Application of COSMO-RS in Investigating Ionic Liquid as Thermodynamic Hydrate Inhibitor for Methane Hydrate

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Abstract

Gas hydrate formation in oil and gas pipelines has resulted in flow assurance issues. To mitigate hydrate formation, recently, ionic liquid (IL) inhibitors have been studied frequently using experimental method. However, experimental testing alone is insufficient to examine all potential ionic liquid combinations due to large amounts of cation and anion. Therefore, in this work, the thermodynamic inhibition ability of ILs have been predicted based on its fundamental property, or specifically hydrogen bonding energy. For this, Conductor-Like Screening Model for Real Solvent (COSMO-RS) software is used to simulate and study the fundamental property of IL-hydrate system. Relationship between IL inhibition ability and hydrogen bonding energy is then justified. The pattern of relationship is next applied to rank the IL inhibition ability. Through this method, pre-screening of ineffective ILs can be conducted and hence narrows down the scope of ILs waiting to be tested experimentally. As consequence, effective thermodynamic hydrate inhibitor could be discovered faster and be applied in industry.

1. Introduction

Methane hydrates are ice-like crystalline compounds that could form in the presence of water and methane gas under a condition of high pressure and low temperature [1]. Its formation in oil and gas pipelines has affected the flow assurance of natural gas and sometimes, resulted in blockage and rupture of pipe. An approach to prevent this
The issue is to inject chemical inhibitor such as IL to mitigate hydrate formation. As reported by Xiao and Adidharma in 2009 [2], an IL has dual functionality in mitigating hydrates. It can act as a thermodynamic hydrate inhibitor (THI) and a kinetic hydrate inhibitor (KHI). THI prevents the formation of hydrate by shifting the thermodynamic equilibrium curve of gas hydrate to a lower temperature and higher pressure [3]. Meanwhile, KHI slows down the nucleation and growth rate of hydrate.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>COSMO-RS</td>
<td>Conductor-Like Screening Model for Real Solvent</td>
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<tr>
<td>THI</td>
<td>Thermodynamic hydrate inhibitor</td>
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<tr>
<td>KHI</td>
<td>Kinetic hydrate inhibitor</td>
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<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>$E_{\text{HB}}$</td>
<td>Hydrogen bonding energy</td>
</tr>
<tr>
<td>$E_{\text{INT}}$</td>
<td>Total interaction energy</td>
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It works on the principle of lengthening the formation time of hydrate to be longer than the residence time of gas in pipelines [4]. Since the discovery of its dual functionalities, different kinds of ILs have been tested by means of experimental work to determine their effectiveness. Nevertheless, experimental work that is the primary method in testing IL inhibition ability is costly and time consuming. Given the fact that there are limitless combinations of anions and cations to form ILs and by considering the rate of experimental work being done now, experimental testing alone is insufficient. It will take an unacceptably long time until all possible ILs are tested. As consequence, the potential of IL could not be fully utilized and applied to industrial processes. Hence, a noble approach is to use fundamental properties to predict ILs inhibition ability. With this, ineffective ILs could be easily identified, pre-screened away and thus narrow down the amount of potential ILs for experimental testing.

For this purpose, COSMO-RS software that could estimate fundamental properties of ILs system has been integrated into this work. Introduced by Klamt et al. [5], COSMO-RS is a new method to predict the thermodynamics properties of fluid and liquid mixture based on quantum chemistry concept of density functional theory (DFT). In COSMO-RS, charge density, $\sigma$, of surface molecules is the basis of all functions. As the first step, charge densities of all interest species are calculated based on the structure of each molecule. Then, chemical potential, $\mu$ of each molecule in liquid or solvent is calculated using the charge density [6]. Lastly, other thermodynamic properties such as hydrogen bonding, gas solubility and activity coefficient are derived from the chemical potential data [7]. In simple words, by only providing the structure of molecules, charge density, $\sigma$ that is needed for COSMO-RS prediction could be calculated. This signifies that COSMO-RS does not require any functional group parameter or any experimental data to work. As a result, it is able to work with virtually all ILs and mixtures, even the unusual and complex combinations [8].

In this context, COSMO-RS is aimed to provide a better understanding on IL-hydrate system at thermodynamic level. COSMO-RS is adopted to simulate IL-hydrate system, which will then generate values that explains about the fundamental properties of IL-hydrate system. Among many types of fundamental properties that are generated, hydrogen bonding energy is the interest of this work. It is chosen due to the fact that it has been reported to have close relation with the inhibition ability of IL. In the work of Xiao and Adidharma [2], it is reported that the inhibition ability of IL is provided by hydrogen bonding of ILs with water. This statement is reinforced by Xiao et al. who stated that hydrogen bonding of IL with water could severely affect the effectiveness of IL as inhibitor [9]. Generally, a good IL inhibitor creates strong hydrogen bonding with water. Since water is now bonded strongly by IL, less water molecules will be free to react with each other to form hydrate later on [10].

In COSMO-RS, hydrogen bonding energy is no longer a new parameter that is studied intensively. For instance, Claudio et al. [11] had obtained values of hydrogen bonding energies from COSMO-RS and studied its relationship with the pairing of ions. In their work, they have proven reasonable linear relationships between hydrogen-bond basicity values and the hydrogen bonding energy. This indicates that different pairing of ions could affect hydrogen bond basicity, which further has a linear correlation on hydrogen bonding energy. Moving on, from COSMO-RS simulation, Zhou et al. [12] reported that hydrogen bonding interactions between anions and molecules (water) will
directly affect the solubility of IL in water. They suggested that the solubility of IL in water is directly proportional to the strength of hydrogen bonding interaction between anion and water. Furthermore, COSMO-RS had also been applied for the purpose of ILs screening including determining extraction solvent and improving separating process [13]–[16]. Through all these works, it is proven that COSMO-RS is an applicable and reliable method to study the hydrogen bonding interaction of IL systems.

In short, this work is started with the extraction of experimental values of IL inhibition ability from recognized papers. Next, the exact IL-hydrate systems as reported in papers are simulated in COSMO-RS to obtain the values of fundamental property. The relationship between IL inhibition ability and fundamental property is then justified. The pattern of relationship is next applied to provide a faster way in screening out ineffective ILs. With this, scope of ILs to be experimentally tested could be greatly narrowed down and hence, potential of IL as thermodynamic hydrate inhibitor could be maximized. Although applying COSMO-RS to simulate IL-hydrate system is a relatively new and unique concept, this work is justifiable by the successful implementation of previous works in predicting thermodynamic properties for different IL system.

2. Methodology

2.1. Computational method of COSMO-RS

COSMO-RS calculation of interaction energies was basically a two-steps calculation. Firstly, the generations of geometries and electronic density for cations and anions were conducted by TURBOMOLE6.1 program package that follows density functional theory (DFT), using the BP functional B88-86 with a triple-zeta valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation [17]. This was then followed by the estimation of interaction energies performed by COSMOthermX, utilizing the parameter file of BP\_TZVP\_C30\_1301 (COSMOlogic GmbH & Co KG, Leverkusen, Germany).

A total of three basic types of interaction energies are estimated by COSMO-RS. There are the hydrogen bonding energy ($E_{\text{HB}}$), electrostatic-misfit energy ($E_{\text{MF}}$) and van der Waals energy ($E_{\text{VdW}}$). The computational details of these three kinds of interaction energies are described in equations 1-4 below. Lastly, the summation of these three energies formed total interaction energy ($E_{\text{INT}}$).

\[ E_{\text{HB}} = a_{\text{eff}} C_{\text{HB}} \min(0; \sigma_{\text{donor}}^{\alpha} + \sigma_{\text{HB}}^{\alpha}) \times \max(0; \sigma_{\text{acceptor}}^{\alpha} - \sigma_{\text{HB}}^{\alpha}) \]  

\[ E_{\text{MF}} = a_{\text{eff}} \left( \frac{\sigma + \sigma'}{2} \right)^2 \]  

\[ E_{\text{VdW}} = a_{\text{eff}} \left( \tau_{\text{VdW}} + \tau_{\text{VdW}}' \right) \]  

\[ E_{\text{INT}} = E_{\text{HB}} + E_{\text{MF}} + E_{\text{VdW}} \]

The five parameters that affect the energies are interaction parameter ($a'$), effective contact area ($a_{\text{eff}}$), threshold for hydrogen bond ($\sigma_{\text{HB}}$), strength of hydrogen bond ($C_{\text{HB}}$), and lastly $\tau_{\text{VdW}}$, specific van der Waals interaction parameters for each element [18].

In COSMO-RS calculations, IL is treated as equimolar mixture of anion and cation [6], [7]. All simulations for this study were conducted at 10wt% IL at 10°C.

2.2. Extraction of experimental inhibition value

Since this work does not involve any experimental testing, to develop a correlation, the Y values (IL thermodynamic inhibition ability) have been obtained from the experimental results of several recognized papers
In this work, the experimental inhibition ability of IL is represented by average temperature depression (ΔT), which could be calculated by equation [9].

\[ \bar{\Delta T} = \frac{\sum \Delta T}{n} = \frac{\sum (T_{0,p_i} - T_{1,p_i})}{n} \]  

where \( T_{0,p_i} \) is the dissociation temperature of methane in a blank sample without IL and \( T_{1,p_i} \) is the dissociation temperature of methane in a sample with IL inhibitor. The values of both dissociation temperatures should be obtained from the same \( p_i \) and \( n \) refers to the number of pressure point considered.

### 3. Results and discussion

#### 3.1. Identification of relationship between type of energies and IL inhibition ability

Different types of predicted energies have been plotted against average temperature depression as shown in Fig. 1. The purpose of this graph is to determine besides EHB, is there any type of energies that could affect IL inhibition ability. The low regression (R2) value of EMF and EVdW line however indicates that they are insignificant in affecting inhibition ability. The inability of EVdW to affect IL inhibition ability could be due the fact that it is the weakest type of intermolecular attractions [22]. Although EINT, which is summation of three types of energies, shows an even higher R2 value than EMF and EVdW, it still has a lower R2 value than EHB. Among all four types of energies, EHB with the highest R2 value, has proved itself to be the main type of energy to affect IL inhibition ability. This is due to the fact that hydrogen bonding exerted between IL and water could reduce the amount of free water molecules to form hydrate [2], [9], [10], [23]. To verify the consistency of EHB in affecting IL inhibition ability, R2 values have been continuously shown in upcoming graphs.

![Fig. 1. Average temperature depression from Sabil et al. work vs types of predicted energy.](image)

#### 3.2. Effects of different IL anions

Solubility of IL in water affects its performance as hydrate inhibitor. A hydrophilic IL is a better inhibitor, as it can easily dissociate and bond with water molecules [24], [25]. Peng et al. [26] once reported that the solubility of IL in water is dominated by anion’s ability to form hydrogen bonding with water. Hence, Fig. 2 is plotted to illustrate the effect of different anions on solubility and subsequently IL inhibition ability, by showcasing two sets of ILs with fixed cations but different anions. As observed, inhibition ability for both sets increases with increasing \( E_{HB} \) (becoming more negative). This indicates that when cation is fixed, additional \( E_{HB} \) provided by different kind of
anions is beneficial for inhibition ability. In fact, it is found out that when cation is fixed, IL inhibition ability increases with electronegativity of anion. In the BMIM-cation IL set in Fig. 2, the highest inhibition ability goes to BMIM-Cl, followed by BMIM-Br > BMIM-I > BMIM-BF$_4$. Clearly, it is seen that the rank of IL inhibition ability is same as the rank of anion electronegativity where Cl$^-$ > Br$^-$ > I$^-$ > BF$_4^-$. This similar trend of IL inhibition ability has been also reported in the work of Tariq et al [10]. Hence, it is inferred that the higher the electronegativity of anion, the higher the additional $E_{\text{HB}}$ provided by anion [27]. Subsequently, higher $E_{\text{HB}}$ creates more bonding between IL and water which results in higher inhibition ability.

Fig. 2. Average temperature depression from Xiao et al. work vs predicted hydrogen bonding energy (fixed cation)

Fig. 3. Average temperature depression from Xiao et al. work vs predicted hydrogen bonding energy (when EMIM and BMIM based ILs are categorized as only one data set)
Another interesting finding observed from Fig. 2 is the separation of EMIM and BMIM based ILs into two different data sets, instead of one. This step is necessary as the combination of all ILs into one data set may lower the linearity of relationship. This statement is supported by Fig. 3, which is basically a similar graph, but with both EMIM and BMIM based ILs combined into one data set. As seen, the $R^2$ value decreases significantly. This inferred that linear relationship only exists when ILs with same cation are compared. An early deduction is that to ensure a linear relationship for a set of data, only one single ion, which is either cation or anion, can vary while another one must be fixed. The relationship could yet to be applied to predict ILs with different cations and anions. This deduction is also supported by Fig. 4, which the anion of the data set is fixed. The graph proves that when only one type of ion is allowed to vary, linear relationship exists.

### 3.3. Effects of different cations

Next, the effect of cations on inhibition ability is illustrated in Fig. 4, which has its anion fixed as Cl$^-$. When anion is fixed instead, the gradient of the graph is totally opposed as to the graph of fixed cation. This indicates that additional cation $E_{\text{HB}}$ worsens IL inhibition ability. This is because IL cation is non-polar in nature, but water molecule, due to its amphoteric character, tends to have higher affinity only with polar molecules [23]. As a result, water does not like to interact with IL cations [28]. On the other hand, the electronegative IL anion is polar in nature. This makes it to become the main component in IL to interact with water molecules to prevent hydrate formation, whereas cation merely contribute slightly in the process [26], [27]. Since cations have low affinity with water molecules, it is deduced that most of the cations in water will continue to bond with anions. In that case, the additional cation $E_{\text{HB}}$ is actually unbeneﬁcial as it will be used by cation to create stronger bond with anion [29]. This stronger IL bond then reduces the amount of free anions to interact with water because more energy is needed to break the bond [27]. Ultimately, the additional cation $E_{\text{HB}}$ reduces the IL inhibition ability.

![Graph showing relationship between Predicted $E_{\text{HB}}$ and temperature depression for Cl$^-$ anion](image)

*Fig. 4. Average temperature depression from Li et al. work vs predicted total interaction energy (fixed Cl$^-$ anion).*

Furthermore, the trend in Fig. 4 could be explained by the size of cation. In this work, COSMO-RS calculation shows that when anion is fixed, the larger $E_{\text{HB}}$ (more negative) is normally provided by a larger size cation. To serve as a good inhibitor, a large size cation is never preferable. This is because as the size of cation increases, it becomes bulkier, thus harder for it to interact with water molecules. This increased hydrophobicity of cation will in turn reduce the inhibition ability of IL [10], [19], [30]. This statement is supported by the work of Xiao et al.
Conclusion

In conclusion, through this work, $E_{\text{HB}}$ is proven to be the main type of energy that affects IL-water interaction and subsequently altering the inhibition ability of ILs. It is learnt that to study the relationship between $E_{\text{HB}}$ and inhibition ability, either cation or anion must be fixed. Furthermore, it is found out that $E_{\text{HB}}$ provided by cation and anion has opposite effect on IL inhibition ability. Additional anion and subsequently altering the inhibition ability of ILs. It is proven to be the main type of energy that affects IL-water interaction and subsequently altering the inhibition ability of ILs. Additional anion and subsequently altering the inhibition ability of ILs. It

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Reference


