Dehydration of natural gas using choline chloride based deep eutectic solvents: COSMO-RS prediction

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ABSTRACT

Water removal from natural gas is one of the most potent techniques widely used in the pre-treatment processes required for avoiding industrial problems such as corrosion and hydrate formation. Due to its accuracy and precision, conductor-like screening model for a real solvent (COSMO-RS) has recently attracted the attention of researchers around the globe in many applications. In this article, COSMO-RS investigation on the dehydration of natural gas using choline chloride (ChCl) based deep eutectic solvents (DESs) was conducted. The structural combination of the DESs and their water absorption mechanism were well interpreted by performing mixture job to form the DESs and measuring the activity coefficient, σ profile and σ potential of the involved species using COSMO-RS. In addition, vapor pressures for the formed DESs were reported. The activity coefficients of H_2O in DESs were also investigated. The results found in this work imply that DESs can be good alternative to the conventional absorbents for natural gas dehydration. To the best of our knowledge, this is the first report implements COSMO-RS in dehydration of natural gas using DESs.

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1. Introduction

Water in natural gas (NG) is the most undesirable impurity; due to its industrial problems (Gandhidasan et al., 2001). NG must be dried before it enters distribution pipelines stage, to control corrosion and prevent formation of solid hydrocarbon/water hydrates (Lin et al., 2012). Water removal from NG using dehydration process is an important operation in gas processing industry. In current industrial processes, the standard method for NG dehydration is by absorption of water using triethylene glycol (TEG) (Twu et al., 2005). TEG is highly hygroscopic and can remove water from natural gas down to the concentrations specified for pipelines to avoid hydrate formation (Satyro et al., 2011). However, the conventional solvent TEG causes some industrial problems such as: (1) Glycol solutions may be contaminated by dirt, scale, and iron-oxide. (2) Overheating of glycol solution may lead to decomposed products and cause some loss of efficiency. (3) Glycol losses due to foaming, degradation, inadequate mist extraction, etc (Economides, 2009). The above mentioned industrial problems encouraged researchers to develop and improve new and alternative solvents to replace TEG (Xiuli Wang, 2009).

New generation of solvents, named deep eutectic solvents (DESs), has emerged at the beginning of this century (Zhang et al., 2012). DES is defined as a mixture of hydrogen bond donor (HBD) with hydrogen bond acceptor (HBA) that has a melting point less than 100 °C. Their physicochemical properties resemble those of ionic liquids (ILs) (Ruß and König, 2012). DESs are not considered as volatile organic solvents and not flammable, making their storage convenient (Zhang et al., 2012). In addition, DESs have attracted the attention of researchers because they can be biodegradable, nontoxic, and compatible with enzymes (Zhang et al., 2012; Maugeri and Domínguez de María, 2014). DESs are relatively cheap to produce because they are made from inexpensive starting materials and are easy to prepare. DESs can be considered as a good low-cost alternative to ionic liquids in many applications, such as in CO_2 capture, pharmaceuticals, nanotechnology, enhancing oil recovery, electrodeposition, purification of biodiesel, drug solubilization and other various chemical and industrial applications (Ghareh Bagh et al., 2015; Morrison et al., 2009; Gu et al., 2015; Abbott et al., 2015; Mohsenzadeh et al., 2015; Abo-Hamad et al., 2015; Wu et al., 2012).

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In this study, ChCl based DESs were introduced as absorbents for H_2O from NG. Theoretical systems for the prepared DESs by mixing HBDs (TEG, diethylene glycol (DEG), ethylene glycol (EG) and glycerol (GL)) with ChCl as HBA were performed using COSMO-RS and TURBOMOLE software. The combination mechanisms of the formed DESs and their interactions with water have been investigated by determining σ-profiles, σ-potentials and the activity coefficient of H_2O in DESs. Additionally, vapor pressures of the formed DESs were calculated and compared with experimental results for glycols reported in the literature. This article motivates more investigations on the implementation of DESs in gas technology.

2. Computational details

The conductor-like screening model for a real solvent (COSMO-RS) is based on a unimolecular quantum chemical calculation which is combined with statistical thermodynamic approaches to describe thermodynamic behavior of pure compounds and mixtures of compounds (Mulyono et al., 2014). COSMO-RS can be implemented to predict various thermodynamic properties and mixture behaviors, such as vapor liquid equilibrium phase diagrams, measurement of activity coefficient, σ-profiles, σ-potentials, vapor pressure and many other properties. There are mainly two steps to conduct 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. Table 1 illustrates the composition and abbreviation of DESs involved in this work.

2.1. TURBOMOLE calculation

This study involves six molecules namely; HBDs (TEG, DEG, EG and GL), HBA (ChCl) and H_2O. Fig. 1 shows the molecular structure and charge density performed by TmoleX for (a): DES$_1$ (ChChl:TEG), DES$_2$ (ChCl:DEG) and (b): DES$_3$ (ChCl:EG), DES$_4$ (ChCl:GL). Fig. 2 illustrates the absorption mechanism of H_2O in the four DESs performed by TmoleX. Building 3D molecular structure is the first step toward ground state geometry optimization of a molecule. The geometry optimization was performed at the Hartree-Fock level and def-TZVP basis set for each molecule. 3D molecular structure and geometry optimization were conducted using Turbomole 6.4 software package (TmoleX) (E and A development, 2013).

It should be noted that geometry optimization jobs for HBDs and HBA were performed with TmoleX, and then cosmo files were created using the same software. The created cosmo files were imported by COSMOtherm for mixture job to combine the HBDs with HBA to form the DES$_s$. The DESs formed were imported by TmoleX for geometry optimization again. For the cosmo file creation, jobs were performed at Hartree-Fock level and def-TZVP basis set. Water molecule was included in COSMOthermX data without need of geometry optimization.

2.2. COSMO-RS implementation

Cosmo files for all species involved were imported by COSMO-thermX software (Eckert, 2013). After the geometry optimization of

Table 1
Composition and abbreviation of DESs used in this work.

Salts	Abbreviation	HBD	Molar ratio	Symbol
Choline Chloride	ChCl	TEG	1:3	DES$_1$
		DEG	1:3	DES$_2$
		EG	1:3	DES$_3$
		GL	1:3	DES$_4$

the HBDs and HBA, the theoretical combination mechanism of forming DESs was performed in COSMOthermX by mixing the HBD with its corresponding HBA. In addition, H_2O absorption mechanism in DESs was performed using COSMOthermX. The probability distribution of finding a surface segment with a specific screening charge density was investigated by calculating σ profile. The affinity of a solvent for a molecular surface of polarity σ was investigated by calculating σ potential. Moreover, the activity coefficient of H_2O in DESs and vapor pressure of the DESs were determined. All above jobs were retrieved from COSMOthermX.

3. Results and discussion

3.1. Combination mechanism of DESs and their absorption behavior with H_2O

Hydrogen bonding is important in systems containing strongly positively polar hydrogen atoms as donors and negatively polar heteroatomic lone pairs as acceptors. In such systems, donors and acceptors may form a very short-ranged and directed pseudobond -the hydrogen bond- (Klamt and Eckert, 2000). DESs are prepared by mixing HBD with its corresponding HBA at specific temperature and atmospheric pressure. Fig. 1 (a), (b) and Fig. 2 (a), (b) illustrate the chemical structure, charge density and combination mechanism of HBDs (TEG, DEG, EG and GL), HBA (ChCl) and combined DESs (DES$_1$, DES$_2$, DES$_3$ and DES$_4$). The charge density represented in Figs. 1 and 2 for the involved species show in red color the negative charge of the anion Cl$^-$ allocated in free space with choline cation. In addition, the negative charge of O atom contained in the glycol molecules and choline cation was also represented in red color. In contrast, the positive charge of the H atom attached with O atom of glycol molecules was represented in blue color. It should be noticed that the positive charge of N atom allocated in the center of the choline cation was not represented due to its position which is in between C and H atoms. In Fig. 1 (a) the anion Cl$^-$ attracts the nearest H atom allocated in the choline cation. The combination of DES$_1$ was by hydrogen bonding interaction between Cl$^-$ anion and H atom attached with O atom of TEG as it is shown in Fig. 1 (a). Similarly, for all formed DESs, Cl$^-$ anion attracts the nearest H atom allocated outside the choline cation. However, hydrogen bond interaction for the combined DES$_2$ was represented in Fig. 1 (b) between H atom attached with O atom of DEG and between O atom of DEG with H atom of choline cation. For DES$_3$ and DES$_4$, Fig. 2 (a) and (b) show similar hydrogen bond interaction between Cl$^-$ anion and H atom linked with O atom of EG and GL as it is for DES$_1$.

Fig. 3 and Fig. 4 illustrate the combination of H_2O with the four prepared DESs and the charge density of each involved species. The combination mechanism of H_2O with DES$_1$ was represented by hydrogen bond interaction between O atom of water with H atom of TEG in DES$_1$. The charge density of H_2O and DES$_1$ describes more the interaction mechanism by showing the negative charge in red color and positive charge in blue color. Water behaves as HBA when O atom of water was directed to H atom of DES$_1$ due to the electronegativity of O atom represented in red color. Similar behavior was observed for H_2O with DES$_2$ and DES$_3$ as represented in Fig. 3 (b) and Fig. 4 (a). In contrast, Fig. 4 (b) shows that DES$_4$ combination with H_2O was different from other investigated DESs. The oxygen atom of H_2O was not attracted by H atom of DES$_4$ which belongs to GL. The hydrogen bond interaction of DES$_4$ with H_2O was between O atom of H_2O represented by the negative charge with red color and H atom of choline cation. Other hydrogen bond interaction of DES$_4$ with H_2O was represented in Fig. 4 (b). The H atom of choline cation was directed to O atom of H_2O due to the high electronegativity of O. The charge density in Figs. 4 and 5 also describes the absorption mechanism of H_2O in DESs and the