Journal of Molecular Structure 1141 (2017) 451–456

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Theoretical investigation on the microstructure of triethylene glycol based deep eutectic solvents: COSMO-RS and TURBOMOLE prediction

Tayeb Aissaoui [a, b], Yacine Benguerba [a, b, *], Inas M. AlNashef [c, d]

[a] Department of Processes Engineering, Université Ferhat Abbas, Sétif-1, 19000, Sétif, Algeria
[b] Laboratoire de Génie des Procédés Chimiques, Université Ferhat Abbas, Sétif-1, 19000, Sétif, Algeria
[c] Department of Chemical and Environmental Engineering, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates
[d] Department of Chemical Engineering, Khalifa University for Science and Technology, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form
12 March 2017
Accepted 3 April 2017
Available online 5 April 2017

Keywords:
COSMO-RS
Chemical structure
Deep eutectic solvent
Triethylene glycol
Phosphonium salt
Hydrogen bond donor
FTIR

ABSTRACT

The in-silico combination mechanism of triethylene glycol based DESs has been studied. COSMO-RS and graphical user interface TmoleX software were used to predict the interaction mechanism of hydrogen bond donors (HBDs) with hydrogen bond acceptors (HBA) to form DESs. The predicted IR results were compared with the previously reported experimental FT-IR analysis for the same studied DESs. The sigma profiles for the HBD, HBAs and formed DESs were interpreted to identify qualitatively molecular properties like polarity or hydrogen bonding donor and acceptor abilities. The predicted physicochemical properties reported in this study were in good agreement with experimental ones.

© 2017 Published by Elsevier B.V.

1. Introduction

In last decades, novel green media named Deep Eutectic Solvents (DESs) have been emerged as an alternative to conventional solvents and ionic liquids (ILs). DESs have gained considerable academic and industrial interest due to their easy preparation, low economic cost and environmental friendly advantages [1]. These new solvents are simply prepared by mixing hydrogen bond donors (HBDs) with hydrogen bond acceptors (HBAs) at specific molar ratio, temperature and atmospheric pressure [2]. Their melting points are lower than that of HBDs and HBAs [2].

Since DESs are designed by properly combining various quaternary ammonium or phosphonium salts (e.g. ChCl) with different hydrogen bond donors (HBD), they are chemically tailorable solvents [3–6]. Significant investigations have been reported dealing with DESs physicochemical properties (e.g., freezing point, viscosity, density, conductivity, pH and water content) [7–11]. Further studies were performed where DESs have been introduced for several industrial applications such as nanotechnology [12], enhancing oil recovery [13], catalysts for biodiesel production [14], CO_2 capture [15], and many other applications. DESs have proven to be excellent extracting agents in the separation of some components from their mixtures. The tunable properties of the DESs allow to tailor-make optimal solvents for the given application [16–19]. The DESs are also used as a green reaction media in different metal-catalyzed organic reactions [20].

However, microstructures of DESs were not well investigated. Few works were dedicated to report the structures of DESs and their combination mechanism. Therefore, investigating nanoscopic characteristics of DESs is highly recommended. Sun et al. (2013) have reported theoretical study on the structures and properties of mixtures of urea and choline chloride by performing molecular dynamic (MD) simulations [1]. In addition, groups interaction, structure analysis and identification for ChCl–urea–$MgCl_2$, ChCl–EG–$MgCl_2$, and ChCl–Gl–$MgCl_2$ have been investigated by Wang et al. (2012) using FT-IR spectroscopy [21]. In their recent article, Hammond et al. [22] found that the DES reline have a strong and complex hydrogen-bonding network between species, and that the delicate balance of these strong forces is sufficient to

* Corresponding author. Department of Processes Engineering, Université Ferhat Abbas, Sétif-1, 19000, Sétif, Algeria.
E-mail address: benguerbayacine@yahoo.fr (Y. Benguerba).

http://dx.doi.org/10.1016/j.molstruc.2017.04.009
0022-2860/© 2017 Published by Elsevier B.V.

prevent the crystallization of the mixture at room temperature, thereby accounting for the deep eutectic behavior of reline. Ashworth et al. [23] found that the covalency of doubly ionic H-bonds can be greater than, or comparable with, neutral and ionic examples. In contrast to many traditional solvents, an "alphabet soup" of many different types of H-bond (OH···O=C, NH···O=C, OH···Cl, NH···Cl, OH···NH, CH···Cl, CH···O=C, NH···OH, and NH···NH) can form. In this context, some other articles were published [24–26] but the gap still not covered.

This article investigates the structural characteristics of triethylene glycol based DESs using COSMO-RS and TURBOMOLE predictions. Molecular interactions of HBD with HBAs were predicted with an interpretation of sigma profile and IR spectra. Moreover, theoretical results of the density and IR analysis for the studied DESs were compared with previous experimental work published by Hayyan et al. (2015) for the same triethylene glycol based DESs [2]. This study is a further work to encourage more investigations dealing with DESs microstructure characteristics.

2. Computational details

Two main steps are required to perform COSMO-RS calculations: 1) Geometry optimization of each species involved using TURBOMOLE (graphical user interface TmoleX). 2) COSMO-RS implementation and calculation using COSMOthermX software.

2.1. TURBOMOLE calculation

The systems in this study involves six molecules namely: HBD (triethylene glycol (TEG)) and HBAs (methyltriphenylphosphonium bromide (MTPB), benzyltriphenylphosphonium chloride (BTPC), allyltriphenylphosphonium bromide (ATPB), choline chloride (2-hydroxyethyl-trimethylammonium chloride (ChCl) and N,N-diethylethanolammonium chloride (DAC)), Fig. 1 illustrates the molecular structure and charge density for the involving molecules HBD, HBAs and DESs. The first step toward ground state geometry optimization of a molecule is to build its 3D molecular structure. After building the molecules, geometry optimization was performed at the DFT level and def-TZVP basis set for each molecule. Both 3D molecular structure and its geometry optimization were conducted using Turbomole 6.4 software package (TmoleX) [27]. Geometry optimization of the molecules DES_1 (TEG:MTPB), DES_2 (TEG:BTPC); DES_3 (TEG:ATPB), DES_4 (TEG:ChCl), DES_5 (TEG:DAC) were also performed using TmoleX. Furthermore, creating Cosmo files for the investigated DES molecules is a further operation conducted by TmoleX. For the Cosmo file creation, tasks were performed at DFT level and def-TZVP basis set. In addition, IR spectra prediction was reported using TmoleX.

2.2. COSMO-RS implementation

The conductor-like screening model for a real solvent (COSMO-RS) links chemical engineering thermodynamics and quantum chemistry at a molecular level without requiring experimental data on the involved system [28]. COSMO-RS can be applied to predict various thermodynamic properties and behavior of a mixture [29]. Cosmo files for all species involved were imported by COSMOthermX software [29]. After the geometry optimization of the HBD and HBAs, the theoretical combination mechanism of forming DESs was performed in COSMOthermx by mixing the HBD with its corresponding HBA. The probability distribution of finding a surface segment with a specific screening charge density was investigated by calculating σ profile. Moreover, theoretical densities of DESs were measured and compared with experimental results. All above operations were retrieved from COSMOthermX software.

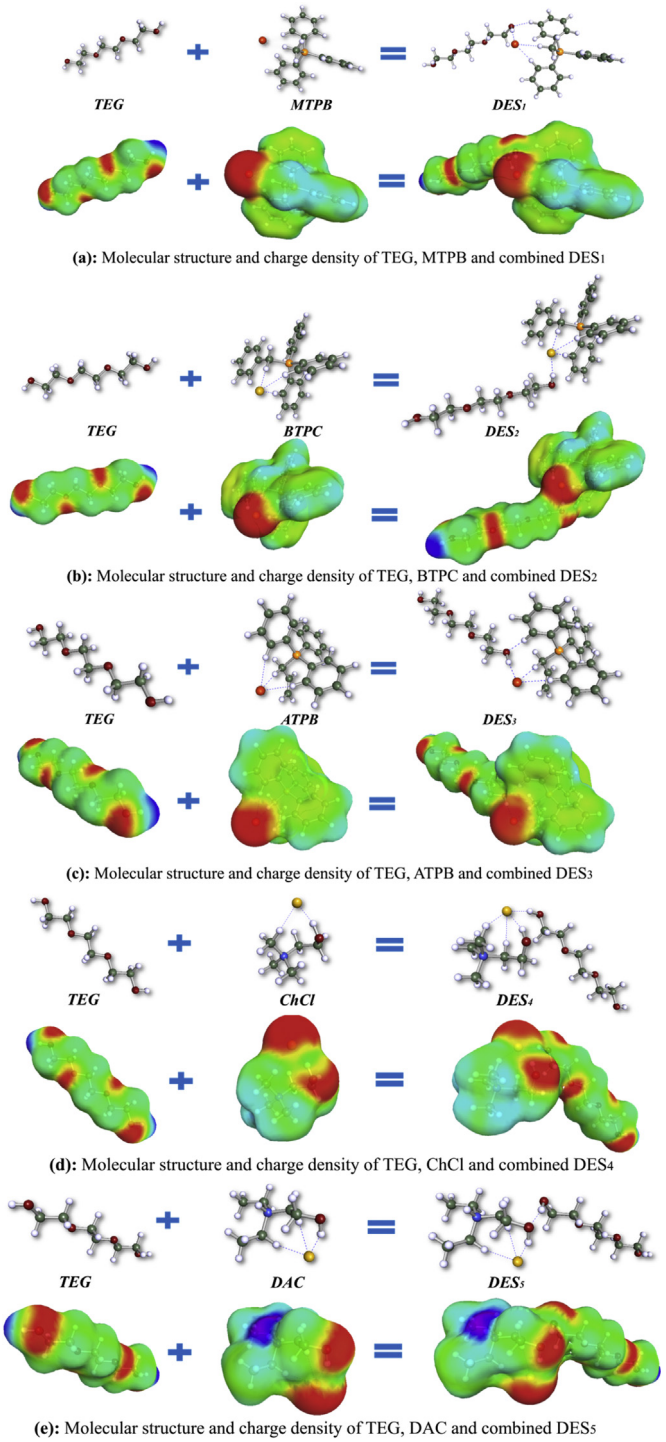

Fig. 1. Molecular structure and charge density of (a) TEG, MTPB and DES_1, (b) TEG, BTPC and DES_2, and (c) TEG, ATPB and DES_3. Molecular structure and charge density of (d) TEG, ChCl and DES_4, (e) TEG, DAC and DES_5.

3. Results and discussion

3.1. Combination mechanism and molecular interactions

The constituents of the DES are three distinct species, i.e. cation, anion and Complexing Agent (CA) [29]. Table 1 illustrates cations, anions and CA involved in this investigation.

After the geometry optimization of the molecules and creating

Download English Version:

https://daneshyari.com/en/article/5161131

Download Persian Version:

https://daneshyari.com/article/5161131

Daneshyari.com