground state which typically evolves in few picoseconds (i.e., ~ 5 -10 ps). Fourier transform (FT) of the time-domain interferogram yields the Raman spectrum. The experimental set-up is similar to a femtosecond broadband transient absorption spectrometer and is described elsewhere [18,19]. Briefly, an ultrashort Raman pump pulse (>1 mW) centered on 580 nm with a maximum detectable Raman shift of ~ 600 cm^{-1} (obtained from the non-collinear optical parametric amplifier (NOPA, TOPAS Light Conversion, pumped by Libra, Coherent)) and a broadband probe pulse (< 10 μW) (obtained by pumping sapphire crystal) are used and the corresponding spectra are shown in Fig 1(c).

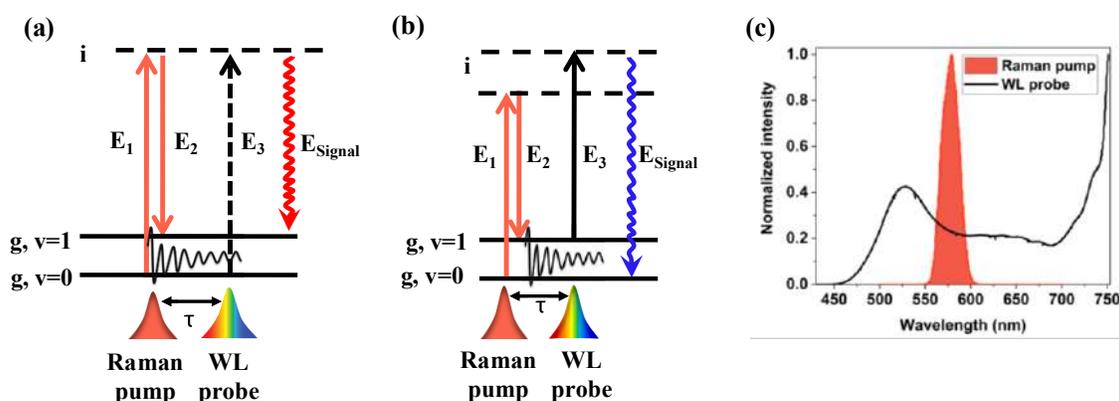


Fig 1. Energy level diagram for (a) red-shifted (Stokes) signal, (b) blue-shifted (coherent anti-Stokes) signal in ISRS (solid/broken arrows represent the electric field interaction with the bra/ket side of the density matrix); (c) normalized spectra of Raman pump and broadband probe.

A data analysis procedure (skipping coherent artifact, baseline correction, zero padding, applying a Hanning window function, and Fourier-transforming the time-domain data) is adopted to obtain the Raman spectra from raw time-domain data using Matlab programming. For a detailed discussion on the principles and methodology, see Ref 19.

3 Results and discussion

Steady-state studies

Preliminary studies to investigate the various interactions between DES and DMSO are performed using steady-state Raman spectroscopy. Raman spectra of DES with its individual components (Chcl and 1,3-Propanediol) and its binary mixture with DMSO are shown in Fig 2 (a, b). Numerous vibrational modes are obtained corresponding to individual components of DES and the intermolecular interactions within DES and DES/DMSO binary mixture, along with a substantial increase/decrease in the Raman intensities indicating the hardening/softening of bond interactions.

Blue and red-shifts are observed in vibrational modes of varying compositions of DES/DMSO shown in Fig 3, as previously reported [20]. On the other hand, the weak interactions associated with the lower vibrational wavenumber are difficult to capture through steady-state. Therefore, ISRS studies are carried out to investigate these low-frequency vibrational modes.

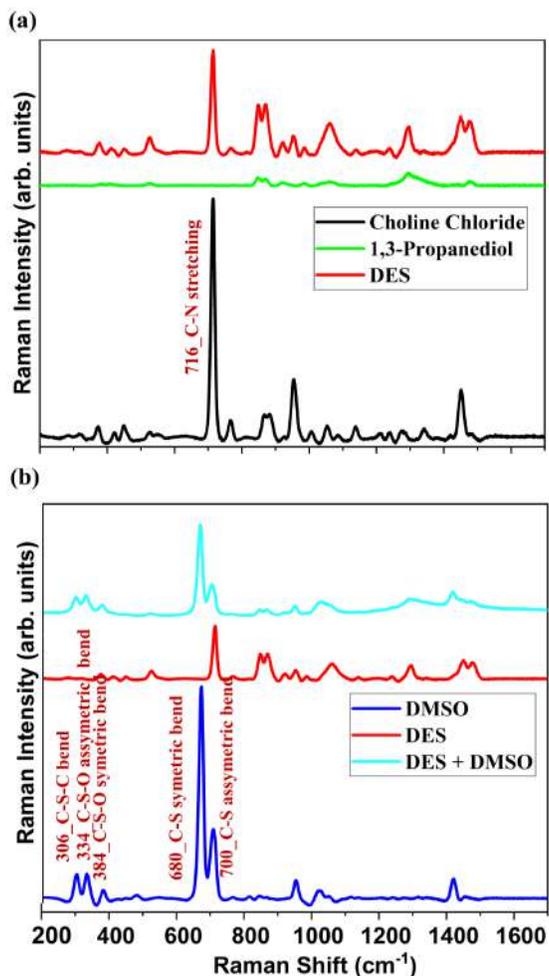


Fig 2. Steady-state Raman spectra (a) of DES with its individual components (b) of DES, DMSO, and equimixture of DES and DMSO.

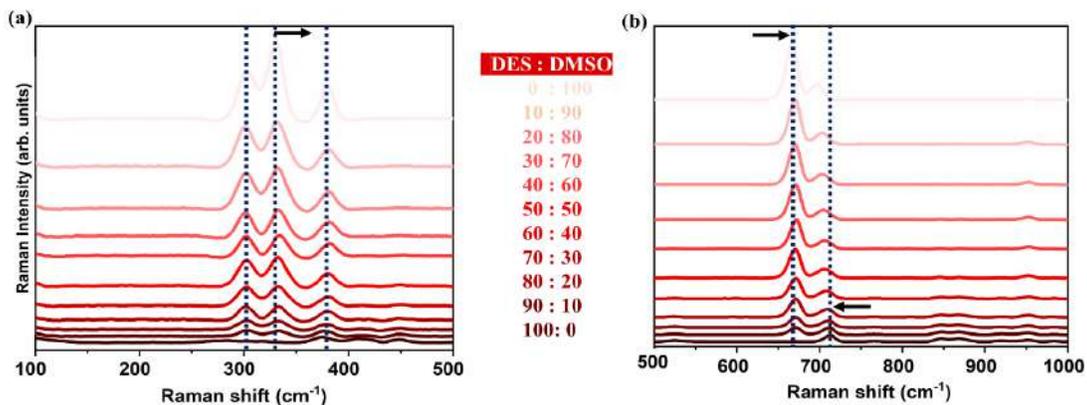


Fig 3. Steady-state Raman spectra for varying compositions of DES and DMSO; (a) for 100 to 500 cm^{-1} region (b) for 500 to 1000 cm^{-1} region

Time-resolved studies

The raw time-domain data of pure DES is displayed in Fig 4(a) and divided into two different regions of the probe spectrum (region A: 500-541 nm and region B: 625-750 nm). For an improved signal-to-noise ratio, the FT of summing over regions A and B is performed as shown in Fig 4(b, c). Significant changes in the vibrational modes are highlighted (within the pink band). In region A, DMSO exhibits three strong vibrational modes at 288 cm^{-1} , 308 cm^{-1} , and 399 cm^{-1} that overlap with the DES modes, thereby making it difficult to track the variations in the vibrational feature of DES within the binary mixture. Quite interestingly, for 40% and 80% DMSO composition, a new mode appears at 261 cm^{-1} which is more prominent in region B and appears at 259 cm^{-1} in 40% composition of DMSO.

This new mode is likely to correspond to the intermolecular interaction between the individual components (Chcl and 1,3-Propanediol) of DES, the intensity of which is enhanced in presence of DMSO (known as the ‘synergistic effect’), or it may correspond to a new intermolecular interaction specific to the binary mixture of DES and DMSO [21-25]. This, however, warrants further theoretical studies to identify the key interactions responsible for this characteristic peak in the Raman spectrum.

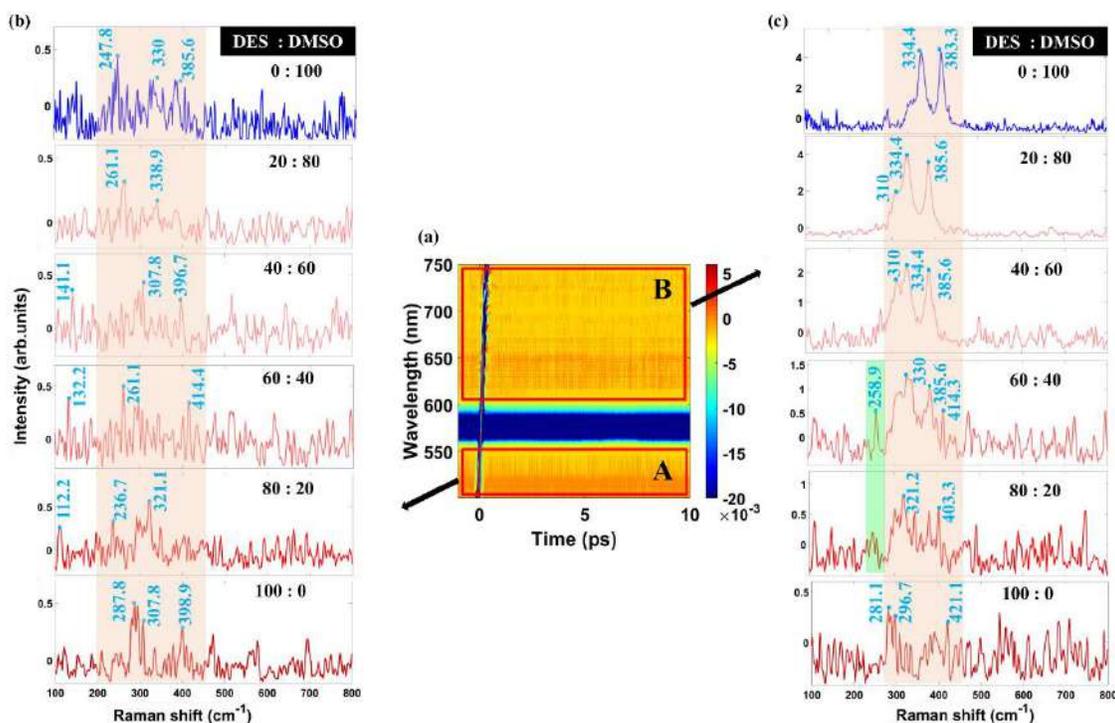


Fig 4. (a) Pump-probe contour map of pure DES and Raman spectra of DES with varying DMSO composition showing summed FT of (b) region A and (c) region B.

Furthermore, using the advantage of employing a broadband probe, the information of vibrational modes across the whole region of detection wavelength can be obtained through the FT contours depicted in Fig 5 (a, b) for both regions [19,26-29]. These contours provide a clear picture of vibrational modes and their intensities as well. In data for pure DES, the vibrational modes exclusive to DESs are observed in region A, while in the binary mixture, modes obtained in region A are contributed from both DES and DMSO, and modes obtained in region B are contributed primarily from DMSO.

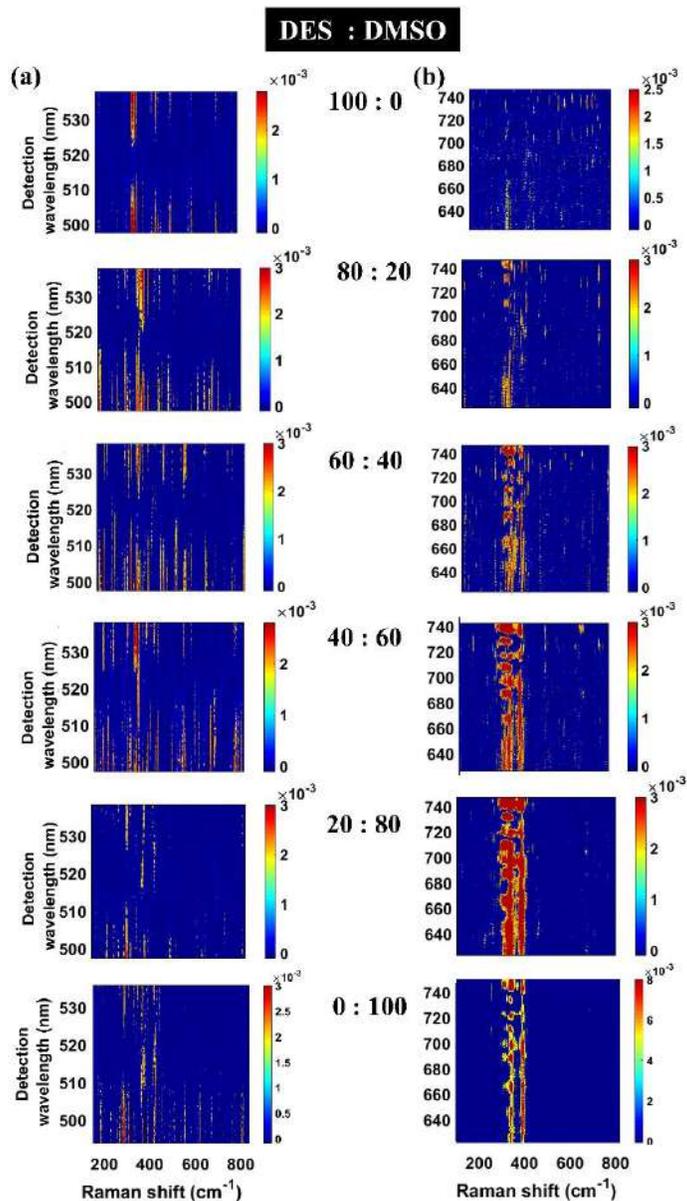


Fig 5. Contours representing the FT for varying ratios of DES/DMSO for: (a) region A (500-541 nm) and (b) region B (625-750 nm).

4 Conclusion

In summary, using impulsive stimulated Raman spectroscopy, we identified a new low-frequency vibrational feature (at $\sim 259 \text{ cm}^{-1}$) arising due to specific intermolecular interaction in the binary mixture of DES with DMSO at a particular composition (i.e., 40% composition of DMSO in the binary mixture) which is not captured by the conventional steady-state studies. Thus, ISRS studies proved to be an intriguing technique to monitor low-frequency vibrational modes in complex systems.

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