

Chemical Engineering Thermodynamics

COSMO-RS: An ionic liquid prescreening tool for gas hydrate mitigation☆

Cornelius B. Bavoh, Bhajan Lal^{*}, Omar Nashed, Muhammad S. Khan, Lau K. Keong, Mohd. Azmi Bustam

Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia

ARTICLE INFO

Article history:

Received 28 December 2015

Received in revised form 1 June 2016

Accepted 14 July 2016

Available online 25 July 2016

Keywords:

Gas hydrates

COSMO-RS

Hydrogen bonding energies

Ionic liquids

Tuning

ABSTRACT

Recently ionic liquids (ILs) are introduced as novel dual function gas hydrate inhibitors. However, no desired gas hydrate inhibition has been reported due to poor IL selection and/or tuning method. Trial & error as well as selection based on existing literature are the methods currently employed for selecting and/or tuning ILs. These methods are probabilistic, time consuming, expensive and may not result in selecting high performance ILs for gas hydrate mitigation. In this work, COSMO-RS is considered as a prescreening tool of ILs for gas hydrate mitigation by predicting the hydrogen bonding energies (E_{HB}) of studied IL inhibitors and comparing the predicted E_{HB} to the depression temperature (T) and induction time. Results show that, predicted E_{HB} and chain length of ILs strongly relate and significantly affect the gas hydrate inhibition depression temperature but correlate moderately ($R = 0.70$) with average induction time in literature. It is deduced from the results that, T increases with increasing IL E_{HB} and/or decreases with increasing chain length. However, the cation–anion pairing of ILs also affects IL gas hydrate inhibition performance. Furthermore, a visual and better understanding of IL/water behavior for gas hydrate inhibition in terms of hydrogen bond donor and acceptor interaction analysis is also presented by determining the sigma profile and sigma potential of studied IL cations and anions used for gas hydrate mitigation for easy IL selection.

© 2016 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Gas hydrates are non-stoichiometric ice-like crystalline inclusion compounds formed by the physical combination of water and gases [1–5]. Common gas hydrate formers are methane, propane, and carbon dioxide; more so, there are basically three gas hydrate structures; cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH). Gas hydrate can be formed in oil and gas production, transportation, and processing facilities which cause serious operational, economic, and safety problems [2]. Therefore, gas hydrate continues to be the major flow assurance challenge facing oil and gas industries. According to Xiao-Sen *et al.* [6], the maintenance of flow assurance in the oil and gas industry amounts to over 200 M USD annually due to gas hydrate formation and aggregation. Water removal, depressurization, heating and chemical inhibition are the main methods of mitigating gas hydrate, but currently chemical inhibition is used due to high economic cost, impracticability and/or ineffective implementation of the other methods [7].

Strong electrostatic force and hydrogen bonding ability with water molecules are the molecular characteristics of gas hydrate inhibitors (such as methanol (MeOH) and ethylene glycol (EG)). These molecular characteristics result in strong hydrogen bonding between the inhibitor molecules and the water molecules reducing the activity of water to form hydrates with gas molecules. This effect changes the thermodynamic and kinetic conditions of hydrate formation [8].

Recently, experimental studies [6,9–18] have introduced organic salts with low melting point, known as ionic liquids [19] as dual function gas hydrate inhibitors (*i.e.* they shift the equilibrium hydrate curve to high pressure and low temperature regions and increase hydrate formation nucleation time). The uniqueness of ILs for inhibiting gas hydrate is that, they show strong electrostatic force and form hydrogen bonding with water molecules. MD simulation and modeling study of ILs on gas hydrate shows that the hydrogen bonding ability of ILs, which strongly depends on the anion type, and hydrophobicity (which depends on the cation chain length) are the critical parameters for gas hydrate inhibition [20,21]. Therefore high inhibition depends on the anion–cation pairing or tuning of ILs. The hydrate inhibition strength of chemical inhibitors is generally determined by calculating the average depression temperature of the hydrate–liquid–vapor curve as;

$$\bar{T} = \frac{1}{n} \sum_{i=1}^n \Delta T \quad (1)$$

where n is the number of data points and ΔT is the difference between measured hydrate dissociation temperature in the presence of inhibitor and pure water at constant pressure.

Currently, no desirable extent of gas hydrate inhibition in the presence of ILs has been achieved by IL gas hydrate researchers. For example at 10 wt.% concentration, shift of equilibrium hydrate temperature curve with studied ILs ranges from 0.7 to 1.50 K while that of

☆ Supported by the Universiti Teknologi PETRONAS.

^{*} Corresponding author. Fax: +60 53757619.E-mail addresses: bhajan.lal@petronas.com.my, bhajan200575@gmail.com (B. Lal).

conventional methanol and EG (ethylene glycol) at the same concentration is about 3.5–5.0 K and 2–2.50 K [18] respectively. Nevertheless the huge database and promising nature (low vapor pressure, tunable and dual functionality) of ILs still make them potential candidates for gas hydrate mitigation when carefully tuned. Presently, no available method has been proposed for tuning ILs for gas hydrate inhibition. Previous studies have shown that, researchers tuning ILs base on literature findings and trial and error random selection.

The aforementioned selection mechanism of ILs for gas hydrate inhibition is based on random speculations making these methods probabilistic *i.e.* they may or may not inhibit gas hydrate when experimentally investigated. This may result in high cost and time wastage since the cost of purchasing ILs and gases is relatively high. Similarly, the time required in performing gas hydrate experiment is considerably longer. For a break through, there should be a predictive tool or method to pre-screen and tune ILs by predicting the gas hydrate inhibition properties of ILs, such as hydrogen bonding basicity, cation chain length and cation–anion pairing type, in order to select potential IL inhibitors before synthesis or purchase for hydrate studies. Structural–interpolation group contribution methods (GCMs) such as UNIQUAC Functional-group Activity Coefficients (UNIFAC) are widely and reliable methods used for predicting the thermophysical properties of solvents with less experimental data [22]. GCMs are less accurate and face prediction challenge when very less experimental data of some compound mixtures are used. A more efficient and accurate method that presents necessary data and significant description of molecular interactions of compounds in solution is the conductor like screening model for real solvents (COSMO-RS). In addition, COSMO-RS uses very less experimental data compared to GCMs, and can be used as a tool for tuning ILs for gas hydrate mitigation.

COSMO-RS is a software which combines quantum calculation and statistical thermodynamics introduced by Klamt and Schuurmann. COSMO-RS is an efficient method which allows fast thermodynamic calculations and screening of solvents [22]. COSMO-RS has wide applications in chemical engineering, pharmaceutical study for drug development [23] and modeling thermodynamic properties of ILs [24–26]. COSMO-RS has been reported as a screening tool of IL properties for carbon dioxide capture and solubility studies [27–31]. Most recently, COSMO-RS was presented as a method for tuning ILs for natural gas dehydration [32], however there is no open literature regarding the use of COSMO-RS to screen ILs for gas hydrate studies. Claudio *et al.* [33] used COSMO-RS to predict the hydrogen bonding energies (E_{HB}) of ILs, which is defined as the energy between IL acceptor and donor in hydrogen-bonding interaction [34]; and reported that, COSMO-RS predicted E_{HB} have a strong relationship with the experimental hydrogen bonding basicity (ability of ILs to accept hydrogen atoms [35]) of ILs [20,21]. Klamt [36] described the interaction mechanism between water and solute compounds by determining their sigma-prolife and sigma-potentials in COSMO-RS and concluded that COSMO-RS effectively describes water–solvent interactions of precompounds. Therefore COSMO-RS can be used as a predictive tool for prescreening IL hydrogen bonding basicity for gas hydrate purposes.

This work presents COSMO-RS as a new prescreening tool of ILs for gas hydrate mitigation by predicting their hydrogen bonding energies (E_{HB}), and analyzing the effect of predicted E_{HB} on the average depression temperature (T) and induction time of studied ILs reported in the literature. It also discusses factors that affect E_{HB} of ILs and presents a visual and better understanding of IL–water behaviors in terms of hydrogen bond donor and acceptor. This is done by determining the sigma profile and sigma potential of some commonly studied IL cations and anions for gas hydrate mitigation. More so, this work is aimed at saving cost, time, and to aid in successive selection of more effective ILs for gas hydrate mitigation using COSMO-RS.

2. Materials and Methods

The experimental work in this paper is reported elsewhere in reference [12]. The details of experimental data from reported literatures

used in this work are shown in Table 1. These literatures were chosen for analysis because they present many types of ILs with the same cations, which open doors for data plotting and analysis. For simplicity, we considered thermodynamic and kinetic studies separately because thermodynamic of gas hydrates is well understood compared to kinetics. In addition, kinetics of hydrate formation is stochastic and depends on the type of apparatus used, rate of agitation, subcooling *etc.* Also, the data is analyzed differently due to some differences in reported results for same ILs by various research groups (see Table 1) which may be credited due to data validity. However the data validity cannot be questioned much since the differences can be related to, accuracy and calibration of equipment, and more importantly the purity level of the ILs used.

The typical studied concentrations of thermodynamic and kinetics of hydrate inhibitors are 10 wt.% and 1 wt.% respectively. Therefore the average depression temperature (T) and average induction time of ILs for gas hydrate mitigation in this work were selected accordingly.

2.1. Conductor like screening model for real solvents (COSMO-RS)

In COSMO calculations, the solute molecules are calculated in a virtual conductor environment inducing a polarization charge density on the interface of the molecule and the conductor. Details on theory and application of COSMO-RS can be found in literature [24]. The hydrogen-bonding energies, E_{HB} , are described by the following equation [24];

$$E_{HB} = a_{eff} c_{HB} \min(0, \min(0; \sigma_{donor} + \sigma_{HB}) \min(0; \sigma_{acceptor} - \sigma_{HB})) \quad (2)$$

where ($\sigma_{acceptor}$, σ_{donor}) is a function of the polarization charges of the two interacting segments, c_{HB} is the threshold for hydrogen bonding; a_{eff} is the effective contact area between two surface segments. The lowest energy conformer is used in the COSMO-RS calculations with the parameter file BP_TZVP_C21_0111.ctd. Furthermore, independent equimolar cation–anion and water mixture are used to predict the E_{HB} values of pure ILs. Sigma surface, sigma profile and sigma potential are determined by using independent IL cations and anions. Furthermore, statistical analysis was performed at p -value of ≤ 0.05 .

3. Results and Discussion

The COSMO-RS predicted E_{HB} for studied ILs in literature data are presented in Table 1.

3.1. Predicted hydrogen bonding energies (E_{HB})

3.1.1. Effect of predicted hydrogen bonding energies and chain length on thermodynamic hydrate inhibition (THI)

The average depression temperature (T) is used to measure the hydrate inhibition performance of ILs. This property describes the ability of ILs to shift the hydrate phase equilibrium curve to high pressure and low temperature conditions [18]. Fig. 1 shows the plot of T verses COSMO-RS predicted E_{HB} of selected studied ILs in this work.

In Fig. 1, results show that predicted hydrogen bonding energies (E_{HB}) of selected ILs strongly relate linearly to experimental average depression temperatures (T) of IL gas hydrate inhibitors reported in selected literature. Ionic liquids with shorter cation alkyl chain (EMIM base) demonstrated high inhibition impact than those with longer alkyl chain (BMIM base). This implies that, IL cation chain length affects gas hydrate inhibition as reported by Xiao *et al.* [10]. It is observed that the average depression temperatures increase with increasing E_{HB} for ILs with the same cation chain length but decrease with increasing cation chain length with the same anion. The variation in average depression temperatures in Fig. 1 of BMIM base ILs studied by different authors [10,12] is due to data validity as mentioned earlier.

For further analysis, a multiple regression analysis is performed to examine the effect of ILs E_{HB} and chain length on the average depression

Table 1Experimental details of reported literature used in this work and COSMO-RS predicted hydrogen bonding energies (E_{HB})

Author	Ionic liquid (IL)	Gas	Test type	Conc/wt. %	E_{HB} predicted/ $\text{kJ} \cdot \text{mol}^{-1}$	IL chain length	Average temperature deviation/K	Average induction time/h
Xiao-Sen et al. [6]	1,3-Dimethyl-imidazolium iodide [MMIM]-I	CH ₄	THI	10	−15.99154	1	0.844	
	1-Ethyl-3-methyl-imidazolium iodide [EMIM]-I				−15.80808	2	0.822	
Xiao & Adidharma [9]	1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM]-BF ₄	CH ₄	THI/KHI	10	−11.51698	2		6.48
	1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM]-BF ₄				−11.10226	4		3.94
	1-Ethyl-3-methylimidazolium dicyanamide [EMIM]-N(CN) ₂				−18.97839	2		1.03
	1-Ethyl-3-methylimidazolium ethyl sulfate [EMIM]-EtSO ₄				−19.03374	2		0.56
	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM]-CF ₃ SO ₃				−13.2242	2		0.40
Zare et al. [11]	1-Butyl-3-methylimidazolium methyl sulfate [BMIM][MeSO ₄]	CH ₄	THI	10	−18.34148	4	1.03	
	1-Ethyl-3-methylimidazolium hydrogen sulfate [EMIM][HSO ₄]				−42.30824	2	0.99	
	1-Ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO ₄]				−19.03374	2	0.67	
	1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF ₄]				−11.10226	4	0.46	
Sabil et al. [12]	1-Butyl-3-methylimidazolium hydrogen sulfate [BMIM][HSO ₄]	CH ₄	THI	10	−41.9339	4	1.103	
	1-Butyl-3-methylimidazolium chloride [BMIM][Cl]				−30.62388	4	0.887	
	1-Butyl-3-methylimidazolium bromide [BMIM][Br]				−23.2777	4	0.758	
	1-Butyl-3-methylimidazolium dicyanamide [BMIM][N(CN) ₂]				−19.10425	4	0.663	
	1-Butyl-3-methylimidazolium trifluoromethane sulfonate [BMIM]-CF ₃ SO ₃				−13.03396	4	0.617	
	1-Butyl-3-methylimidazolium methyl sulfate [BMIM][CH ₃ SO ₄]				−18.34148	4	0.585	
	1-Butyl-3-methylimidazolium perchlorate [BMIM][ClO ₄]				−4.59349	4	0.37	
Xiao et al. [10]	1-Ethyl-3-methylimidazolium chloride [EMIM]-Cl	CH ₄	THI/KHI	10/0.1	−30.98246	2	1.22	1.47
	1-Ethyl-3-methylimidazolium bromide [EMIM]-Br				−23.64372	2	1.03	2.04
	1-Propyl-3-methylimidazolium iodide [PMIM]-I				−15.68538	3	0.80	1.29
	1-Butyl-3-methylimidazolium chloride [BMIM]-Cl				−30.62388	4	0.69	1.85
	1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF ₄)				−11.51698	2	0.60	5.70
	1-Butyl-3-methylimidazolium bromide [BMIM]-Br				−23.2777	4	0.58	2.45
	1-Butyl-3-methylimidazolium iodide [BMIM]-I				−15.45325	4	0.50	5.21
	1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF ₄)				−11.10226	4	0.27	

temperatures of studied ILs. The analysis shows that, E_{HB} and chain length significantly affect T , with the p -values of 1.21×10^{-5} and 0.000871 respectively and an adjusted R -Square of 0.83. The multiple regression coefficients suggest that, (1) the average depression temperature increases with increasing E_{HB} and/or decreasing cation chain length. (2) IL cation chain length is very sensitive to gas hydrate inhibition impact compared to E_{HB} . The reason could be credited to the inhibition mechanism for gas hydrate by reducing activity of water molecules in hydrate formation by forming hydrogen bonds with water molecules. An increase in IL cation chain length increases the hydrophobicity of the ILs, therefore reducing

the interaction ability or the accessibility of the ILs with/to water molecules and restricting hydrogen bond formation between ionic liquid and water molecules. In other words the hydrogen bonding ability of ILs with water molecules depends on hydrophobic nature of ILs. For example BMIM-Cl (−30.62388 $\text{kJ} \cdot \text{mol}^{-1}$) has higher E_{HB} than EMIM-Br (−23.64372 $\text{kJ} \cdot \text{mol}^{-1}$) but the average depression temperature of the latter (1.03 K) is greater than that of the former (0.69 K) because EMIM-Br has less chain length therefore has the ability to access water molecules and form more hydrogen bond compared to BMIM-Cl.

3.1.2. Effect of predicted hydrogen bonding energies and chain length on kinetic hydrate inhibition (KHI)

The measurement of induction time is used by researchers as kinetic gas hydrate inhibition indicator. Considering the stochastic nature of induction time and factors affecting hydrate formation as stated earlier, it is assumed that, at least a decrease in one order of magnitude of kinetic measurement accuracy relative to thermodynamic measurement of hydrate formation can be accepted [1]. The challenges with induction time measurement resulted in difficulties in comparing COSMO-RS predicted E_{HB} to average induction time as shown in Fig. 2. However, in Fig. 2, correlation analysis was performed to determine how average induction time correlates to E_{HB} as reported in literature [9,10].

Fig. 2(a) and (b) shows $R = 0.70$ suggesting that experimental average induction time moderately correlated high with E_{HB} . This implies that, E_{HB} and IL chain length play a role in kinetic inhibition of gas hydrate and likewise in thermodynamics agreeing with the result reported in literature [21]. In contrary to thermodynamic inhibition of gas hydrates discussed, decreasing E_{HB} and longer IL cation chain length increase the average induction time of hydrate formation in the presence of ILs. In view of this, COSMO-RS can be used to pre-screen ILs to obtain a critical E_{HB} and chain length for high dual functional inhibition of gas hydrate. For further understanding and detailed analysis with respect to E_{HB} and kinetics of gas hydrate, a predictable parameter such as hydrate growth rate can be considered rather than the induction time, since the induction time measurements are stochastic.

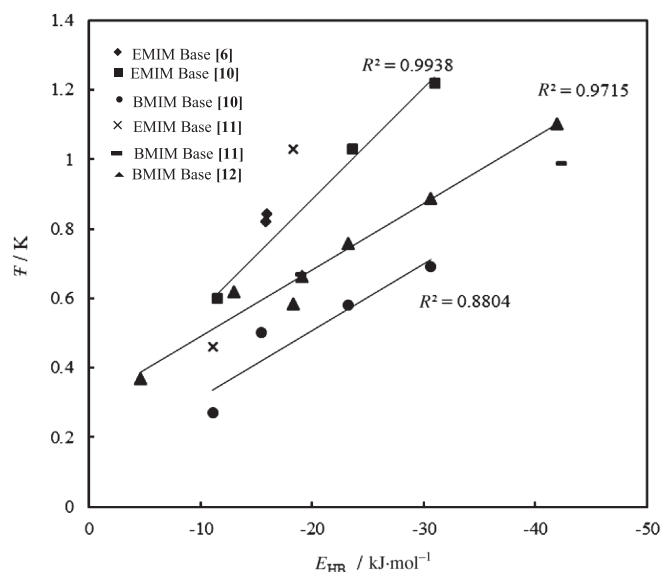


Fig. 1. Regression between average depression temperature (T) and hydrogen bonding energies (E_{HB}) predicted by COSMO-RS.

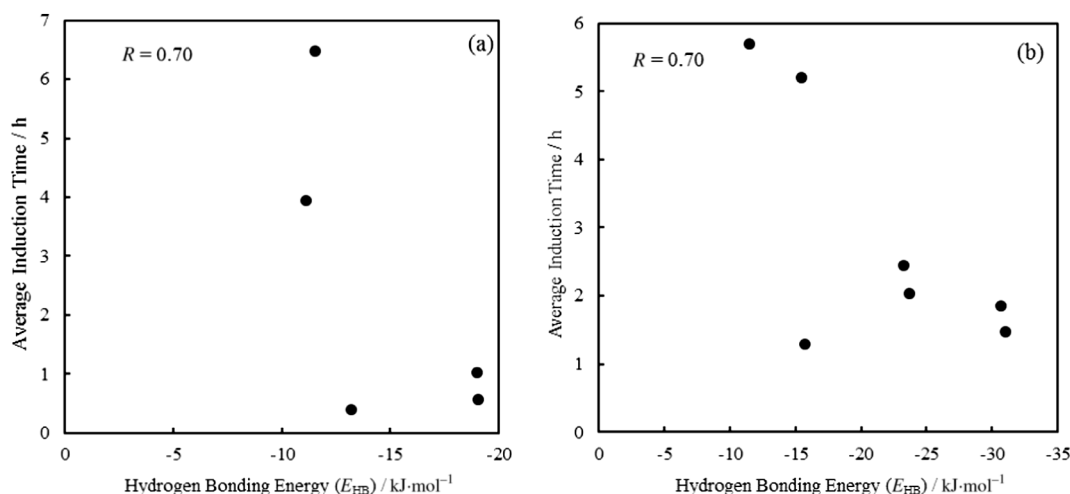


Fig. 2. Correlation between average induction time and hydrogen bonding energies (E_{HB}) predicted by COSMO-RS: (a) reference [9] at 10 wt.%; (b) reference [10] at 1 wt.%.

3.2. Factors affecting ionic liquid hydrogen bonding energies

Aiming at proposing a method to screen ILs for hydrate mitigation, further comparisons were performed to determine the effect of IL cation alkyl chain length and different cation–anion pairing on the E_{HB} of IL predicted by COSMO-RS. It is reported that the hydrogen basicity of ILs depends on the anion while the acidity on the cation [37]. In

Fig. 3(a) and (b), for a specific anion, there is no significant difference in predicted E_{HB} for different IL cation alkyl chain lengths, but in Fig. (3c), a significant difference in predicted E_{HB} values are shown for specific ionic liquid anion with different cation types. This implies that, cation chain length has negligible effect on IL E_{HB} , but significantly affects IL hydrophobicity. Presented earlier as a critical parameter that affects gas hydrate inhibition impact. IL cation–anion pairing affects the

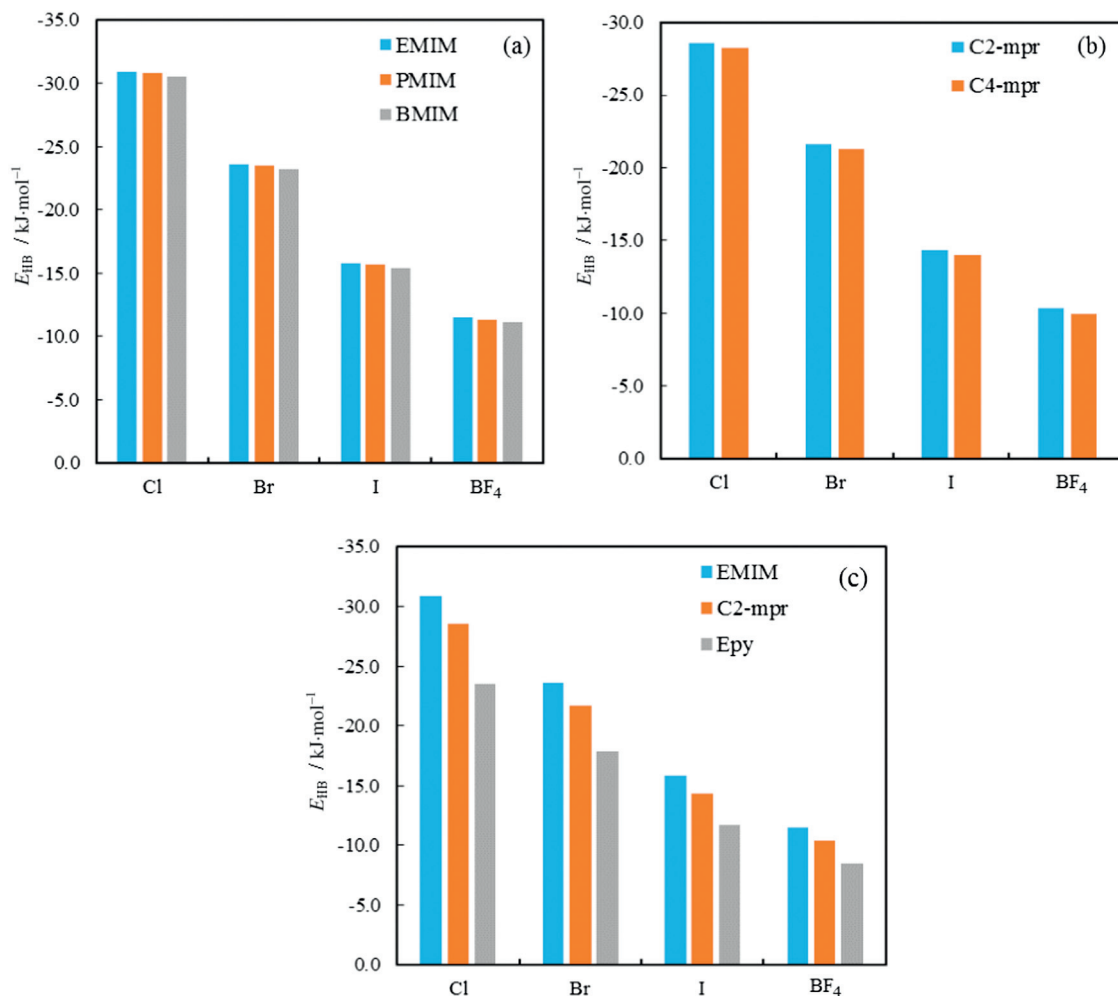


Fig. 3. Effects of chain length and cation type on hydrogen bonding energies (E_{HB}) of halide anions predicted by COSMO-RS: (a) effect of different chain lengths of imidazolium base ILs; (b) effect of different chain lengths of pyridinium base ILs; (c) effect of different IL cations.

E_{HB} agreeing to the finding reported by [15,22]. Therefore in order to increase the E_{HB} of an ILs for hydrate mitigation, the cation–anion pair must be considered critically. Furthermore, incorporating hydroxyl group into IL cations is known to also increase the hydrogen bonding strength of ILs and gas hydrate inhibition impact [12,18].

3.3. COSMO-RS σ profile and sigma (σ) potential

COSMO-RS σ -surface, σ -profile and σ -potential of IL cations and anions can be employed for the prescreening of ILs for gas hydrate mitigation in addition to IL hydrogen bonding energies. The σ -surface, σ -profile and σ -potential give a good explanation of IL cation and anion interaction behavior with water in a visualize and simple way by describing their electro-negativity and electro-positivity. Since in gas hydrate mitigation, one major aim of inhibitors (ILs) is to distract the activity of water molecules from hydrate formation through hydrogen bonding interaction with water molecules. Therefore, a pre-visual comparison of the interaction of ILs with water using COSMO-RS through σ -surface, σ -profile and σ -potential will aid in the selection of desired ILs for gas hydrate mitigation.

Fig. 4 shows the σ -surface and σ -profile of water, MeOH, DEG and commonly studied IL anions for gas hydrate studies. The blue area on the σ -surface of water describes a strong negative (≥ -100 eV·nm⁻²) of the hydrogen bond (HB) donors, the red area shows a strong positive (≤ 100 eV·nm⁻²) of HB-acceptors and the green area describes the non-polar nature of the compound (≥ -1 non-polar ≤ 100 eV·nm⁻²) [36]. Water and commercially used inhibitors (MeOH, DEG) exhibit two peaks of HB affinity (donor and acceptor) whereas the studied IL anions only exhibit strong HB acceptor affinity (positive side) in an increasing order of tetrafluoroborate (BF₄) < iodide (I) < dicyanamide (C₂N₃) < bromide (Br) < chloride (Cl) (Fig. 4). The σ -profile result agrees with finding reported in Table 1 by various hydrate research groups. Considering IL anions in Fig. 4, for the same cation (e.g. BMIM) the T increases in the same order as observed in the σ -profile. This further explains why Cl is known to show high gas hydrate inhibition as reported in the literature [10], because Cl interacts strongly with water molecules by accepting hydrogen atoms from water molecules.

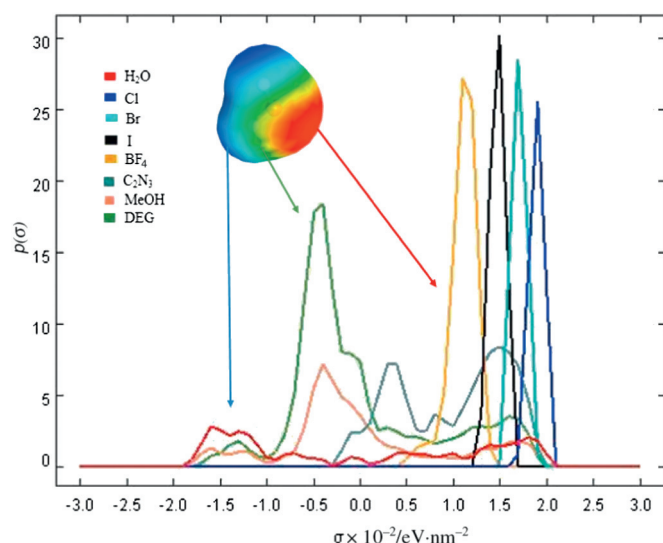


Fig. 4. σ -Surface and σ -profiles of water, some commercially used inhibitors and commonly studied IL anions for gas hydrate studies.

In Fig. 5, IL cations turn to be more non-polar, accounting for the high induction time demonstrated by IL cations with high longer chain length. According to MD simulation studies by Ebrahim *et al.* [21] IL

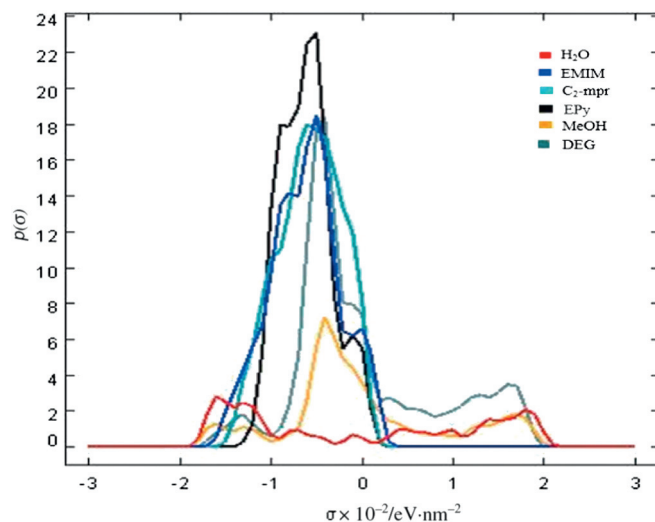


Fig. 5. σ -Profiles of water, some commercially used inhibitors and commonly studied IL cations.

cations sticks to gas hydrate surface, reducing hydrate formation rate and growth. However they exhibit relatively weak hydrogen bond donor affinity and weakly interact with water molecules, resulting to poor gas hydrate thermodynamic inhibition impact. EMIM shows the strongest hydrogen bond donor affinity among selected IL cations in this work. On the other hand, MeOH and DEG (commercial inhibitors) exhibit strong hydrogen bond donor affinity. They exhibit strong HB donor and acceptor affinity with water molecules. This explains why they show high gas hydrate inhibition impact. Employing the σ -surface and σ -profile method using COSMO-RS, one can identify and/or select which IL cation and anion have strong affinity to form hydrogen bonding with water for high gas hydrate inhibition and promotion purposes.

A better and detailed understanding of IL/water behavior can be achieved in the σ -potentials as shown in Figs. 6 and 7. Though the σ -potential results are similar to σ -profile/ σ -surface, nevertheless σ -potential gives a detailed result with simplicity, making peak analysis easy to interpret when compared to σ -profile/ σ -surface peaks which looks much clustered and sometimes difficult to interpret. For example, in Fig. 4, it's quite difficult to interpret the hydrogen bond acceptor affinity of dicyanamide, but its interpretation is simply achieved in the σ -potential in Fig. 6.

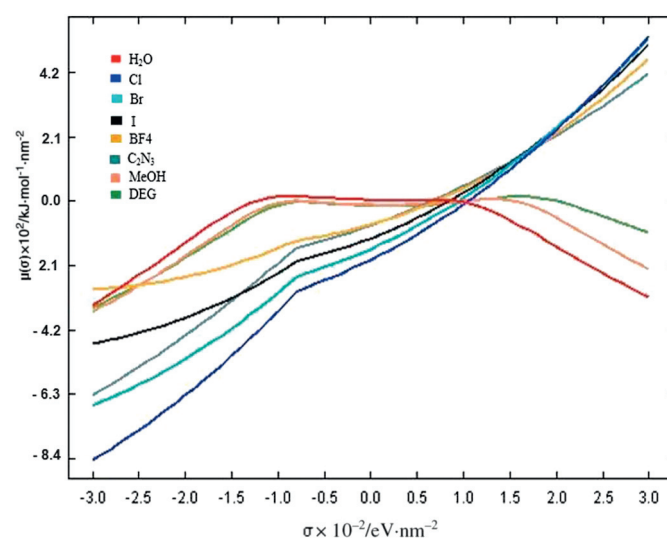


Fig. 6. σ -Potentials of water, some commercially used inhibitors and commonly studied IL anions for gas hydrate studies.

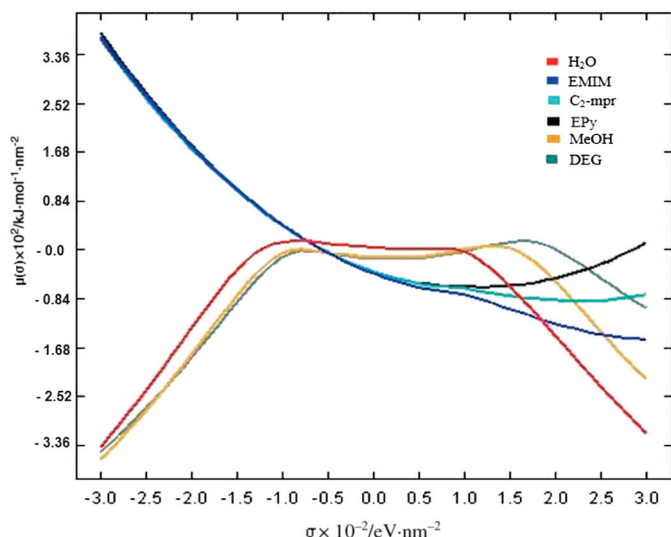


Fig. 7. σ -Potentials of water, some commercially used inhibitors and commonly studied IL cations.

It is observed from the σ -profile and σ -potential that studied ILs (cations and anions) on gas hydrate inhibition impact exhibit strong HB acceptor affinity than HB donor affinity, as compared to commercially used inhibitors, therefore restricting hydrogen bonding interaction to HB donor affinity of water, causing the free HB acceptor of water to be less involved in hydrogen bonding. For high gas hydrate inhibition, gas hydrate researchers must screen for ILs that exhibit strong hydrogen bond acceptor and HB donor affinity for active engagement in hydrogen bonding with both HB acceptor and donor of water. Furthermore, due to the huge IL database, specific ILs cannot be generally proposed. However it is recommended that IL cations with strong HB donor affinity and less non-polarity should be selected for hydrate mitigation.

4. Conclusions

This study shows that COSMO-RS can be used as a prescreening tool of ILs for gas hydrate purposes via predicting IL E_{HB} , adjusting IL cation-anion pairing and cations alkyl chains, and understanding IL/water behavior by determining the σ -surface, σ -profile and σ -potential of IL cations and anions. The results suggested that T increases with increasing E_{HB} and/or decreasing cation alkyl chains of ILs. E_{HB} and cation chain length of ILs did not only relate to T , but they also correlated relatively with the average induction time, therefore suggesting COSMO-RS as a tool to prescreen ILs in order to achieve higher gas hydrate inhibition impact for the oil and gas industry.

Nomenclature

a_{eff}	effective contact area between two surface segments
c_{HB}	threshold for hydrogen bonding
E_{HB}	hydrogen bonding energies
$\sigma_{acceptor}$	function of the polarization charge of hydrogen acceptor segment
σ_{donor}	function of the polarization charge of hydrogen donor segment

References

- [1] E.D. Sloan, C.A. Koh, Clathrate hydrates of natural gases, third ed. CRC Press, Boca Raton, 2007.
- [2] C.A. Koh, E.D. Sloan, A.K. Sum, D.T. Wu, Fundamentals and applications of gas hydrates, *Annu. Rev. Chem. Biomol. Eng.* 2 (2011) 237–257.
- [3] C. Sun, W. Li, X. Yang, F. Li, Q. Yuan, L. Mu, et al., Progress in research of gas hydrate, *Chin. J. Chem. Eng.* 19 (2011) 151–162.
- [4] X. Peng, Y. Hu, L. Yang, C. Jin, Decomposition kinetics for formation of CO₂ hydrates in natural silica sands, *Chin. J. Chem. Eng.* 18 (2010) 61–65.

- [5] L. Chen, C. Sun, G. Chen, Y. Nie, Z. Sun, Y. Liu, Measurements of hydrate equilibrium conditions for CH₄, CO₂, and CH₄ + C₂H₆ + C₃H₈ in various systems by step-heating method, *Chin. J. Chem. Eng.* 17 (2009) 635–641.
- [6] X. Sen Li, Y.J. Liu, Z.Y. Zeng, Z.Y. Chen, G. Li, H.J. Wu, Equilibrium hydrate formation conditions for the mixtures of methane + ionic liquids + water, *J. Chem. Eng. Data* 56 (2011) 119–123.
- [7] M. Tariq, D. Rooney, E. Othman, S. Aparicio, M. Atilhan, M. Khraisheh, Gas hydrate inhibition: A review of the role of ionic liquids, *Ind. Eng. Chem. Res.* 53 (2014) 17855–17868.
- [8] J. Carroll, Natural gas hydrates a guide for engineers, Elsevier, Third edit, 2014.
- [9] C. Xiao, H. Adidharma, Dual function inhibitors for methane hydrate, *Chem. Eng. Sci.* 64 (2009) 1522–1527.
- [10] C. Xiao, N. Wibisono, H. Adidharma, Dialkylimidazolium halide ionic liquids as dual function inhibitors for methane hydrate, *Chem. Eng. Sci.* 65 (2010) 3080–3087.
- [11] M. Zare, A. Haghtalab, A.N. Ahmadi, K. Nazari, Experiment and thermodynamic modeling of methane hydrate equilibria in the presence of aqueous imidazolium-based ionic liquid solutions using electrolyte cubic square well equation of state, *Fluid Phase Equilib.* 341 (2013) 61–69.
- [12] K.M. Sabil, O. Nashed, B. Lal, L. Ismail, A. Japper-jaafar, Experimental investigation on the dissociation conditions of methane hydrate in the presence of imidazolium-based ionic liquids, *Thermodyn. J. Chem.* 84 (2015) 7–13.
- [13] B. Partoon, N.M.S. Wong, K.M. Sabil, K. Nasrifar, M.R. Ahmad, A study on thermodynamics effect of [EMIM]-Cl and [OH-C₂MIM]-Cl on methane hydrate equilibrium line, *Fluid Phase Equilib.* 337 (2013) 26–31.
- [14] K. Nazari, A.N. Ahmadi, A thermodynamic study of methane hydrate formation in the presence of [Bmim][Bf 4] and [Bmim][Ms] ionic liquids, 17th International Conference Gas Hydrates 2011, Edinburgh, Scotland, United Kingdom 2011, p. 9.
- [15] T. Makino, Y. Matsumoto, T. Sugahara, K. Ohgaki, H. Masuda, Effect of ionic liquid on hydrate formation rate in carbon dioxide hydrates, Proc. 7th Int. Conf. Gas Hydrates (ICGH), Edinburgh, Scotland, United Kingdom 2011, pp. 2–5.
- [16] K. Tumba, P. Reddy, P. Naidoo, D. Ramjugernath, A. Eslamimanesh, A.H. Mohammadi, et al., Phase equilibria of methane and carbon dioxide clathrate hydrates in the presence of aqueous solutions of tributylmethylphosphonium methylsulfate ionic liquid, *J. Chem. Eng. Data* 56 (2011) 3620–3629.
- [17] T. Kitajima, N. Ohtsubo, S. Hashimoto, T. Makino, D. Kodama, K. Ohgaki, Study on prompt methane hydrate formation derived by addition of ionic liquid, *Am. Chem. Sci. J.* 2 (2012) 100–110.
- [18] K. Kim, S.-P. Kang, Investigation of pyrrolidinium- and morpholinium-based ionic liquids into kinetic hydrate inhibitors on structure i methane hydrate, 7th International Conference Gas Hydrates 2011, Edinburgh, Scotland, United Kingdom 2011, p. 6.
- [19] B. Lal, M. Sahin, E. Ayranci, Volumetric studies to examine the interactions of imidazolium based ionic liquids with water by means of density and speed of sound measurements, *J. Chem. Thermodyn.* 54 (2012) 142–147.
- [20] H. Jiang, H. Adidharma, Thermodynamic modeling of aqueous ionic liquid solutions and prediction of methane hydrate dissociation conditions in the presence of ionic liquid, *Chem. Eng. Sci.* 102 (2013) 24–31.
- [21] M. Ebrahim, H. Nasrollah, B. Abareschi, C. Ghotbi, V. Taghikhani, A.H. Jalili, et al., Investigation of six imidazolium-based ionic liquids as thermo-kinetic inhibitors for methane hydrate by molecular dynamics simulation, Proc. 2nd Natl. Iran. Conf. Gas Hydrate 2013, p. 12.
- [22] A. Klamt, F. Eckert, COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids, *Fluid Phase Equilib.* 172 (2000) 43–72.
- [23] A. Klamt, The COSMO and COSMO-RS solvation models, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 1 (2011) 699–709.
- [24] U. Guide, A graphical user interface to the COSMOtherm, *Program* (2012) 1–77.
- [25] L.S. Ferreira, J.O. Trierweiler, Modeling and simulation of the polymeric nanocapsule formation process, *IFAC Proc.* 7 (2009) 405–410.
- [26] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, G. Crespo, Overview of the liquid-liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS, *Ind. Eng. Chem. Res.* 51 (2012) 3483–3507.
- [27] D.I.W. Edward, M. Ishiyama, W.R. Paterson, Modeling and simulation of the polymeric nanocapsule formation process, *AIChE J.* 57 (2011) 3199–3209.
- [28] Z. Lei, B. Zhang, J. Zhu, W. Gong, J. Lü, Y. Li, Solubility of CO₂ in methanol, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and their mixtures, *Chin. J. Chem. Eng.* 21 (2013) 310–317.
- [29] R. Kato, J. Gmehling, Systems with ionic liquids: measurement of VLE and γ^∞ data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(OL), *J. Chem. Thermodyn.* 37 (2005) 603–619.
- [30] K.Z. Sumon, A. Henni, Ionic liquids for CO₂ capture using COSMO-RS: effect of structure, properties and molecular interactions on solubility and selectivity, *Fluid Phase Equilib.* 310 (2011) 39–55.
- [31] J. Palomar, V.R. Ferro, J.S. Torrecilla, F. Rodríguez, Density and molar volume predictions using COSMO-RS for ionic liquids. An approach to solvent design, *Ind. Eng. Chem. Res.* 46 (2007) 6041–6048.
- [32] G. Confa, M.A. Bustam, A.M. Sharif, N. Mohamad, S. Ullah, Tuning ionic liquids for natural gas dehydration using COSMO-RS methodology, *J. Nat. Gas Sci. Eng.* (2015).
- [33] A.F.M. Cláudio, L. Swift, J.P. Hallett, T. Welton, J.A.P. Coutinho, M.G. Freire, Extended scale for the hydrogen-bond basicity of ionic liquids, *Phys. Chem. Chem. Phys.* 16 (2014) 6593–6601.
- [34] M.H. Hao, Theoretical calculation of hydrogen-bonding strength for drug molecules, *J. Chem. Theory Comput.* 2 (2006) 863–872.
- [35] M.H. Abraham, P.L. Grellier, R.M. Doherty, R.W. Taft, The use of scales of hydrogen-bond acidity and basicity in organic, *Rev. Port. Quim.* 31 (1989).
- [36] A. Klamt, COSMO-RS for aqueous solvation and interfaces, fluid phase equilib, 2015.
- [37] H. Ohno, K. Fukumoto, Amino acid ionic liquids, *Acc. Chem. Res.* 40 (2007) 1122–1129.