Studying the Formation of Choline Chloride and Glucose Based Natural Deep Eutectic Solvent at the Molecular Level

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Abstract

In our work, we have studied the formation of choline chloride based NADESs using DFT calculations, and all-atom classical Molecular Dynamics (MD) simulations. In our DFT calculations, the ground state geometry optimizations were performed in the gas phase using DFT B3LYP 6-31+G(d) level of theory. Moreover, all-atom classical Molecular Dynamics simulations were implemented using Gromos force field. The DFT calculation results revealed the formation of NADESs via formation (creation) of binding between chlorine and choline, and chlorine and glucose. Next, the results of all-atom classical Molecular Dynamics simulations, based on the time average of the equilibrated production run of MD simulations, stated that the nitrogen atom of choline ion, and chloride ion have greater interactions, while chloride ion have also greater interaction with glucose during formation of NADES.

Highlights

- Intermolecular interactions of NADES were studied by DFT calculations and all-atom classical Molecular Dynamics simulations.
- Calculated outputs of DFT calculations and all-atom classical Molecular Dynamics simulations for NADES were
- The molecular formation mechanism of NADES was

1. Introduction

More than 1.3 million tons of chemical waste is produced globally per year and its amount continues to increase. Hazardous waste is mainly generated in the chemical industry, the production of petroleum products and coal, in the processing and disposal of waste, the production of agricultural chemicals such as pesticides, fertilizers, etc. The main source of waste is liquid waste from academic laboratories and industrial chemical processes; it's mostly from extraction, separation, chemical synthesis and pretreatment processes. These chemical processes consume a lot of solvents. Solvents include acids, bases, organic solvents of petroleum origin and other inorganic solvents [1]. But hazardous waste also comes from the products we use every day, such as batteries, cosmetics, cleaning products, paints, pharmaceuticals, and electronics.

Consequently, there is a need to develop more environmentally friendly, cheaper, non-toxic solvents that are harmless to humans and the environment. In this regard, deep eutectic solvents (DES) and their derivatives so called natural deep eutectic solvents (NADES) are a new field in the search for green alternative solvents. Ease of manufacture, low cost of components, environmental friendliness are the advantages of DES [2]. Some DES are completely non-toxic or less toxic than conventional organic solvents and ionic liquids (IL).

Since the introduction of the first solvent of choline chloride and urea in 2003 by Abbott et al [3] many other solvents, including binary, ternary and quaternary components of the solvent system have

developed. And interest in these solvents continues to grow, especially in the past decade. This is due to the prospects for the use of these materials in electrochemistry [4, 5], catalysis and gas capture [6–8], polymer synthesis [9, 10], purifications, and extraction [11–14] processes applications. For example, DES using polyols such as glycerin or ethylene glycol typically has lower freezing points and even exists as a liquid below room temperature, and these polyols are also widely used in many industrial applications. The high activity and stability of enzymes in DES can be used to dissolve metal oxides, which is necessary for their extraction, processing, and catalyst preparation [15].

However, insufficient knowledge of the structure and thermodynamic properties of DES and the effect of solvents such as water, alcohols, and alkanes on these properties hinder the possibility of large-scale application of these materials in industry [16].

Garcia et al. [17], in study using Density Function Theory and AIM and with ChCl: urea (1: 2), ChCl: glycerin (1: 2), ChCl: glycerin (1: 3) and ChCl: malonic acid (1: 1) proposed that charge delocalization caused by hydrogen bonding is thought to cause low electron density, which leads to the low melting points seen in DES. However, Zan et al. [18] question this assumption. In a recent study by Ashworth et al. [19] choline Chloride and urea form several complexes with the participation of choline and urea, as well as urea and chloride. This casts doubt on the popular assertion that chloride anion and urea form hydrogen bonds, which are known to be the main force the interaction underlying the formation of DES. Therefore, there is a need for further studies of the molecular basis of DES formation.

The structural properties of a 1:2 mixture of choline chloride and urea and a 1:2 mixture of butyltrimethylammonium chloride and urea, have been investigated by means of Molecular Dynamics simulations in [20]. It was found that the presence or absence of a hydroxyl group on the organic cation strongly affects the DES hydrogen bond network, causing a different three-dimensional arrangement of all particles present in the mixtures. These results may be important for the future development of DES for specific applications. The combination of neutron reflectometry and molecular dynamics (MD) simulations has been shown to provide fresh insights into the structure of solid/DES interfaces [21]. The electrosorption of water limited by graphene in the 1:2 choline chloride - urea (Reline) system in a wide range of surface polarizations has been investigated using atomistic molecular dynamics [22]. It was found that the interfacial structure and water distribution are sensitive to the polarization of the electrode surface. Local intermolecular interaction with reline particles and electrostatic interaction with a graphene electrode strongly affect the electrosorption of water. A theoretical study using both ab initio molecular dynamics and quantum chemistry calculations to clarify the role of water in the nanostructure of a mixture of urea and betaine was carried out in Ref. 23. Facilitating the water association between urea and betaine, increasing the network of hydrogen bonds and inhibiting the aggregation of urea molecules, was established from preliminary modeling results. In situ studies of the formation of iron oxide nanoparticles in DES and observation of the effect of water on the reaction were carried out in [24] using SANS, SAXS, EXAFS, neutron and X-ray diffraction, and atomistic modeling. Solute-solvent interactions of glucose, sucrose, erythritol, cellobiose, starch and cellulose in five different choline chloride-based DES are studied in [25] using size exclusion chromatography, NMR and differential scanning calorimetry. In

general, carbohydrates showed good solubility and some similarities were observed between aqueous solutions and ionic liquids. Ethylene showed the best performance because it had the lowest viscosity and did not degrade carbohydrates. The effect of ethylene glycol, malic acid, tartaric acid, glycerol and oxalic acid with choline chloride acceptor in the formation of supramolecular structures have been studied in [26] using the molecular dynamics simulations approach. In compared to other solvents, choline chloride with tartaric acid at a 2: 1 ratio has a better polarizability, entropy, thermal stability and heat capacity. At the same time, choline chloride with Ethylene Glycol at a ratio of 1: 2 has the highest conductivity, dipole moment, electron mobility and hole mobility.

In this regard, we have done DFT calculations, and all-atom classical Molecular Dynamics (MD) simulations to study the intermolecular interactions within the NADESs at the molecular level. In particular, we have selected NADESs, that is, ChCl/Glu (1:1) as theoretical model for ab initio calculation and all-atom classical MD simulations to understand its formation mechanism at the molecular level. The choice of the NADESs is based on the available experiments and simulation parameters, as we explain below.

2. Methodology

2.1 Ab initio calculations

GAUSSIAN09 with GausView5.0.9 was used for DFT calculation in order to get optimized structure, calculate molecular orbital densities, molecular electrostatic potential maps, bond distances, and binding energies. Moreover, we have selected choline (Ch) chloride (Cl) and D(+)glucose (glucose) based NADESs. Electronic ground state geometries for ChCl, glucose, and their mixture as the NADES in the gas phase were optimized using Density Functional Theory (DFT) and B3LYP 6–31 + G(d) level of theory (Fig. 1). The optimized conformations of ChCl and glucose were taken from the ATB server [27]. By analytical calculation of the second energy derivatives, all stationary points were confirmed to be true minima on their respective potential energy surfaces [28].

2.2 All-atom classical MD simulations

A mixture of ChCl, glucose and water was taken as a representative model of NADESs, while the representative segment models were illustrated on Fig. 1. After that, the optimized force field parameters, and optimized coordinates for the ChCl, glucose, and water were obtained from the ATB database [27]. The Lennard-Jones (LJ) parameters were taken from the standard gromos54a7 force field [29].

A $10 \times 10 \times 10 \text{ nm}^3$ initial simulation box with a limit on force of 500 kJ/mol/nm on any atom at 298 K and 1 bar implemented for energy minimization. Next, NPT and NVT equilibrations were done at 298 K and 1 bar for 1 ns each. After the equilibrium, Molecular Dynamics (MD) simulations were performed for 10 ns with temperature and pressure of 298 K and 1 bar.

LINCS constraint algorithm was implemented for all bonds during the simulation. Long-range interactions computed via Particle Mesh Ewald summation [30], [31]. In addition, V-rescale method was maintaining temperature, and Berendsen pressure coupling was maintaining system pressure. Periodic boundary conditions were used as well.

Table 1

Details of the simulation system for studying formation of the NADESs at 298 K and 1 bar.

#	ChCl	Glucose	Water (/wt.%)	Purpose
1	400	-	-	Pure ChCl
2	400	400	413 (5.5)	NADESs

All-atom classical MD simulations were initially performed on the individual components of the NADESs: pure ChCl (400 molecules) for reference (system 1; see Table 1). Next, a mixture of ChCl/Glucose/Water (system 2; see Table 1) at molar ratio of 1:1 was simulated to explore interactions within the NADESs and compare it with its constituent components (Fig. 1). In MD simulation, the choice of forcefield parameters is very important for our designed system. As a result, there is a good agreement between experimental and computed results and these data justify the selection of the force field (Table 2).

Table 2

Densities of system 1 and 2 at 298 K and 1 bar.

Compounds	Computed density	Experimental density
ChCl	1.009 (g/mL)	1.100 (g/mL) [31]
NADES	1.18 (g/mL)	1.27 (g/mL) [32]

3. Results And Discussion

3.1 DFT results

We have constructed and optimized the structure of a cluster of NADES ChCl + glucose using the optimized structures of molecules ChCl and glucose. Figure 2 shows the resulted structure of NADES as well as its molecular electrostatic map. One may see that chlorine atom acts as a connecting agent between Ch and glucose molecules. The dashed lines in Fig. 2 (A) demonstrate the shortest distances (from 2.11 Å to 2.95 Å) between chlorine ion and hydrogen atoms, where hydrogen atom of glucose was the closest atom to chlorine. The structure of glucose does not demonstrate any significant changes after formation of NADES except rotation of two O-H bonds toward Cl. The only observed changes in structure of ChCl under formation of NADES were elongations of distances between H and Cl, which is mostly due to appearing of attraction of Cl to glucose. According to Fig. 2 (B) Cl ion accumulates excessive negative

charge while hydrogens have the positive one. Therefore, there is strong attraction between hydrogens and Cl in ChCl and NADES.

Figure 3 demonstrates visualization of HOMO-1 (H-1), HOMO (H), LUMO (L) and LUMO + 1 (L + 1). In ChCl and NADES H-1 and H are formed by π orbitals of Cl ions while L and L + 1 in ChCl and NADES are localized on choline molecules. H-L gap is large > 5.4eV indicating high stability of NADES.

In Table 3 we present the results of calculation of total energy, electronic energy, zero-point correction energy (ZPE) and Δ_{excess} , where Δ_{excess} was calculated using formula 1 for every component of energy.

$$\Delta_{\text{excess}} = E_{\text{NADES}} - (E_{\text{ChCl}} + E_{\text{D(+)glucose}}) \quad (1)$$

Relatively low values of Δ_{excess} may indicate that melting point of NADES should be lower than for pure ChCl or glucose.

Table 3
Energies for formation of NADESs

Energy (kJ/mol)	ChCl	glucose	ChCl + glucose	Δ_{excess}
Total energy	-2071913.94	-1804280.43	-3876268.04	-73.66
Electronic energy	-2071913.93	-1804280.43	-3876268.04	-73.66
Electronic energy + ZPE	-2071391.57	-1803764.13	-3875223.83	-68.12

3.2 All-atom classical MD

To link DFT work, we have performed classical all-atom Molecular Dynamics (MD) simulations to understand the formation of Ch Cl and glucose based Natural Deep Eutectic Solvents. Herein, we have investigated ChCl:Gl system via intermolecular interaction energies, hydrogen bonding, and radial distribution functions implementing MD. As observed from MD simulations, the interaction energy between Ch and Cl according to system 1, was around – 86930.89 kJ/mol, which means a strong intermolecular interaction between the Ch and Cl ions. However, the interaction energies between Ch and Cl ions decreased to -46050.96 kJ/mol in the presence of Glucose and Water molecules as can be seen From Table 4. The results show the weakening of intermolecular interactions between the Ch and Cl ions, which is explaining the melting point depression that is observed in Natural Deep Eutectic Solvents formations.

Table 4
Interaction Energies for NADES
components

Interactions	Energies (kJ/mol)
Ch-Cl (Pure)	-46050.96102
Ch-Cl	-30334.70092
Ch-Water	-4956.33706
Cl-Glucose	-57707.01762
Cl-Water	-14449.19286
Glucose-Water	-9322.065128

Moreover, the results of interaction energies from Table 4 implies that there is a formation of bonding between Ch and water with -4956.33 kJ/mol, chlorine (Cl) and glucose with -57707.01 kJ/mol, chlorine (Cl) and water with -14449.19 kJ/mol, glucose and water with -9322.06 kJ/mol for system 2. Moreover, the intermolecular formation of NADESs is explained in general via hydrogen bonding. In this regard, the number of hydrogen bonds were computed via employing that the distance between acceptor and donor is less than 0.35 nm and the angle is 30^0 degree. The classical all-atom MD simulation was performed for system 2. The results implied that there are around 800 hydrogen bonds between glucose and chlorine ion as can be seen from Fig. 4.

However, the number of hydrogen bonds for Ch/glucose, chlorine/water, chlorine/glucose, and glucose/water systems are around 350, which are second most contributing agents for formation of NADESs as can be seen from Fig. 4. Finally, there are some 100 hydrogen bonds for Ch/water bonding as can be seen from Fig. 4.

Next, Fig. 5 shows the radial distribution functions between Ch, Cl, Glucose, and water molecules respectively. The results indicated that the chlorine with water, and chlorine with glucose have the highest bonding strength, while the next trends belong to Ch/glucose, choline/water, Ch/chloride, and glucose/water.

Conclusion

Initially, we performed DFT calculations for one molecule of choline, chloride, and glucose as a NADES system. As a result, the structure of glucose did not show any significant changes after intermolecular formation of NADES except rotation of two O-H bonds toward Cl. The only observed changes in structure of ChCl under formation of NADES were elongations of distances between H and Cl, which is mostly due to the appearance of attraction of Cl to glucose.

Next, the classical all-atom MD simulation was performed for the ChCl, glucose and water based NADESs. As can be noted from interaction energies, the formation of NADESs happened via weakening of choline and chloride bonds. As a result, after mixing with glucose and water, it was found that the higher number hydrogen bonds are higher for glucose and chlorine ion, Ch/glucose, chlorine/water, chlorine/glucose, and glucose/water. Moreover, the results of radial distribution function implies that there is strong bonding between chlorine/water, and chlorine/glucose components.

In general, we performed multiscale work from DFT to MD simulations. The results of both simulations are in good agreements. This computer aided modeling could help us to rational design of NADESs in the future.

Abbreviations

DFT – Density Functional Theory

MD – Molecular Dynamics

ILs – Ionic Liquids

DESs – Deep Eutectic Solvents

NADESs – Natural Deep Eutectic Solvents

ChCl – Choline Chloride

Glu – Glucose

Declarations

The authors have no relevant financial or non-financial interests to disclose.

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Availability of data and material:

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Authorship contribution:

Zhassulan Sailau: Methodology, Formal Analysis, Writing – original draft

Anuar Aldongarov: Methodology, Formal Analysis, Writing – original draft

Nurlan Almassov: Conceptualization, Formal Analysis, Writing – review & editing

Kainaubek Toshtay: Formal Analysis

Dmitry Murzin: Writing – review

Code availability:

DFT calculations were performed using Gaussian 09 Rev. E.01 program package.

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Figures

A) **B)**

Figure 1

Structure of A) ChCl, and B) glucose. Color key: Carbon: grey, hydrogen: white, nitrogen: blue, oxygen: red, chloride: green.

A)

(ChCl)

(Glucose)

(NADESs)

B)

(ChCl)

(Glucose)

(NADESs)

Figure 2

(A) Optimized structures and (B) Molecular Electrostatic Maps for ChCl, glucose, and NADESs. Color key: white: hydrogen, grey: carbon, blue: nitrogen, green: chloride, red: oxygen.

Figure 3

Representations of H-1, H, L, and L+1 Molecular Orbital Density for optimized electronic ground state geometries of ChCl, glucose, and the NADESs.

Figure 4

A number of hydrogen bonding between NADES components.

Figure 5

A comparison of radial distribution functions between choline (Ch), chlorine (Cl), glucose (Glu), and water components of NADESs.