

# Molecular Diffusion

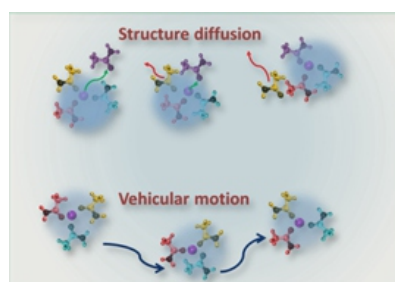
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## Microscopic Diffusion Mechanisms in Deep Eutectic Solvents

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Schematic representing structure diffusion and vehicular motion mechanisms of lithium transport

### ABSTRACT

Deep eutectic solvents (DESs), widely used in industrial and pharmaceutical applications, still lack a complete understanding of their physicochemical properties from a microscopic perspective. The control and efficiency of applications utilizing DESs hinge significantly on their transport properties. In this article, we report our simulation and theoretical studies on DESs unravelling the microscopic diffusion mechanisms which provide an insight into the emergence of their macroscopic transport properties. We investigate how the properties of DESs depend on their components and composition, with a focus on the pivotal role played by molecular interactions. Additionally, we explore the modulation of these interactions by water to analyze the correlation between water concentration and molecular diffusion rate in these systems. Our findings suggest that a thorough understanding of complex formation and kinetics in DESs can provide the necessary link to interpret the emergence bulk transport properties from molecular diffusion.

**KEYWORDS:** Deep eutectic solvents, Molecular dynamics simulations, Diffusion, Neutron scattering

### Introduction

Over the past two decades, deep eutectic solvents (DESs) have garnered significance due to their expanding applications across various industrial sectors [1,2]. Their popularity is driven by enhanced eco-friendliness and preparation protocols when compared to ionic liquids (ILs). Despite sharing similar physicochemical properties with ILs, DESs differ as they are not exclusively composed of ions; rather, they contain a substantial molecular component. Further, the constituents of the DESs are typically sustainable and biodegradable, as a result they are considered as green solvents [3]. Generally, DESs are created through mixtures of hydrogen bond donors (HBDs) and salts, offering versatility through the diverse options of HBDs (based on amides, glycols, phenols) and salts available for their preparation [1,4].

Deep eutectic solvents (DESs) have become valuable in a wide array of applications, including nanoscale synthesis [3,5], electrochemical processing [1,6], drug solubilization [7], and serving as electrolytes in batteries [4,8,9]. The intriguing functional aspects of DESs have ignited interest in exploring their fundamental properties. Understanding the molecular mechanisms responsible for their unique functionalities is essential for designing and synthesizing new DESs with tailored properties. Transport properties, particularly in non-aqueous solvents, play a crucial role in various industrial and pharmaceutical processes utilizing DESs. For example, in catalytic applications, achieving lower solvent viscosity is favourable for improving reaction rates, especially in diffusion-controlled reactions. Similarly, for electrochemical processes such as electroplating/ batteries, ionic conductivity, which is the key parameter, is also significantly controlled by solvent viscosity. Hence, understanding the microscopic diffusion processes that lead to their emergence is essential for gaining

insights into the adjustability of their overall transport properties. These properties hold significance across various applications.

As a multicomponent mixture comprising both ions and molecules, DES displays complex microscopic transport phenomena due to the various intermolecular interactions present in the solvent. Furthermore, it exhibits glass-forming features, suggesting a strong interplay between structural relaxation and transport phenomena. These structural relaxations are facilitated by the relaxation of extensive intermolecular H-bond networks and complexes formed within the DES. Consequently, adjusting the intermolecular interactions within the DES emerges as a valuable approach to modulate its transport properties. In this context, water, being a strongly polar compound, serves as an effective agent for controlling molecular interactions and, consequently, adjusting both microscopic and bulk transport properties within the system.

This article unveils a collection of research conducted by our group, delving into the microscopic diffusion landscape and its origins arising from molecular interactions within DESs. The exploration is undertaken through a combination of molecular dynamics (MD) simulations, the theory of stochastic processes, and neutron scattering [4,8,10-13]. Our studies are focussed primarily on DESs based on acetamide and lithium salts. These DESs are shown to be potential candidates for electrolytes in lithium-ion batteries and supercapacitors [9,14,15]. It is observed that diffusion of acetamide in these systems exhibit a cage-jump mechanism which is linked to the nature of complexes formed in the DES. Further, at the microscopic level, the DESs exhibit dynamical heterogeneity which inherently emerges as a consequence of cage-jump mechanism. Owing to the ability of water to disrupt the hydrogen bond network and complexes, it is observed that addition of water makes the systems significantly more

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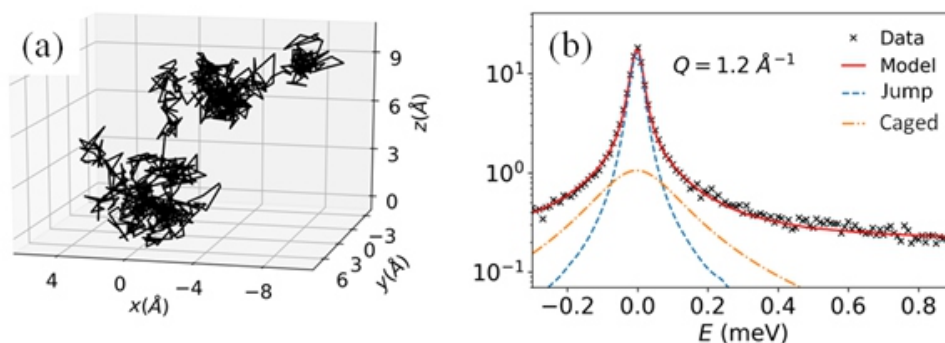


Fig.1: (a) Simulated trajectory of acetamide COM molecules in DES. (b) QENS spectra of acetamide + LiClO<sub>4</sub> DES at  $Q = 1.2 \text{ \AA}^{-1}$ . The model function is based on cage-jump mechanism and the individual components for jump and caged diffusion are also indicated.

dynamic. Studying the dynamics at different water concentrations offers a pathway to investigate the correlation between diffusivities and complex lifetimes in DESs. This becomes particularly relevant due to notable impact of water on the transport properties of DESs.

### Cage-jump Mechanism of Diffusion

Classical molecular dynamics (MD) simulations on DES based on acetamide and lithium perchlorate were carried out to understand the microscopic diffusion within the system [10]. In Fig.1 (a), we present the centre of mass (COM) trajectories of acetamide in the DES, revealing distinct patterns of local clustering and jump-like motions. This diffusion behaviour is characteristic of liquids with an extensive network of hydrogen bonding (H-bonding). The rationale behind this behaviour can be explained by considering the following arguments: At any given time, molecules within the system are typically either complexed or H-bonded with their neighbours, leading to localized caged diffusion. However, this cage is transient and is influenced by the lifetime of the formed complex or H-bonds. Subsequent to the relaxation of the cage, the molecules undergo jump-like translations, after which they reform their complexes with a different set of neighbours.

The cage-jump diffusion model can be verified using quasielastic neutron scattering (QENS) experiments [10], which distinctly probe the diffusion of acetamide molecules. This sensitivity is primarily attributed to the significant incoherent scattering cross-section of hydrogen atoms, making QENS particularly adept at probing the dynamics of hydrogen within the system. In fact, cage-jump diffusion model was also used to explain the QENS data of supercooled water and glycerol based DES. In Fig.1 (b), we show the data from QENS

experiments on the DES and its model description based on a combination of jump and localized caged diffusion. The suitability of the data with the model clearly vindicates the presence of the cage-jump diffusion mechanism in this system. To comprehend the mechanism of cage-jump diffusion, it is crucial to explore the formation of various complexes within the deep eutectic solvent (DES) using molecular dynamics (MD) simulation data.

### Formation of Complexes

Our analytical approach centers on categorizing acetamide molecules into distinct states determined by their interactions with neighbouring molecules and ions. Two states of acetamide molecules were predominantly found – one corresponding complexes with lithium and the other free acetamide [8] – classified as bound and free acetamide, respectively. Typically, 35% of acetamide molecules were found to be in bound state and around 60% in the free state. Notably, the diffusion of bound acetamide in DES was observed to be  $\sim 3$  times slower than the free acetamide molecules in the system. The formation of these complexes vindicated the transient caging of acetamide molecules during the diffusion process. This could be validated through studying the distribution of acetamide molecules around each lithium ion in the system. The typical time-evolution of number of acetamide molecules ( $N_{ACM}$ ) in the first solvation shell of lithium ions is shown in the inset Fig.2 (a). The complete probability distribution,  $P(N_{ACM})$  calculated from MD simulations are also shown in Fig.2 (a), indicating that 3 and 4 are the most dominant coordination of acetamide around lithium ions. The snapshots of these complexes are indicated in Fig.2 (b).

The formation of complexes has important consequences to the mechanism of lithium transport within

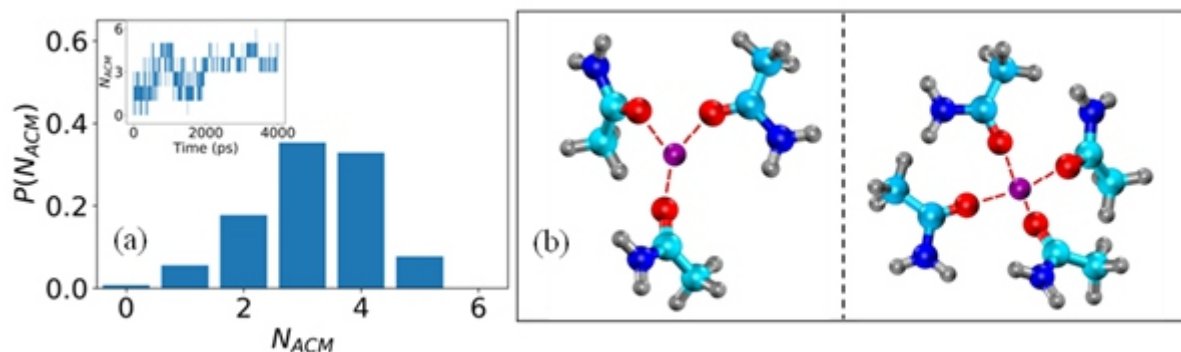


Fig.2: (a) Probability distribution of  $N_{ACM}$  for the lithium ions in the DES. (inset) Time evolution  $N_{ACM}$  of a random lithium ion the system. (b) Simulation snapshots of lithium ion complexed with 3 and 4 acetamide molecules.(hydrogen – gray; oxygen – red; carbon – cyan; nitrogen – blue; lithium – magenta; chlorine – purple).

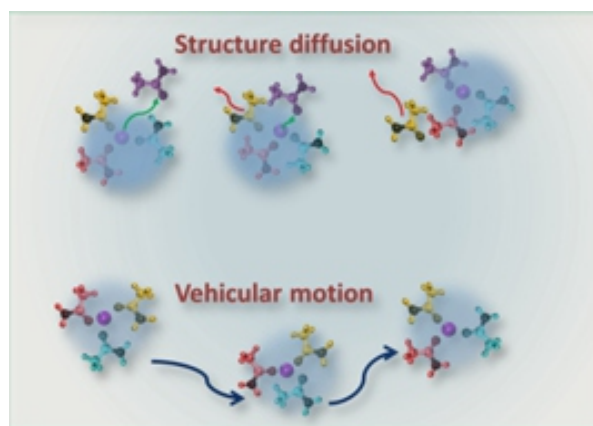


Fig.3: Schematic representing structure diffusion and vehicular motion mechanisms of lithium transport.

DESs. In liquid electrolytes, there are two typical mechanisms through which lithium ions are transported—structure diffusion and vehicular motion, as represented in Fig.3. In structure diffusion, the lithium ions are transported by exchanging its neighbours and forming new complexes in the process of diffusion. Meanwhile, in vehicular motion, the lithium ions diffuse along with their first solvation shell without breaking the complex with acetamide. In the DES, it was observed that all the lithium ions were complexed with the different acetamide molecules in the DES and they're found to follow the diffusion of the bound acetamide molecules in the system [8]. This striking observation indicated that the mechanism of lithium transport in this system is most likely propagated by vehicular motion. In order to validate this, we also calculated the lifetime of these complexes using bond autocorrelation functions obtained from MD simulations. The typical lifetimes of these complexes between acetamide and lithium was estimated to be  $\sim 1$  ns, suggesting that majority of lithium diffusion is propagated while the complex is intact [8].

#### Modulation of Diffusion by Water

MD simulations of aqueous mixtures of the DES (acetamide +  $\text{LiClO}_4$ ) were also carried out to investigate the effect of water on microscopic diffusion in the system [11,12]. Our studies revealed that the underlying solvation structure of lithium ions substantially changed due to the addition of water in the system. With increasing water content, acetamide molecules were displaced from the lithium solvation shell, replaced by water molecules, leading to availability of free acetamide. This change in lithium complexes leads to an increased diffusion of both acetamide and lithium in aqueous DES. The diffusion of different species in the DES more than doubled for water at 20 wt% [11]. It was observed that the diffusivity of acetamide, lithium, and perchlorate increases at least by a factor of two at just 5% water by weight. Subsequently, they continue to increase with water content and become about 4 times of their values at 20 wt% of water. The addition of water alters the nature of the complexes formed in the DES and also destabilizes the complexes resulting in a decreased lifetime. These two effects comprehensively lead to substantially enhanced diffusion within the DES. Further, the decrease in their diffusivities can also be associated to increase in the ionic conductivity and decrease of bulk viscosity.

The presence of dynamical heterogeneity in deep eutectic solvents (DESs), associated with a significant deviation from Brownian motion, is a well-established phenomenon [13,16]. By characterizing dynamical heterogeneity through the non-Gaussian parameter computed

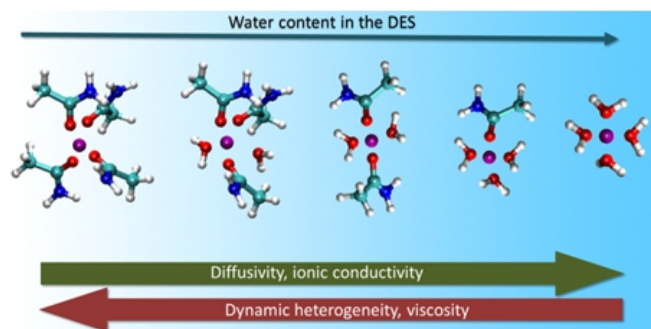


Fig.4: Schematic showing the evolution of the complexes between lithium ions, water and acetamide in aqueous mixtures of acetamide based DES. As the concentration of water increases, dynamic heterogeneity and viscosity of the DES decrease, and diffusivity and ionic conductivity increase.

from molecular dynamics (MD) simulations, it was observed that the introduction of water led to a reduction in non-Gaussianity within the system [11]. This implies that the addition of water contributes to restoring homogeneity in the dynamics of the system. The impact of water concentration on diverse dynamical and structural properties of the DES is illustrated in Fig.4.

#### Conclusions

Our comprehensive simulation studies on deep eutectic solvents (DESs) reveal a non-Brownian diffusion behaviour characterized by a cage-jump mechanism. The transient cages formed during diffusion result from the prolonged lifetimes of ion-molecule complexes. The formation of these complexes hinders the free movement of molecules, significantly slowing down the diffusive motion and thereby contributing to poor transport properties in DESs. To address this issue, we investigate the addition of water to the solvent, finding that water disrupts and destabilizes these complexes, leading to increased diffusion rates and reduced viscosity. The insights gained from our studies provide a mechanism for understanding how the controlled addition of water can finely adjust the microscopic diffusion properties of DESs. Moreover, these findings support the notion that the intricate molecular relaxation processes within the system are interconnected with the bulk transport properties that manifest as a consequence of such relaxation behaviour.

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