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Effect of the alkyl chain length of Hydrogen bond donor on the intermolecular interaction in eutectic solvents

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Abstract

The binary mixtures of L-menthol and a series of fatty acids such as Acetic acid (C2), Butyric acid and (C4), and Decanoic acid (C10) have been prepared. The structural properties of the deep eutectic solvents were investigated using radial distribution functions (RDF), combined distribution functions, and hydrogen bond networks. The results proved dipole strong intermolecular dipole-dipole interaction and hydrogen bond network in the deep eutectic solvents.

Keywords: L-menthol, Molecular dynamics simulations, Deep eutectic solvents, Structural properties, Dipole-dipole interaction

Introduction

Deep eutectic solvents are defined as mixtures with a low melting point compared to the two pure components [1]. DESs are created by combining a salt with a molecular hydrogen bond donor (HBD) which has a clear liquid phase. These novel solvents are sometimes created as a result of a hydrogen bond interaction between two components. DESs frequently exhibit non-flammability, great thermal stability, and low volatility [1] . L-menthol is a common ingredient in flavoring, foods, and medications [2]. This compound has become interesting as a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in the design of hydrophobic deep eutectic solvents. The saturated fatty acids are obtained from meat fats and plant oils such as coconut oil and palm kernel oil [3]. The fatty acids are important compounds that can have wide applications in the chemical as solvents [4]. The study of the interaction between fatty acids and L-menthol is expected to provide valuable information regarding the interaction between different alkyl chains. Furthermore, fatty acids are found in biodiesel fuels of plant origin that have been considered fossil fuels. It is very difficult to separate fatty acids from the mixtures because these compounds undergo thermal decomposition easily. The fatty acids and terpenes mixture was proposed as a hydrophobic DES able to extract Metal ions and biomolecules from aqueous solutions. The examination of the distribution syntactic of solvent molecules using radial and spatial distribution functions, along with the justification of observed trends, might yield important insights into thermophysical properties. Therefore, one other theme of this study is investigating the possible effect of intermolecular interactions on the structural properties of deep eutectic solvents based on L-menthol and fatty acid. The results proved dipole strong intermolecular dipole-dipole interaction and hydrogen bond network in the deep eutectic solvents.

Simulation Details

The binary mixtures of FAs and L-MEN were prepared using the PACKMOL package. All MD simulations were performed using the NAMD 2.14 software package [5]. The simulation studies of binary mixtures were performed with the CHARMM force fields. The partial charges for L-menthol and Fatty acid (e.g., acetic acid, butyric acid and Lauric acid) species were calculated at the MP2/6-31G* level by fitting the RESP (restricted electrostatic potential). The systems were then allowed to stabilize for 50 ns in an isothermal-isobaric (NPT) ensemble at a temperature of 298.15 K and a pressure of 1 atm. The desired temperature was maintained using the Langevin dynamics method. Finally, intermolecular interactions were investigated in a menthol-based eutectic solvent.

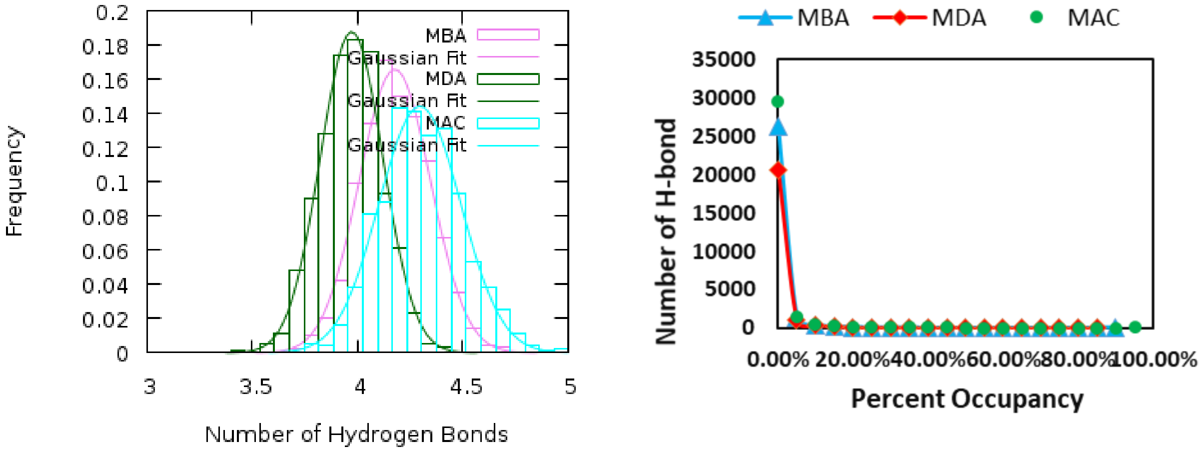
Results and discussion

Hydrogen bond networks

The significant variation in the observed melting point of L-menthol is correlated readily with the strength and number of hydrogen bonds between HBA and HBD. In this work, the importance of intramolecular hydrogen bonding in the orientation of molecules was discussed. The hydrogen bond plugin in VMD was used to obtain the number of Hydrogen bonds [6]**.** Gaussian functions fitted to the number of H-bond data were used to determine the average number of H-bonds (Eq.1).

$$F(X) = \frac{a}{\sigma\sqrt{2\pi}} exp^{\frac{-(X-\bar{X})^2}{2\sigma^2}} \qquad (1)$$

, where $\bar{X}$ is the mean of the distribution, σ is the standard deviation[7]. The average numbers of H-bonds are clearly seen in Figure 1 (a). It is found that the carboxyl group (-COOH) of FAs and hydroxyl group (—OH) of L-menthol plays a key role in the formation of hydrogen bonds between two components. The L-MEN···DEC hydrogen bond with a value of 4 is again shorter than the L-MEN···BUA hydrogen bond with an average value of 4.25 (for each molecule). The hydrogen bonds occupancy analysis shows that the H-bond between decanoic acid and L-menthol molecules is much stronger than acid and makes a stable interaction in the mixture (see Figure1)



(a) (b)

Figure 1. Number of hydrogen bonds (a) and the distribution of the hydrogen bond between the FAs and L-MEN, (b) Hydrogen bond percent occupancies between the FAs and L-MEN

Dipole-dipole interaction energies

The obtained results put in evidence the importance of hydrogen bonding formed between the HBA and HBD in DES synthesis, they are nevertheless key contributors to the overall strengths of HBA–HBD interactions. Therefore, the dipole-dipole interaction energies were obtained using Eq.2:

$$\langle V(r)\rangle = \frac{-1}{3}\frac{\mu_A^2\mu_B^2}{(4\pi k\varepsilon_0)^2}\frac{1}{r^6}\frac{1}{k_B T} \quad (2)$$

where T, r, and μ are temperature, distance, and dipole moment. The j, k_B, and ε_0 are the relative permittivity of the medium, permittivity of free space, and Boltzmann constant. The energy of dipole-dipole interactions is the source of van der Waals interactions. It is often possible to characterize the well-known Keesom energy as a function of intermolecular distance (r) (see Eq. 2).

The electrons may be asymmetrically distributed at a given moment, therefore, the value of dipole moment assigned to a molecule is usually a time average. The average values of the dipole moments of solvent components were obtained by fitting the Gaussian Eq. (1). The normalized-Gaussian distribution has a mean of 2.693 Debye for the L-menthol in the deep eutectic solvent based on acetic acid, while the mean value is 2.7850 Debye in the Decanoic acid-based DES with the longer chain. As can be seen, the dipole moment for the L-menthol molecule in the system containing DEC is greater than that of the mixture MAC, and this can be attributed to the presence of more hydrogen bonds between the L-menthol and Decanoic acid. Also, a negligible difference can be seen for the corresponding average values of the dipole moments of L-MEN in the mixtures MAC and MBA (liquid phase). The dipole-dipole interaction energies are reported in Table 1. The energy of the dipole-dipole interactions between menthol molecules and acid species follows the order [MEN] [ACE] < [MEN] [BUA] < [MEN] [DEC]. In the system containing Ace, the energy of ion-dipole interaction in the case of the acid molecule, is slightly more than the system containing butyric acid, and this is due to the lower electronegativity of this Ace, compared to BUA. It should be noted that the dipole – dipole interaction occurs when the angles between the dipole moment vector of L-MEN and the dipole moment vector of DEC are 80 degrees (see Figure 2).

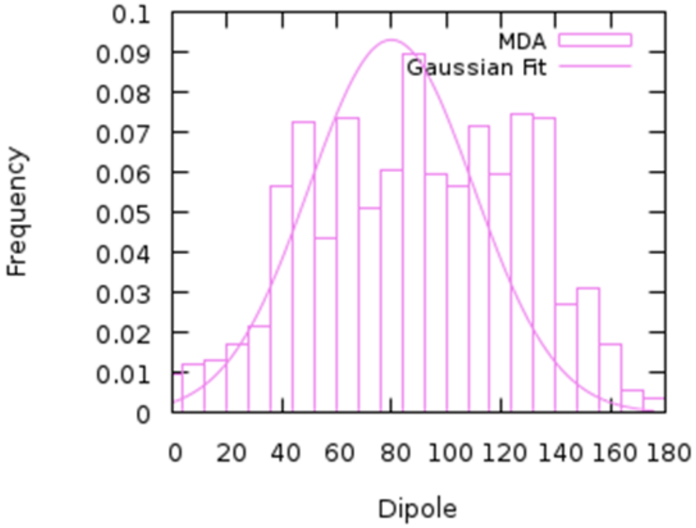


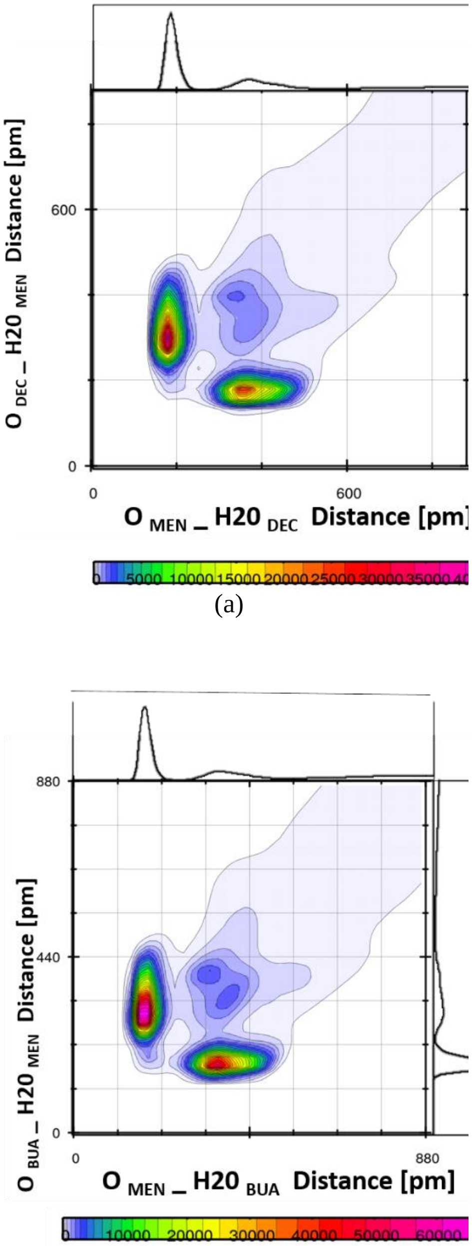
Figure 2. The obtained dipole moment distribution between Decanoic acid and L-menthol molecules at 298.15 K.

Table. 1. Calculated dipole moment of species (in Debye) in the liquid phase.

Interaction	**MAC**	**MBA**	**MDA**
ACE _ MEN	54.4177		
MEN _ MEN	52.5699		
BUA _ MEN		56.2903	
MEN _ MEN		60.1626	
DEC _ MEN			56.4539
MEN _ MEN			60.1726

Tracking the Bridge Species Using the Respective CDFs

For the binary mixtures, the corresponding distance/distance CDFs of the three neighboring species (L-MEN⋯FAs⋯L-MEN) are computed to track the bridging role of species in solutions. The TRAVIS package was used to draw the CDFs. As seen in Fig.3, we looked into the possibility of connecting two [FAs] molecules as the H-bond donors by a one [MEN] bridge in the binary mixture. As shown in the CDFs, one of the axes of CDF represents the distance between the hydrogen of the Decanoic acid bridge, H1, and hydroxyl oxygen of one neighbor DEC, O2, and the other axis belongs to the distance between the O1 atom of the acid bridge and H1 atom of another menthol (see Figure 3). An intense probability region for the two distances of L-menthol - Decanoic acid neighbors (O1-H1) and (O2−H1) is apparent at about 2 Å /2 Å. Since the color spectrum of the CDF graphic for L-MEN - DEC interaction is slightly larger than that of L-MEN - BUA, the average value of the distribution function of the H-bond of L-MEN -DEC molecules surrounding menthol has more numerical values.



(a)

(b)

Figure 3. CDFs showing one [FAs]− bridge between two [MEN] molecule

Conclusions

In this work, the structural properties of four Eutectic Solvents based on L-menthol and fatty acids (L-MEN: ACE, L-MEN: BUA, and L-MEN: DEC) have been investigated using MD simulations. Based on the findings of structural investigations, it is likely that the hydrogen bonds that form between HBD and HBA are what cause the menthol molecules in the mixtures to lose their aggregation. In addition, Dipole-dipole interaction energy was increased with the increase of alkyl chain length.

References

[1] Smith, E.L.; Abbott, A.P.; Ryder, K.S.; Chem. rev. 2014, 114, 11060-82.
[2] Oshima, T.; Ito, M.; J. nat. med. 2021, 75, 319-25.
[3] O'Connor, S.; Rudkowska, I.; Adv. Food Nutr. Res. 2019, 87, 43-146.
[4] Aouf, C.; Durand, E.; Lecomte, J.; Figueroa-Espinoza, M.-C.; Green Chem. 2014, 16, 1740-54.
[5] Barhaghi, M.S.; Crawford, B.; Schwing, G.; Hardy, D.J.; Stone, J.E.; Schwiebert, L.; J. Chem. Theory. Comput. 2022, 18, 4983-94.
[6] Balabin, I.A.; Hu, X.; Beratan, D.N.;. J. Comput. Chem. 2012, 33, 906-10.
[7] Pour, S.B.; Sardroodi, J.J.; Ebrahimzadeh, A.R; Fluid Phase Equilibria. 2022, 552, 113241.