



Prediction of Ionic Liquids Methane Hydrate Average Depression Temperature via COSMO-RS

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Abstract

COSMO-RS is a tool used to pre-screen and pair ionic liquids for gas hydrate mitigation. However, the ionic liquids properties estimated from COSMO-RS lack direct connectivity to the determination of the safety margin (hydrate depression temperature) the inhibitor can alter on the hydrate phase boundary conditions. In this study, a parametric function that relates COSMO-RS estimated ionic liquid surface area and hydrogen bonding energies to the methane hydrate average depression temperature (ΔT) have been presented. The statistical model in this study was developed using multiple linear regression techniques on about 90 data samples at 10 wt.% ionic liquids. The developed model in this work accurately predicts the methane hydrate average depression temperature with standard error of 3.14 and average deviation error of 0.92. Also, the ionic liquid surface area and hydrogen bonding energy contribute to hydrate inhibition by 23% and 77%, respectively. The model could predict the methane hydrate average depression temperature in the similar range as reported in literature. The findings in this work provide a simple and fast method of pre-screening and developing efficient ionic liquids gas hydrate inhibitors for use in the oil and gas industry.

Keywords: Ionic liquids, Surface area, Hydrogen bonding energies, Gas hydrates, Pre-screening, Thermodynamic hydrate inhibitors

Introduction

Since the introduction of ionic liquids as thermodynamic gas hydrate inhibitors in 2009,¹ there has been several experimental works in literature to develop highly effect thermodynamic ionic liquids-based gas hydrate inhibitors.²⁻⁹ However, despite the existing studies, there is still no desirable gas hydrate inhibition in the presence of ionic liquids (ILs).¹⁰ By far at ionic liquids concentration of 10 wt.%, the methane equilibrium temperature shift is from 0.7-1.50K while that of conventional methanol and ethylene glycol (EG) at the same concentration is about 3.5-5.0K and 2-2.50K, respectively.¹¹ Nevertheless, the huge database and promising nature (low vapour pressure, tuneable and dual functionality) of ILs still make them potential candidates for gas hydrate mitigation when carefully tuned.²

To effectively develop novel ionic liquid-based gas hydrate inhibitors, Bavoh *et al.*¹¹ proposed a screening model for Real Solvents (COSMO-RS) method for pre-screening hydrate additives.

The COSMO-RS method uses very less experimental data tunes or design ILs for gas hydrate mitigation by combining quantum and statistical thermodynamics calculation.^{12,13} The main screening or evaluation parameter for this method was the hydrogen bonding energies of the ILs.¹⁴⁻¹⁷ Since hydrate crystal inhibition is mainly achieved by disrupting water activity via hydrogen bonding, Other factors such IL alkyl chain length, hydrophobicity and Van der Waals forces are also considered.¹¹ Several studies have adopted this method to improve its application in the hydrate research community.^{15,18,19} However, most of these works merely use these parameters to describe the possible inhibition behaviour or as a justification for explaining experimental results. Also, there is a poor usage of these parameters to directly predict the methane hydrate equilibrium temperature shift.

Bavoh *et al.*^{11,15} and Khan *et al.*¹⁶ proved that COSMO-RS could be used to explain gas hydrate inhibition behaviour. Khan *et al.*^{14,20} established or confirmed the relationship between the methane equilibrium temperature shift and ILs hydrogen bonding energies.

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Received: 17 April, 2024

Published: 01 May, 2024

Citation: Harrison Osei, Cornelius B Bavoh, Richard Amorin. Prediction of Ionic Liquids Methane Hydrate Average Depression Temperature via COSMO-RS: Research Article. *Trends Petro Eng.* 2024;4(1):1-5. DOI: [10.53902/TPE.2024.04.000536](https://doi.org/10.53902/TPE.2024.04.000536)

However, they did not develop a correlation for such predictions. Qasim *et al.*²¹ also discussed the effect of hydrogen bonding energies on the hydrate equilibrium temperature shift of quaternary ammonium salts. The hunger for a COSMO-RS based model for predicting the methane hydrate equilibrium temperature shift is the motivation for this work. The development of such model would eliminate the trial-and-error testing of ILs as hydrate inhibitors. It would also speed up the tuning of ILs hydrate inhibitors with less cost and time.

Therefore, this work pre-proposes a simple linear empirical correlation for predicting the methane hydrate equilibrium temperature shift using COSMO-RS ILs data. The model is developed by using ILs gas hydrate inhibitors experimental data at 10 wt.%. The main variables used in this study for the predictions are the ILs hydrogen bonding energy and the ILs total surface area. It is believed that the findings in this work would provide an accurate methane hydrate equilibrium temperature shift predictions for ILs based on COSMO-RS data. This would mark the beginning of finding powerful ILs based gas hydrate inhibitors at low cost and time.

Methods Used

COSMO-RS simulation

The Conductor-like Screening Model for Real Solvents (COSMO-RS) software is used to predict the hydrogen bonding energies and surface area of ionic liquids.²² In this work, the COSMO-RS predictions are performed using COSMOthermX, Version C2.1 in the compound list with the parameter file BP_TZVP_C21_0111.ctd (COSMOlogic GmbH & Co KG, Leverkusen, Germany) using the lowest energy conformer.^{11,15} Then the hydrogen bonding energies and surface areas are generated. Figure 1 shows the flowchart for predicting the ionic liquid surface area and hydrogen bonding energies using COSMO-RS.²³

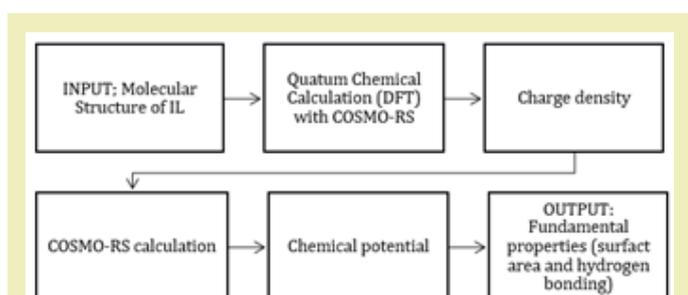


Figure 1: Flowchart on the methodology of predicting fundamental properties in COSMO-RS

COSMO-RS simulation

Using quality data is very critical to developing a strong statistical model.²⁴ Therefore, the variables used to develop the model in this work were carefully selected to accurately represent gas hydrate phase equilibrium shifting behaviour. In this study, the ionic liquids surface area and hydrogen bonding energies were estimated from COSMO-RS. The data consist of over 90 data points

from ionic liquids articles in literature.¹⁰ A brief statistical summary of the data used is presented in Table 1. There were some number of outliers that were removed from the data due to their inconsistency and possible errors in that measurement as discussed by Bavoh *et al.*¹⁰

Table 1: Summary of crude oil assay data used in this work

| Variables | Mean | Max | Min |
|---|--------|--------|--------|
| Hydrogen bonding energy (KJ/mol) | -24.89 | -47.67 | -10.62 |
| Surface area (Å ²) | 258.7 | 373.8 | 165.1 |
| Hydrate depression temperature, ΔT (°C) | 1.24 | 2.09 | 0.3 |
| <i>Max (Maximum); Min (Minimum)</i> | | | |

Model development

The model in this work was developed based on the fundamental gas hydrate inhibition mechanism in ionic liquids. Generally, ionic liquids inhibit hydrate formation by forming strong electrostatic and hydrate gen bonds with water molecules.²⁵

This turns to disrupt the water activity towards hydrate formation. Hence, the use of ionic liquid surface area and hydrogen bonding energies is well justified. Figure 2 shows the adopted model development flow chart. Multiple linear regression (MLR) was used to develop COSMO-RS-based methane hydrate predictions. The MLR model theory in this study constructs a baseline regression that aims at creating a linear relationship between estimated COSMO-RS hydrogen bonding energies and surface area. The MLR model then provides a simple equation of the ionic liquid surface area and hydrogen bonding energies as a linear function of the gas hydrate depression temperature. The MLR model is most suitable for establishing simple and easy-to-use predictive models. The MLR equation for methane hydrate depression temperature prediction in this study is expressed as:

$$\Delta T, ^\circ\text{C} = k_1 S_a + k_2 E_{HB} + k_3 \quad (1)$$

where S_a and E_{HB} are the COSMO-RS estimated surface area and hydrogen bonding energies k_1 , k_2 , and k_3 are the model constants.

The model coefficients were optimised using SPSS 22. The methane hydrate depression temperature model performance was evaluated using root mean squared error (RSME). The specific formulas of the above evaluation indices are defined as follows:

$$\text{RMSE} = \sqrt{\frac{1}{m} \sum_{i=1}^m (y_i - \hat{y}_i)^2} \quad (2)$$

where \hat{y}_i is the MLR model predicted values, y_i denotes the methane hydrate average depression temperature experimental values, and m represents the number of data sets.

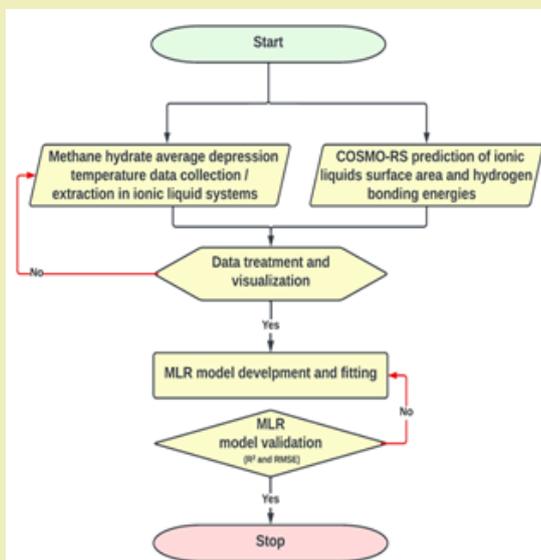


Figure 2: MLR model development flowchart

Results and Discussion

The MLR model was used in this study to provide a simple linear two-parameter function for predicting methane hydrates average depression temperature irrespective of the pressure. The reason for modelling this parameter is to effectively get firsthand information on the thermodynamic safety margin of ionic liquid gas hydrate inhibitors. The developed model in this study effectively predicts methane hydrate average depression temperature as shown in Figure 3. The standard error and average deviation error (ADE) are 0.399 and 0.109, respectively. The methane hydrate average temperature prediction model coefficients parameters for Equation 1 are shown in Table 2. The model coefficients show that both the molecule surface area and hydrogen bonding energies of ionic liquids negatively affects the methane hydrate average depression temperature. This implies that, decreasing surface area and higher hydrogen bonding energies increase the methane hydrate depression temperature. Though it must be noted that the hydrogen bonding energies of the ionic liquids are negative in values. With respect to using this proposed method for developing gas hydrate inhibitors, any ionic liquid with high (negative) hydrogen bonding energy and less surface area would be desirable to beat the existing or conventional inhibitors.

Table 2: Coefficients for equations 1

| Equation parameters | Values |
|---------------------|--------|
| k_1 | -0.005 |
| k_2 | -0.017 |
| k_3 | 2.025 |
| RMSE | 0.399 |
| ADE | 0.109 |

The surface area of the molecules is related to the chain length of the molecule, which governs the solvation behaviour of the ionic

liquids in aqueous systems. A molecule with large surface area seems to be more hydrophobic and would allow poor water and ionic liquid interaction for high gas hydrate inhibition.¹¹

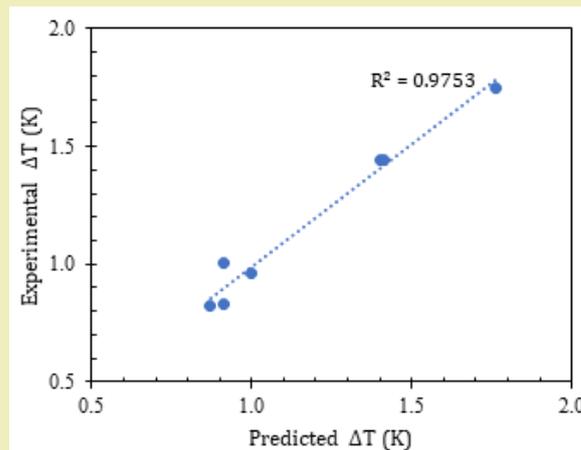


Figure 3: Experimental and predicted methane hydrate average depression temperature of the blind data set

On the other hand, a highly negative hydrogen bonding energy ionic liquid could highly engage the water molecules by disrupting their activity to form hydrates.^{25,26}

In terms of methane hydrate average depression temperature predictor strength, the hydrogen bonding energies of ionic liquids contributes about 77%. While the remaining 23% is controlled by the ionic liquids surface area. This further agrees with most studies that emphasis the critical role of hydrogen bonding strength as a critical property for hydrate mitigation. The constant value represented as k_3 in the model assumes that there is little or negligible ionic liquid surface area and zero hydrogen bonding energy. The methane hydrate depression temperature of about 2K can therefore be achieved, which is almost a half for the performance of conversional gas hydrate inhibitors.²⁷⁻²⁹

The performance of the developed model for predicting crude oil was compared with some existing ionic liquids methane hydrate phase behaviour models. These models are used to predict the hydrate formation temperature which is a direct function of the hydrate average depression temperature. Also, this COSMO-RS based model is advantageous than the conventional once because it is simple and can be used for screening and additives development purposes. Table 3 presents the model performance comparison between this study and those in literature. Interestingly the prediction accuracy of this model out performed some existing models but similar to others.

The developed model in this work was further tested on blind data sets from different locations to appreciate its prediction capabilities. In Figure 3, it is observed that the predicted data agrees with the blind experimental data set with an average depressing error of correlation matrix of 0.9753.

Table 3: Comparison of the performance of the proposed model in this work with conventional methane hydrate phase boundary predictive models in literature

| Model | Errors | Ref. |
|--|--------|-----------------------|
| COSMO-RS and Statistical method | 0.11 K | This study |
| The van der Waals–Platteeuw (vdWP) theory, Peng-Robinson (PR) equation of state (EoS) and the NRTL activity coefficient model. | 0.11 K | Kazemi ²⁷ |
| Dickens and Quinby-Hunt (electrolyte) model and CSMGem | 0.24 K | Nashed ²⁸ |
| Dickens and Quinby-Hunt (electrolyte) model and CSMGem | 0.48 K | Qasim ²¹ |
| The van der Waals–Platteeuw (vdWP) theory, Peng-Robinson (PR) equation of state (EoS) and the NRTL activity coefficient model. | 0.4 K | Ghaedi ²⁹ |
| The van der Waals–Platteeuw (vdWP) theory and the Pitzer and Mayorga model based on osmotic coefficient activity model. | 0.6 K | Partoon ³⁰ |

Conclusion

In this study, a statical model to predict ionic liquid methane hydrate average depression temperature using COSMO-RS parameters such surface area and hydrogen bonding was developed. The developed model exhibited suitable ionic liquid methane hydrate average depression temperature prediction with an average depression temperature deviation of 0.11K. The model parameters informed that, both ionic liquids surface area and hydrogen bonding energies control the hydrate inhibition properties by increasing the ionic liquids solvation and hydrogen bond affinity to water. It was further suggested that reducing the ionic liquids surface area by playing with the chain length of the anion size could yield desirable hydrate inhibition that could match or exceed the existing conventional inhibitors. The findings in this study are useful for pre-screening and developing effective ionic liquids-based gas hydrate inhibitors.

Acknowledgments

The authors acknowledge University of Mines and Technology for their support in terms of laboratory equipment to undergo this study.

Funding

This Research Article received no external funding.

Conflicts of Interest

Regarding the publication of this article, the authors declare that they have no conflict of interest.

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