

## Structure, Dynamic, and Solvation of a New Class of Designer Solvents by Ultrafast Nonlinear Infrared Spectroscopy

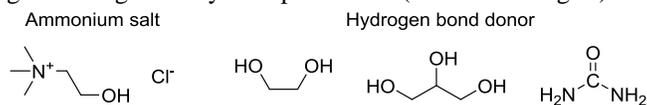
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Deep eutectic solvents (DESs) are a new type of designer solvent based on the eutectic phenomenon in which the fusion point of the DES is lower than the melting points of the individual components of the mixture. In particular, DESs can be formed by the mixing of an ionic compound with a hydrogen-bond donor, both with melting temperatures well above room temperature. Due to their simple preparation, the physical or chemical properties can be tailored by the various components employed based on the different purpose of applications. Thus, DESs have been proposed as new designer solvents. However, DESs have many attractive characteristics such as being inexpensive and green which makes them a contentious alternative to conventional solvents and other designer solvents, such as ionic liquids. The number of DESs that can be prepared by mixing different HBAs and HBDs is very large ( $\sim 10^7$ ). Thus, it is easy to envision on-demand preparation of DESs with properties tailored to their use. However, to make a use-tailored DES, a priori knowledge of the relationship between the microscopic structure and the macroscopic properties is required. In DESs, the connection between macroscopic and microscopic properties is not well understood because many different types of molecular interactions with similar energetics contribute to their physicochemical properties. The diversity of interactions arises from the various chemical structures of the DES components. The possibility having spatial heterogeneities in the DES molecular structure is a good example of the intricate energetic balance in DESs. Thus, a thorough characterization of the DES molecular structure and interactions will help us not only to gain a deeper understanding of these complex solvents, but also to rationalize the observed DES physico-chemical properties in terms of their microscopic structure. Thus, our group has engaged in characterizing the structure and the dynamics of structural changes in DES, as well as the interactions that different solutes observe in DES as a function of the component molecular structure.

### 1. Molecular structure of DES

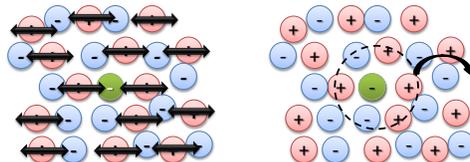
The molecular structure of the DES was investigated from the perspective of the two different DES components; i.e., ionic compound and hydrogen bond donor.

A. **Molecular environment from the anion perspective:** For the investigation of the molecular environment surrounding the anion of the ionic compound, two ionic compounds (azide and thiocyanate ions) in three archetypal DES (Figure 1) were investigated using an array of experimental (IR methodologies) and computational methods.



**Figure 1.** Structure of the component in the three investigated DES.

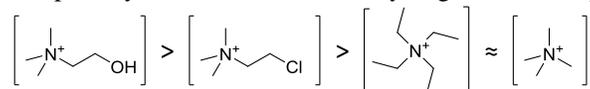
Our experimental results show that the ionic solutes occupy the same places as the chloride ions in the pseudo ionic lattice of the DES since it observes the same type of interactions; i.e., hydrogen bonds with the hydrogen bond donor. However, the dynamics of the environment derived from Two Dimensional IR experiments show a contrasting difference between azide and thiocyanate ions. In the case of the azide ion, the azide ion is observing a similar environment in both solvents; i.e., hydrogen bond with the hydrogen-bond donor. In contrast, the thiocyanate ion shows much different solvation dynamics in the different DES, where two different time scales are clearly observed: a short ( $\tau < 20$  ps) and long characteristic times ( $\tau > 50$  ps). The difference in observed dynamics between azide and thiocyanate ions is due to the symmetry of the anion. The thiocyanate ion can form hydrogen bonds through its sulphur atom without perturbing its nitrile group, but the azide ion interacts through one or both of its nitrogen atoms, and in any of those cases the N3 vibrational mode is directly affected. The molecular motions of the environment surrounding the thiocyanate ion are assigned to in-place and diffusion motions of the cations in the DES (Figure 2).



**Figure 2.** Cartoon representation of the fast (left) and slow (right) molecular motions observed in the DES.

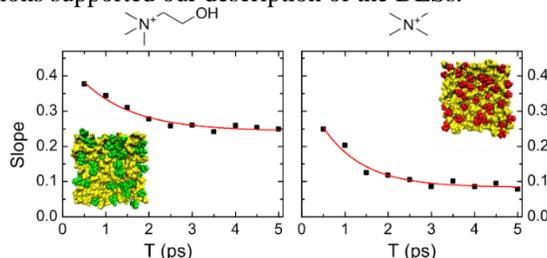
The proposed molecular mechanism behind the solvation dynamics was further confirmed via NMR pulsed field gradient diffusion experiments and computational studies (molecular dynamics simulations and ab initio computations). In addition, our theoretical modeling of the thiocyanate nitrile stretch lineshape suggested that alcohol-based DESs are more structurally disorganized than their amide-based analogues. However, no correlation between the organization of the different DESs and their physical properties, such as density, is observed, indicating that the defects (i.e., hole theory) in the solvent are not sufficient to fully describe the observed properties of DESs.

**B. Molecular environment from the hydrogen bond donor perspective:** For studying the molecular environment of the hydrogen bond donor, the liquid structure of five different amide-based DESs was studied as a function of the chemical structure of the hydrogen bond acceptor. Our studies demonstrated that the amide solvation is not significantly affected by the chemical structure and symmetry of the HBA cation. In addition, it was derived from our studies that the different DESs do not show appreciable differences in the level of disorganization. The solvation dynamics showed that the DESs present a fast dynamical component with a time scale of  $\sim 1$  ps irrespective of the hydrogen bond acceptor, which was assigned to hydrogen bond making and breaking between amides. Moreover, all the studied DESs show a slow dynamical component of the solvation dynamics, which is shown to be correlated with the asymmetry and polarity of the moieties of the hydrogen bond acceptor (Figure 3).



**Figure 3.** Slow dynamic component amplitude order and the cation chemical structure.

The overall dynamics was rationalized in terms of a microscopic heterogeneous structure of the DESs where the heterogeneities create domains that slow the hydrogen bond making and breaking (Figure 4). Modeling of the system via molecular dynamics simulations supported our description of the DESs.



**Figure 4.** Solvation dynamics and structure of the cation.

Finally, the presence of nanoscopic heterogeneities was further evidenced by the observation of an endotherm at 23 °C in the differential scanning calorimetry thermogram. This study shows not only that heterogeneities in DES exist, but also that the nanoscopic heterogeneities slow down solvation dynamics of the amides in the system. Finally, this part of the work is important because it demonstrates that molecular aspects of liquids, such as nanoscopic heterogeneities, can be observed through the dynamics of the molecular motions of the environment.

## 2. Solute-solvent interactions

**A. Ionic solutes:** The effect of the chemical structure of the hydrogen bond donor, as shown in previous sections, demonstrates that the interactions between ionic solutes and the hydrogen bond donor, such as hydrogen bonding, are partially conserved in the DES. Interestingly, other experiments showed that the molecular structure of the cation of the hydrogen bond acceptor does not seem to significantly affect the interactions observed by an ionic probe even if the positively charged moiety has a hydrogen bond donor group. Furthermore, the process of hydrogen bond making and breaking is not easily observed in DESs composed with ionic hydrogen bond acceptors having hydrogen bond donating groups such as choline. The interaction picture changes when the hydrogen bond acceptor is non-ionic. In this case, the thiocyanate probe shows the expected hydrogen bond making and breaking.

**B. Non-Ionic solutes:** The study of the effect of the chemical structure of the hydrogen bond donor and acceptor on the interactions observed by a non-ionic probe showed that the chemical structure of the cation in the hydrogen bond acceptor does not modify significantly the observed interactions of a non-ionic probe. A similar observation is made when the ratio of the hydrogen bond donor and acceptor is changed in the DES.

**C. Summary:** Overall our studies show that DESs are liquids with nanoscopic heterogeneities which creates two well-defined regions in the solvent: the ionic region and the non-ionic region. While the former is mostly composed of the ionic hydrogen bond acceptor, the latter is mostly made up of the hydrogen bond donor. Thus, these results show that DES can have a bright future in applications as a solvent, since DESs have two distinct molecular regions which could be used to solubilize different solutes, or different reagents that do not mix in conventional solvents.

## Impact

This project has impacted Dr. Kuroda's faculty career by giving him the funding needed to explore the captivating research area of deep eutectic solvents. The support not only resulted in novel research, but also helped to support two graduate students, one of whom successfully obtained his Ph.D. degree in the topic. Moreover, the realization of this project has enabled Kuroda's group to publish two scientific manuscripts, and at least another publication is expected in the near future from the research products of this work. Finally, one NSF proposal has been developed based on the observations obtained from this project.