COSMO-RS Prediction for Choline Chloride/Urea Based Deep Eutectic Solvent: Chemical Structure and Application as Agent for Natural Gas Dehydration

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Abstract—In recent years, green solvents named deep eutectic solvents (DESs) have been found to possess significant properties and to be applicable in several technologies. Choline chloride (ChCl) mixed with urea at a ratio of 1:2 and 80 °C was the first discovered DES. In this article, chemical structure and combination mechanism of ChCl: urea based DES were investigated. Moreover, the implementation of this DES in water removal from natural gas was reported. Dehydration of natural gas by ChCl:urea shows significant absorption efficiency compared to triethylene glycol. All above operations were retrieved from COSMOthermX software. This article confirms the potential application of DESs in gas industry.

Keywords—COSMO-RS, deep eutectic solvents, dehydration, natural gas, structure, organic salt.

I. INTRODUCTION

AT the beginning of this century, neoteric solvents have been discovered as alternative to ionic liquids (ILs) [1]. DESs are mixture of hydrogen bond donors (HBDs) with hydrogen bond acceptors (HBAs) at specific molar ratio and temperature. Their melting points are lower than that of their HBDs and HBAs [2]. DESs are liquid at room temperature and possess significant physiochemical properties which make them implemented in several industrial applications. DESs are easily prepared comparing to the conventional ILs. The components HBD and HBA can be simply mixed and converted to a total homogenous mixture without any need for further purification [3]. DESs have also potential implementation in many technologies due to their wide liquid range, water compatibility, low vapor pressure, nonflammability, biocompability, and biodegradability [4].

Owing to its null toxicity, biodegradability, and low cost, ChCl was widely used as an organic salt to prepare eutectic mixtures generally with cheap and safe HBD such as urea [2], [5]. The synthesized form of DES by the combination of ChCl and urea at 1:2 molar ratios and 80 °C has been investigated by several researchers in terms of chemical structure, properties and application. Recently, García et al. [5] have investigated the density functional theory combined with a topological analysis of the electronic density for several DESs including ChCl:urea based DES. The direct relationship between the melting temperature and the hydrogen bond

network features was reported in this work. In addition, Shah et al. [6] reported the intermolecular interactions of ChCl:urea and aqueous ChCl:urea solutions by molecular dynamics simulations. Their results indicated the significance of urea-anion interaction to explain the low melting point of DES. Additionally, in the presence of water, the anion was preferentially hydrated as compared to urea or the cation. In the another study, theoretical investigation on the structures and properties of mixtures of ChCl:urea was reported by Sun et al. [7]. Their results indicate reasonable explanation for the low melting point of the eutectic mixture of ChCl:urea with a ratio of 1:2. Moreover, Yue et al. [8] have discussed the microscopic structure of ChCl:urea using Fourier transform infrared spectroscopy (FT-IR) analysis.

In last years, DESs were reported in many industrial implementations such as CO_2 capture technology, electrodeposition, nanotechnology, purification of biodiesel, enhancing oil recovery, drug solubilization, and many other applications [9]-[15]. At the early stage of this research, there were few research papers available in the literature dealing with the applications of DESs in gas technology. Up to now, this is the first article which predicts the dehydration of natural gas by ChCl:urea using the conductor-like screening model for a real solvent (COSMO-RS).

This article investigates the chemical interaction of DES by predicting the chemical combination and mechanism of ChCl with urea and measuring σ profile of the involved species. In addition, the application of the studied DES on water removal from natural gas was predicted. In this context, DES proves to be a good alternative to conventional solvent TEG.

II. COMPUTATIONAL DETAILS

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. COSMO-RS is a statistical thermodynamic approach combined with a unimolecular quantum chemical calculation [16]. To conduct COSMO-RS calculations, two steps are required: 1) Geometry optimization of each involved species using TURBOMOLE (graphical user interface TmoleX). 2) COSMO-RS implementation and calculation using COSMOthermX software.

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A. TURBOMOLE Calculation

In this article, ChCl, urea, and ChCl:urea molecules were investigated. The HBD (urea) was mixed with HBA (ChCl) to form the DES (ChCl:urea) at molar ratio 1:2 and temperature of 80 °C. Fig. 1 illustrates the chemical structure, combination mechanism, and charge density of the involved species. The first step toward ground state geometry optimization of a molecule is to build 3D molecular structure. 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) [17]. After the geometry optimization of the molecules, cosmo files were created by TmoleX. The created cosmo files for ChCl and urea were imported by COSMOthermX for mixture job to form DES (ChCl:urea). The DES formed was imported by TmoleX for geometry optimization again. For the cosmo file creation, jobs were performed at Hartree-Fock level and def-TZVP basis set.

B. COSMO-RS Implementation

Cosmo files for all involved species were imported by COSMOthermX software [18]. After the geometry optimization of the ChCl and urea, the predicted combination interaction of formed DES was performed in COSMOthermX by mixing ChCl with urea. 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 measured. All above jobs were retrieved from COSMOthermX.

III. RESULT AND DISCUSSION

A. Chemical Structure and Combination Mechanism of DES

DESs are obtained by mixing HBA and HBD, which can be associated with each other by means of hydrogen bond interactions [19]. For a DES formed by ChCl:urea, Abbott et al. [1] have reported that a eutectic occurs at a urea to ChCl ratio of 2. The freezing point of the eutectic mixture is 12 °C, which is considerably lower than that of either of the constituents (ChCl = 302 °C and urea = 133 °C) and allows the mixture to be used as an ambient temperature solvent. Abbott et al. deduced that the significant depression of the freezing point must arise from an interaction between urea molecules and the chloride ion [1]. In addition, Sun at al. [7] have reported that in mixtures of ChCl:urea, the urea molecules enter the second layer around the cations, and appear near the H atoms associating with the C atom attached with N atom of the cation to interact mainly with Cl- anions. It was also deduced in this work that a ratio of 1:2 between ChCl:urea is necessary for a reasonable strength of hydrogen bond interaction to maintain the low melting point of the mixtures of ChCl:urea [7]. In contrast, performing mixture job between ChCl and urea by COSMOthermX gives different results. The mixture job of ChCl:urea was performed by using

the lowest energy contact. Fig. 1 illustrates the chemical structure and charge density of ChCl, urea, and formed DES. The combination mechanism indicated by COSMOthermX shows an interaction between O atom which represents the high electronegativity in red color with the less electronegativity of H atom in blue color attached with O atom of the cation of ChCl. The interaction found in this work confirms the hydrogen bond interaction forming DESs and implies that other hydrogen interactions could cause the depressing of the freezing point and not only the interaction between Cl- and urea.
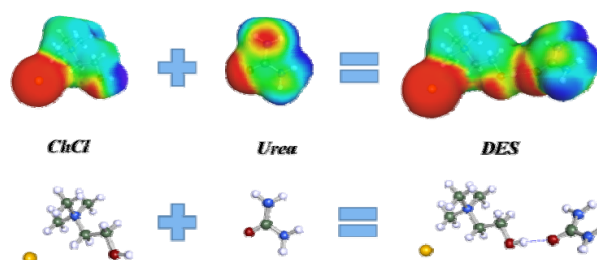

Fig. 1 Chemical structure and charge density of ChCl, urea, and formed DES [23]

Fig. 2 shows the possible hydrogen bond interactions of ChCl and urea. The negative σ values represent positive polarities, and vice versa. There are mainly three regions; HBD region, non-polar region, and HBA region. For ChCl, the positive value σ= +0.019 e $Å^{-2}$ represents the interaction of HBA of the anion Cl- in HBA region. Moreover, the concentrated negative charge of O atom was represented in a positive value of σ=+0.015 e $Å^{-2}$. In HBD region, the less positive charge of H represents the HBD interaction at σ= -0.018 e $Å^{-2}$. For urea, Fig. 2 illustrates the hydrogen atoms attached with N atom at a negative value σ= -0.011 and σ= -0.018 e $Å^{-2}$. Another two peaks which were present in the positive values at +0.018 and +0.015 e $Å^{-2}$ indicate the negative charge of O atom attached with C atom which also represent the interaction of HBDs, and they may also illustrate the less red electronegativity in N atom of urea (Fig. 1 urea). The peaks in non-polar region for urea may represent the non-polar N atom.

B. Dehydration of Natural Gas Using DES

Recently, DESs were introduced as alternative solvents in gas technology. The application of DESs in CO_2 capture technology shows important efficiency [4]. This work proposes DES for water removal from natural gas. The hydrophilic nature of DES finds its applications in many industrial and chemical processes [20]. Infinite dilution activity coefficient of water in ChCl:urea mixture was reported using COSMOthermX. Table I illustrates the measured infinite dilution activity coefficients of water in TEG with that of water in the studied DES at different temperatures. DES shows significant lower results comparing to TEG. At 300.43 K, the infinite dilution activity coefficient of water in DES was 0.1572, whereas that of water in TEG

TEG was 0.5587. Table I demonstrates that the infinite dilution activity coefficient increases with increasing temperature. At 378.32 K, infinite dilution activity coefficient of water in DES reached 0.3198, while that of water in TEG was 0.7257. Clearly, the significant difference between DES and TEG in terms of dilution activity coefficient proves the high affinity of water in DES comparing to the affinity of water in TEG.

The affinity of DES for a molecular surface of polarity σ was investigated by calculating σ potential. Fig. 3 illustrates σ potential of DES and water. In HBD region, high affinity was shown. In contrast, for HBA region, the figure illustrates low interactions in terms of accepting hydrogens by DES.
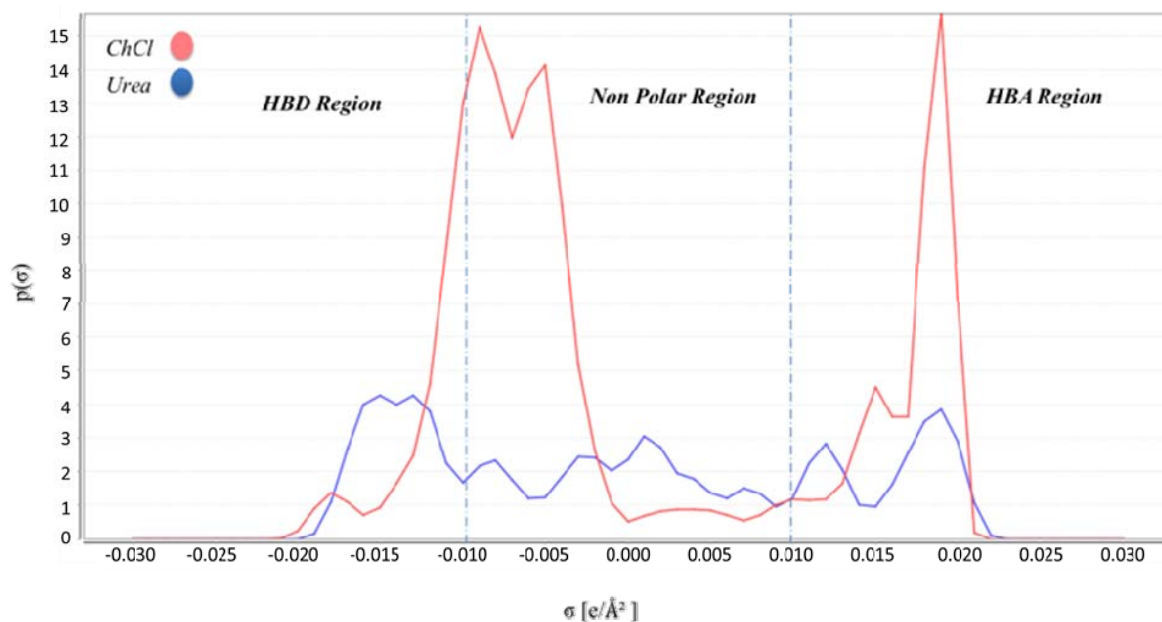

Fig. 2 σ profile of ChCl, Urea

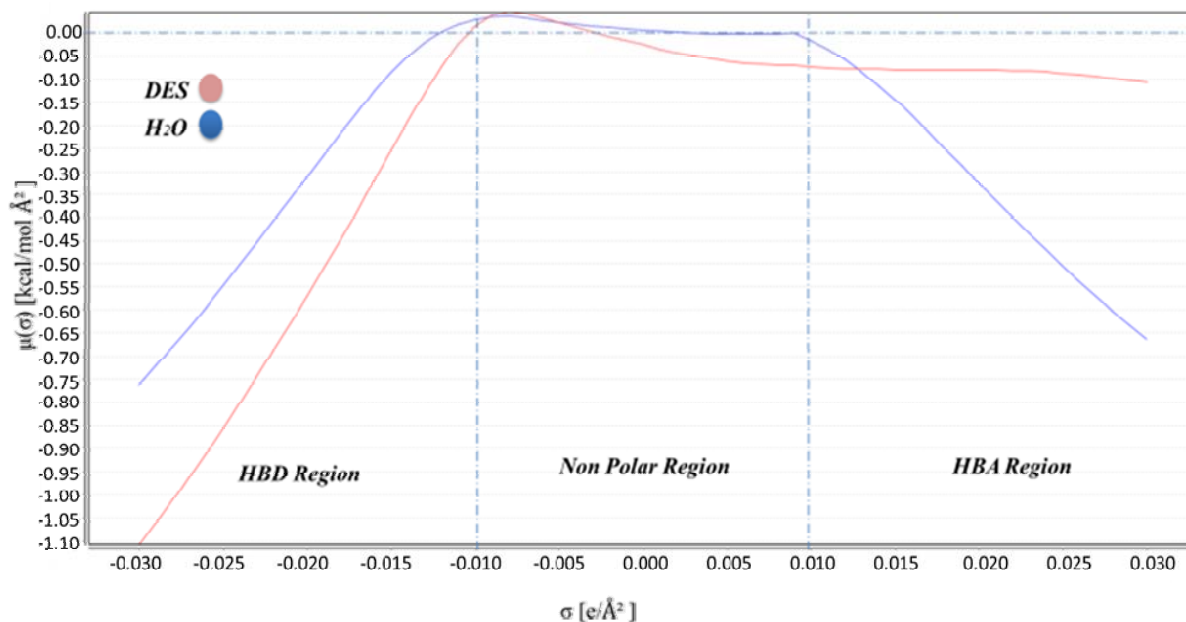Fig. 3 σ potential of DES and water

It is to be noted that glycols are volatile solvents especially during regeneration process. Volatility of glycols is one of their main disadvantages [21]. DES offers potential advantage over TEG in terms of volatility. Table II demonstrates vapor

pressure of TEG and DES. Clearly, DES possesses significant lower vapor pressure comparing to TEG. Consequently, DES has preferential absorption over H_2O due to its affinity with water and very low volatility.

TABLE I
COMPARISON OF PARRISH ET AL. [22] MEASURED INFINITE DILUTION ACTIVITY COEFFICIENTS OF WATER IN TEG WITH THAT OF WATER IN THE STUDIED DES AT DIFFERENT TEMPERATURES

T/K	TEG [22]	DES
300.43	0.5587	0.1572
311.71	0.5826	0.1808
323.26	0.6072	0.2059
333.76	0.6296	0.2299
343.43	0.6503	0.2490
355.93	0.6772	0.2752
364.93	0.6966	0.2922
378.32	0.7257	0.3198

TABLE II
COMPARISON OF MEASURED VAPOR PRESSURE OF TEG WITH PREDICTED VAPOR PRESSURE OF STUDIED DES

Property	TEG experimental result	DES predicted result
Vapor pressure (kPa) at 25 °C	< 0.001 [21]	$2.27.10^{-10}$

IV. CONCLUSION

In this article, chemical structure and combination mechanism of DES were reported. Moreover, DES was considered as neoteric solvent alternates TEG for NG dehydration. It was found that DES proves high affinity with water in addition to its very low volatility, easy preparation and low economic cost comparing to the conventional solvent TEG. This communication presents DESs as promising novel solvents for gas technology implementations. Further investigations are highly required to confirm the available data and highlight more properties and applications of DESs in gas technology.

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