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Molecular Insight into Dynamic and Structural Properties of the Deep Eutectic Solvent Based on Choline Chloride and Stearic Acid: A Molecular Dynamics Study

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Abstract

In this work, the Structural and dynamic properties of eutectic solvents of choline chloride (Ch^+ Cl^-) and stearic acid (STA) were investigated using molecular dynamics simulations. Structural properties of the binary mixture of STA and [Ch^+] [Cl^-] with a molar ratio of 1:1 show a strong interaction between the (COOH) of STA and Cl^- anion in the binary mixture. Compared to the low molecular mass of the chloride anion, the strong interaction between the anion and HBD led to a decrease in the migration of this ion compared to acid. The results showed that Cl^- anion is an effective species in binary mixtures, playing a key role formation of deep eutectic solvents.

Keywords: MD Simulations; Stearic acid; Choline chloride; Deep eutectic solvent; Dynamic and Structural properties.

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Introduction

In order to reduce human damage to the environment, green technology is to be seriously looking g new solvents to replace toxic and volatile organic solvents which produce a part of dangerous air pollutant gases [1]. The synthesis and use of ionic liquids (ILs) are the main developments in this field. Although ILs have attracted a lot of attention and many research articles have been published in this field, these solvents have not been well received in the industry due to their expensively. These solvents, which were called molten salts [2], are liquid at room temperature and they have unique physical and chemical properties such as high thermal stability, non-volatility, non-flammability and, adjustable polarity. Each of these properties can be adjusted by changing anion or cation in ILs [3]. Despite the diverse ability of these compounds, there are many limitations such as poor degradability, toxicity, corrosion, and high cost, which prevent their use in the chemical industry. Therefore, a new generation of solvents has appeared that is called deep eutectic solvents (DESs). DESs have a similar structure to ionic liquids and are a suitable alternative for ILs. The main advantage of DESs to ionic liquids is their easy synthesis. Deep eutectic solvents are a mixture of two or more components in which instability of charge between two donors and acceptor of hydrogen bond components is responsible for reducing the melting point of the eutectic mixture [4]. The common DESs are based on choline chloride as a hydrogen bond acceptor and carboxylic acids, citric acids, succinic acids, and other hydrogen bond donors such as urea and glycerol [5]. Choline chloride is a very cheap, biodegradable, and non-toxic from quaternary ammonium salt (QAS) [6]. Although DESs are made of choline chloride as an ionic species, DESs cannot be considered ionic liquids due to these solvents can be composed of non-ionic species. Though DESs have properties similar to ionic liquids, deep eutectic solvents have many advantages, including low price, easy preparation, nontoxic and biodegradable which can be used in various applications such as extraction. Molecular dynamics (MD) simulation is a new technique that is widely used to investigate the dynamic and structural properties of the binary mixture. In the MD simulation method, molecules are allowed to interact with each other for a certain period of time under the known classical laws. The main basis of this effective method is the solution of Newton's equations of motion for the individual particles (atoms, ions, …). MD simulation provides information at the

microscopic level such as the new position of molecules. In fact, molecular dynamics is the relationship between the structure of molecules and the gradual movement of molecules with time.

The instability of hydrophilic solvents based on ammonium salts in contacting with water has motivated the design of hydrophobic eutectic solvents as green alternatives for organic solvents. Recently, a large number of hydrophobic eutectic solvents based on natural compounds especially menthol, has been used to remove and separate micro-pollutants.

A quick look at the eutectic solvents presented in the literature shows that most of these solvents are very hydrophilic. The instability of hydrophilic solvents based on ammonium salts in contact with water has motivated the design of hydrophobic eutectic solvents as green alternatives for organic solvents. Recently, a large number of hydrophobic eutectic solvents based on natural compounds, especially menthol, have been used to remove and separate micro-pollutants [7]. Also, increasing the solubility of drugs, and extracting drugs from their synthesis environment are the pharmaceutical applications of these solvents [8]. Hydrophobic eutectic solvents based on terpenes and fatty acids are widely used in the extraction of biomolecules such as tryptophan, isophthalic acid, vanillin, and polycyclic aromatic hydrocarbons from aqueous solutions [9].

Therefore, the main goal of this article is to design and describe the structural properties of the eutectic mixture including choline chloride and stearic acid by MD simulation. The liquid phase of the binary mixture of choline chloride and stearic acid in its pure state has been investigated.

The structural and transport properties of the eutectic mixture of choline chloride salt and stearic acid were investigated at 353 K. The transport properties of the species in the binary mixtures were analyzed by studying the mean square displacement (MSD) of the centers of mass of the species, and diffusion coefficients.

Also, assessed structural properties include the radial distribution functions (RDFs), the hydrogen bonding network between species, and spatial distribution functions (SDF). Structural properties of the binary mixture of STA/ Ch^{+} Cl^{-} with a molar ratio of 1: 1 showed a decrease in the strong interaction between Choline and acid.

The analysis of the atom-atom RDFs and Spatial distribution functions (SDF) of the eutectic mixture was indicated the hydrogen atoms that dependent on the hydroxyl group of STA molecules are surrounded by chloride anions. In general, the results of this work are presented

evidence that interactions between chloride anions and the HA atom of the carboxyl groups of stearic acid play a key role in the formation of eutectic solvents based on STA and $Ch^+ Cl^-$.

Results and discussion

Radial distribution function

Radial distribution function or pair correlation function is a useful quantity in molecular dynamics simulation, which represents the probability of finding a molecule at a certain distance from an arbitrary central molecule. This function is widely used to understand effective interactions between molecules and is represented by g(r), where r is the intermolecular distance. The mathematical relationship of this equation is as follows:

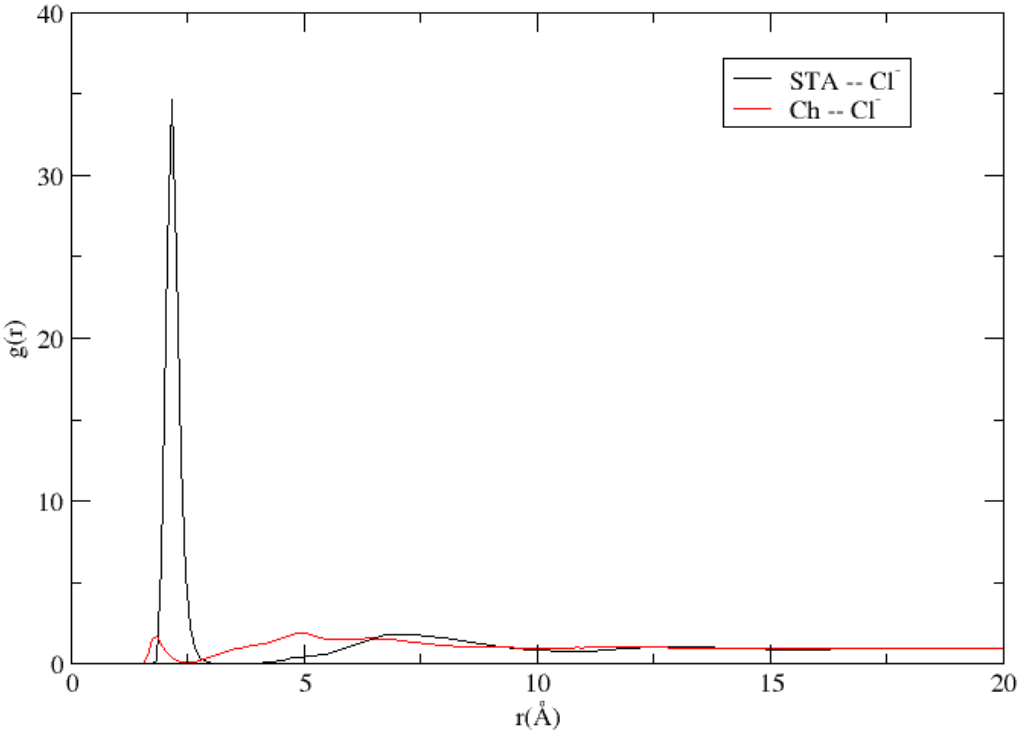
$$g(r) = {dN}/{(4\pi r^2 p)} \qquad (1)$$

In equation (1), dN and ρ represent the number of molecules in a distance of radius (r) around the reference molecule and the average density of system, respectively [10]. The Intensity of the g(r) peak is increased and reduced, respectively, with increasing the number and distance of the molecules around the reference molecule.

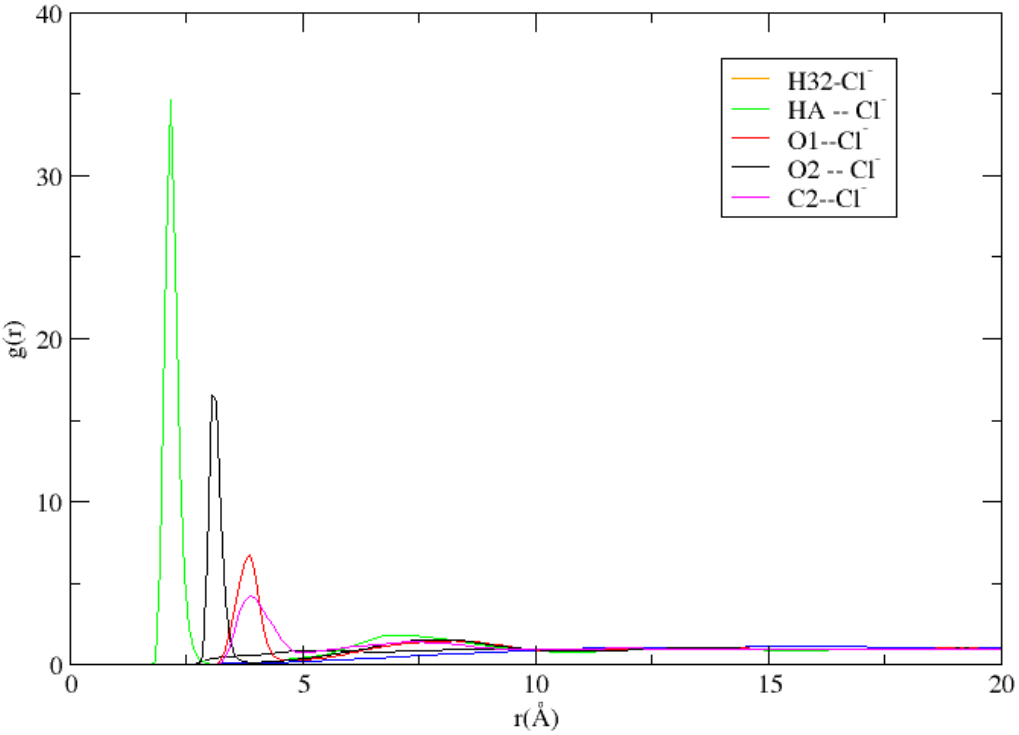
The radial distribution function provides important insights into the structural properties of binary mixtures.

The change in the position of the molecules can be found by observing the difference in the position, height, and width of the peaks. RDF between Cl^- anion around Ch^+ cation and STA in the eutectic mixture is drawn in Figure 1a. RDF related to choline chloride Salt around STA has one sharp peak at distances of 2 Å.

The sharp peak of RDF between Ch^+ and Cl^- in the binary mixture was significantly reduced in the presence of acid molecules. In other words, STA molecules are surrounded by Cl^- anions (see Figure 1b).



(a)



(b)

Figure 1. a) RDF between Cl^- anion around Ch^+ cation and STA in the eutectic mixture at 353 K and b) RDF between Cl^- anion around different atom of STA in the eutectic mixture at 353 K

Hydrogen-Bond Analysis

To understand which of the components of choline chloride can favorably establish strong hydrogen bonds with hydrogen bond donor, the average number of H-bonds between HBD and HBA was evaluated in the binary mixture. The number of hydrogen bonds between HBA and HBD was calculated by the VMD plugin. The cutoff distance of 3.5 Å and an angle cutoff for ∠DHA of 150° were selected for H-bond analysis. The average number of hydrogen bonds is obtained vis the fitting of Equation (2)

$$F(X) = \frac{a}{\sigma\sqrt{2\pi}} exp^{\frac{-(X-\bar{X})^2}{2\sigma^2}} \qquad (2)$$

Where σ, and $\bar{X}$ are the standard deviation and the average number of hydrogen bonds, respectively [11]. The distribution of the number of H-bonds between cation: STA and the anion: STA is shown in Figure 2. The hydrogen of the COOH group of Stearic acid interacts favorably with the anion of salt, forming a hydrogen bond that is stronger than the intermolecular interaction at the pure state.

The number of hydrogen bonds between HBA and HBD of eutectic solvent may not be adequate to justify the interaction between the two species. Hydrogen bond percent occupancies of the HA atoms of STA and Cl^- anion in the binary mixture at 353 K are shown in Figure 3. It is clearly seen that the hydrogen bond between anion and STA is more stable compared to other species.

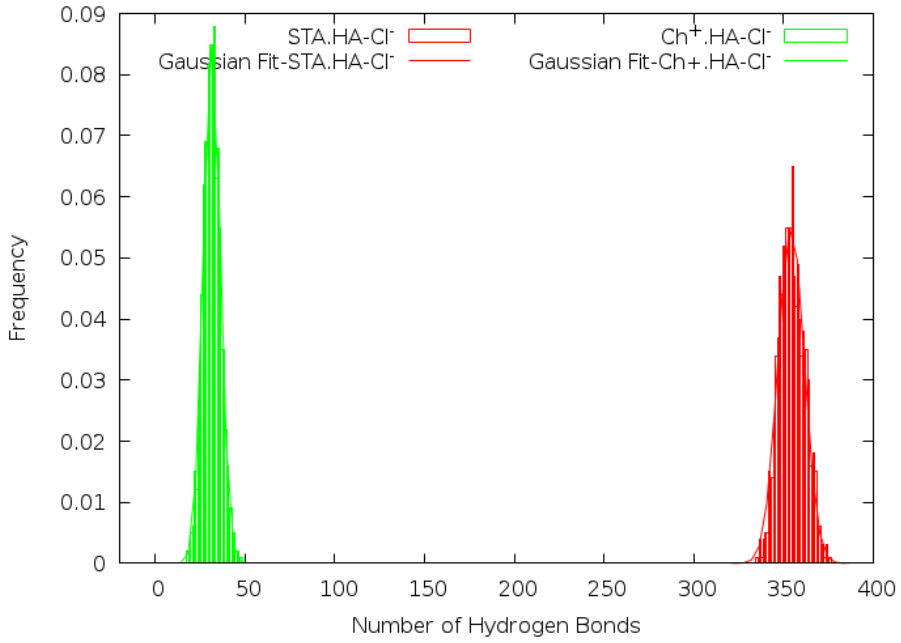


Figure 2. The distribution of the hydrogen bond between STA and Salt in the binary mixture at 353 K

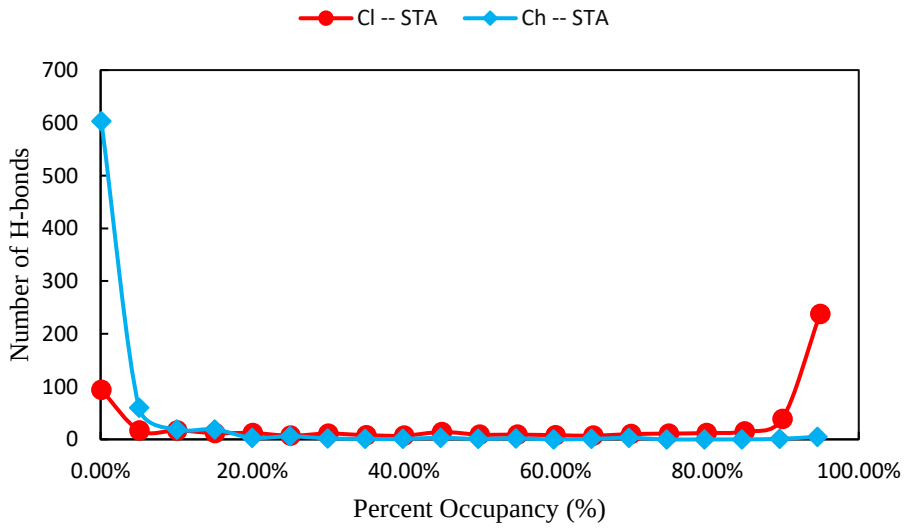
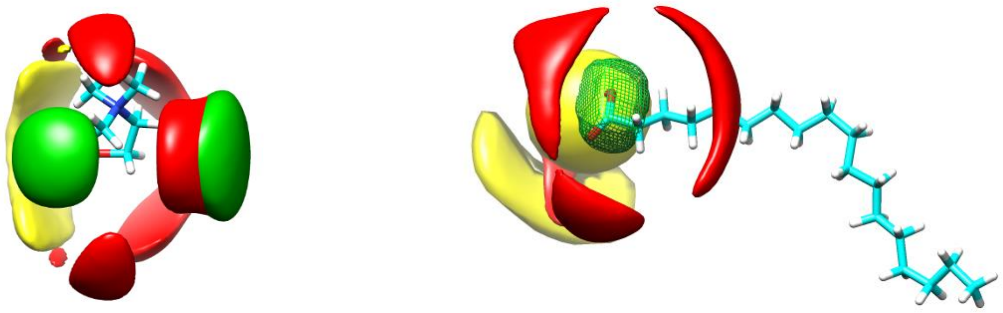


Figure 3. Hydrogen bond percent occupancies for Salt: STA in the binary mixture at 353 K

Spatial distribution function

The spatial distribution function (SDF) is another useful tool to visualize the distribution of molecules, which has provided valuable information about the three-dimensional density distribution of a species around a central molecule. The three-dimensional density distribution of different species around a reference molecule is obtained using TRAVIS software [12]. To determine SDFs in the $[Ch^+]$ $[Cl^-]$ /STA binary mixture,

the C9 atom and N atom are considered as the center of the mass stearic acid molecule and choline chloride, respectively. Investigating the spatial distribution function of the binary mixture shows that the distribution of choline chloride molecules around the carboxylic acid group has the highest value. Also, the distribution of choline chloride and acid molecules around the choline cation as a reference molecule shows the tendency of the hydroxyl group of the Ch^+ cation to form the intermolecular hydrogen bonds between HBA and HBD.



(a) (b)

Figure 4. Spatial distribution functions (SDFs) of the components of the binary mixtures at 353 K. a) SDFs of STA around Choline Chloride molecules in the binary mixture, b) SDFs of Choline Chloride around STA molecules. Green isosurfaces correspond to Cl^-, red isosurfaces are choline Cation

Dynamical and transport properties

Previous studies on deep eutectic solvents have shown that there is a significant relationship between intermolecular interactions and dynamic properties. Thus, self-diffusion coefficients, D_{self}, were calculated for the binary mixture. D_{self} were obtained by the well-known Einstein equation:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt} < \Delta r(t)^2 > \qquad (3)$$

Where $\Delta r(t)^2$ is defined as the distance traveled by the specie i per unit of time or MSD [13]. In order to investigate the dynamic behavior of the molecules, the mean-square displacement (MSD) of the center of mass for each HBA/HBD was calculated in the binary mixture. MSDs of the center of mass for each $[Ch^+][Cl^-]$ /stearic acid as a function of time are drawn in Figure 5. The MSD of the FAs molecule is larger than that of the chloride anion. It seems that the stability of the H-bond

between the HBA and HBD can lead to decreasing the self-diffusion coefficients of species in the binary mixture.

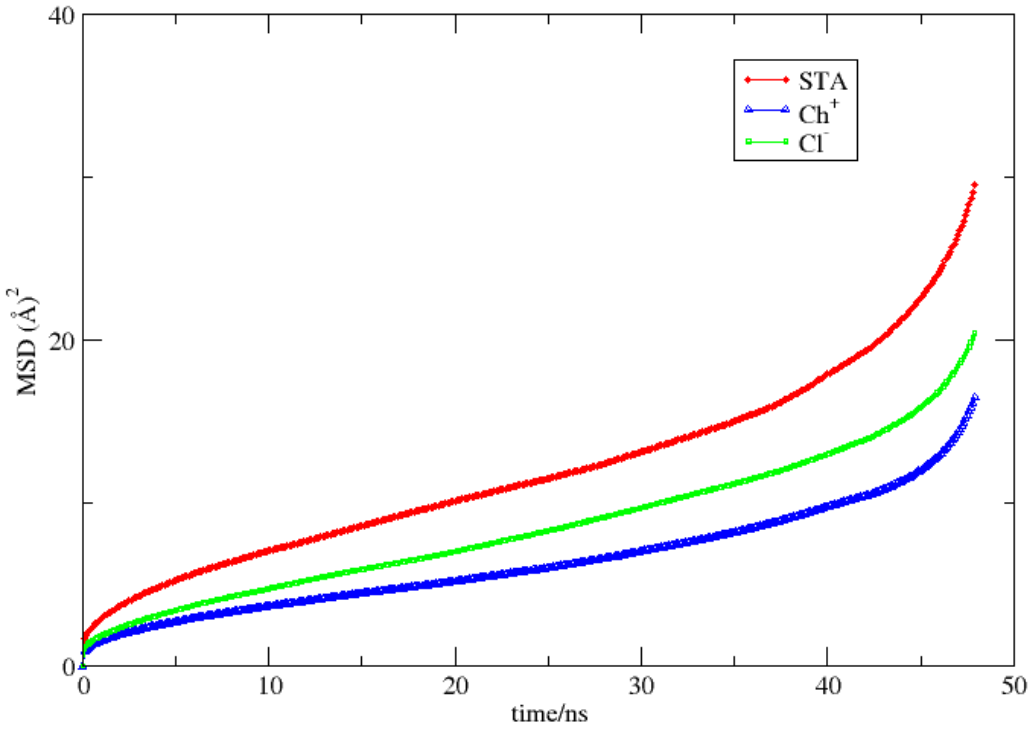


Figure 5. The MSDs of the species for the binary mixtures at 323 K

To ensure the values of Ds, the diffusion coefficient has been calculated in the diffusive region (β = 1). This parameter was proposed to determine the location of the diffusive regime by Del Popolo´ and Voth. In the diffusive region, MSD has a good relationship with time, therefore the Ds are taken in this region.

$$\beta = \frac{\mathrm{d}\log_{10} < \Delta r(t)^2 >}{\mathrm{d}\log_{10} t} \quad (4)$$

$$< \Delta r(t)^2 >= \frac{1}{N}\langle \sum_{i=1}^{N} |r_i^c(t) - r_i^c(0)|^2 \rangle \quad (5)$$

$r_i^c(t)$ and $r_i^c(0)$ are positions of the center of mass of a molecule at time t and 0, respectively [14]. Self-diffusion coefficients for choline (D^+), chloride (D^-) and the HBD (D_{HBD}) at the temperatures listed in Table 1. The hydrogen bonding results confirm the low value of diffusion coefficient of the anion compared to the acid.

Table 1. Self Diffusion coefficients for HBA and HBD in the binary mixture at 353 K

		MSD		
system	**T/K(323)**	**D $_{Ch^+}$ (β)**	**D $_{Cl^-}$ (β)**	**D $_{HBD}$ (β)**
DES	353	0.0391	0.0540	0.7160

Conclusion

The HA $_{STA}$ -- anion RDFs have a main peak at a distance of 2 Å that the H-bonding formation between anion and acid in the binary mixtures. It seems that chloride anion plays a key role in the formation of eutectic solvents based on [Ch^+] [Cl^-] and STA. The structural correlation between anion and acid was confirmed the using spatial distribution function (SDF). The low slope of MSD of anion can be attributed to the stability of the H-bond between anion and hydrogen atoms of carboxyl (-COOH) of STA.

Computational Details

In order to determine whether DESs based on Stearic acid (STA) and choline chloride ([Ch^+] [Cl^-]) can be formed, first, the binary mixtures of STA and [Ch^+] [Cl^-] were simulated at a pure state. Initial configurations of the binary mixtures were prepared using PACKMOL package [15]. The all of MD simulation were carried out by NAMD 2.13 package [16]. For eliminating border effects, periodic boundary conditions (PBC) were used along with the X, Y, and Z-axis. To initiate the simulation, 2000000 steps of minimization was current out to remove the bad contacts of the initial configuration. Then, the binary mixture was heated to 353K in 30000 steps. Finally, the MD simulations were performed for 30 ns in NPT ensembles at 1 bar pressure and desired temperature. For this purpose, the Langevin thermostat, and Nose-Hoover Langevin piston barostat was employed to keep the temperature constant in simulations [17]. The Particle Mesh Ewald (PME) technique was used to calculate the long-range electrostatic interactions [18]. The cutoff distance for the calculation of the short-ranged Lennard-Jones interaction was set at 12 Å [19]. CHARMM36 force field parameters were used for choline chloride salt.

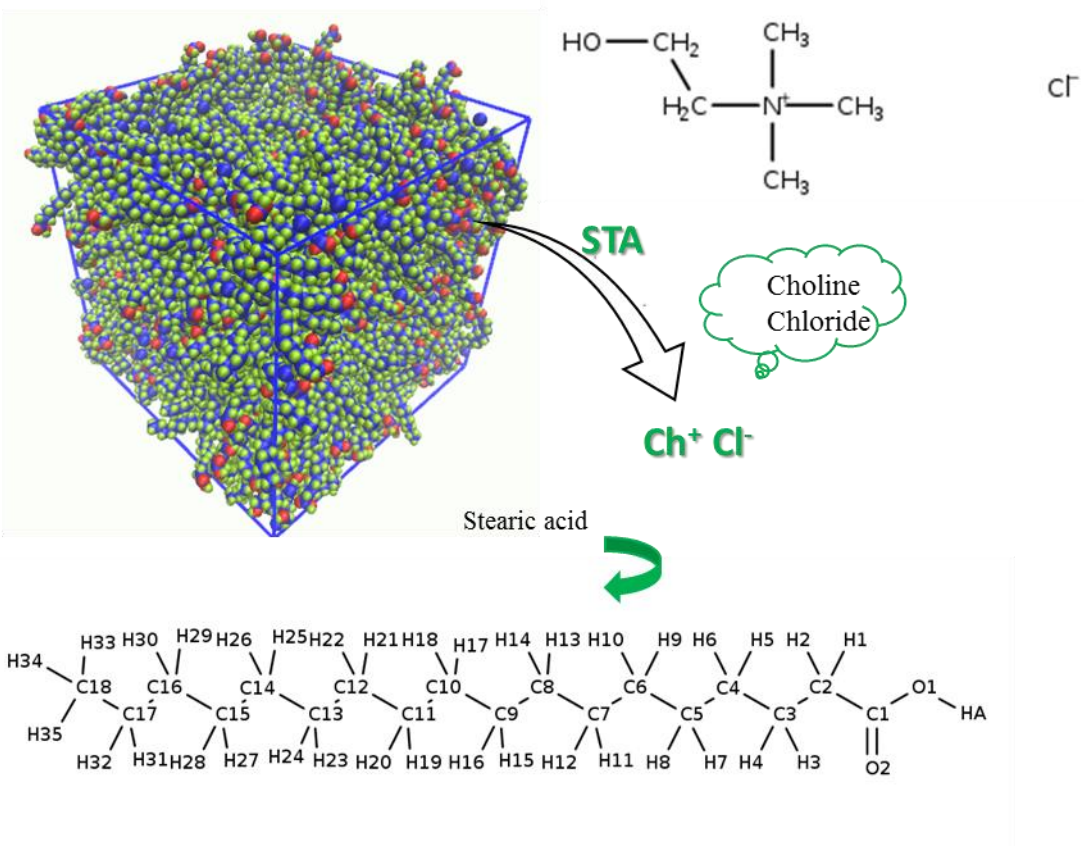


Figure 6. Schematic of the chemical structures of (a) choline [Ch^{+}] and (b) stearic acid with the main atomic labels

Acknowledgments

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