POTENTIAL OF THE BIOMOLECULES FOR GAS HYDRATE INHIBITION IN FLOW ASSURANCE: COSMO-RS BASED ESTIMATIONS

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ABSTRACT: The formation of gas hydrate causes a major flow assurance problem in petroleum industry. Conventional hydrate inhibitors such as, salts, Ionic liquids (ILs), polymers and amino acids are being used to overcome the issues. The usage of conventional hydrate inhibitors has certain limitations in term of low biodegradability and high operational cost. Biomolecules such as Pectin, Sodium-Carboxymethyl Cellulose (Na-CMC), Starch, Glycine and Dextran are some of the biodegradable polysaccharides that can be used as an alternative inhibitors. These biomolecules are complex long chain structures; therefore, before hydrate experiments, their fundamental properties are simulated by a software, Conductor-Like Screening Model for Real Solvents (COSMO-RS). Surface charge distribution, sigma potential, sigma profile and hydrogen-bonding energy of monomers with H_2O, methane (CH_4) and carbondioxide (CO_2) is estimated. By working as a pre-screening tool, the software predicted that Na-CMC and Dextran have higher electropositive distribution. While Starch, Pectin and Glycine shows an almost equal distribution of electropositive and electronegative charges on their surfaces. Pectin, Glycine, Na-CMC and Dextran shows strong hydrogen-bonding with H_2O molecules. Starch, on the other hands, shows less effective hydrogen-bonding activity with H_2O.

KEYWORDS: *Gas Hydrate; Biomolecules; COSMO-RS; Sigma Profile; Hydrogen Bonding Energy*

1.0 INTRODUCTION

Gas hydrates are solid crystalline inclusion compounds formed by some encaged small gas molecules (former) through the hydrogen-bonded H_2O network [1]. The gas former can be a small guest molecule consisting of methane, ethane and propane entrapped within H_2O molecules and form clathrate hydrate. Gas hydrates can form three types of structures identified as structure I, II, and H. Structure I hydrates are made up by small molecular weight gases consist of methane, ethane, carbon dioxide, etc. Structure II accommodates higher molecular weight gases such as propane, isobutene, etc., while Structure H holds natural gas hydrates [2].

The initiative of developing hydrate inhibitors was based on the salts, which are naturally present in the sea H_2O and inhibit the hydrate formations. The presence of salts in sea H_2O has shifted the phase equilibrium conditions to lesser temperature and more pressure. It led to many types of research to generate more efficient inhibitors to prevent flow assurance problem, including the introduction of methanol into the system that manages to reduce hydrate formation at a certain level [3]. Recently, ILs also catch research interest as a potential gas hydrate inhibitor because of their ionic properties that can form hydrogen-bonding (HB) with H_2O molecules [4].

However, the introduction of foreign chemicals into the system may lead to many environmental issues since more concern are being stressed into sustainable development. The use of methanol and ILs are less preferable for sustainable operations, especially in offshore production because of their storage in large amount. However, usage of polymers is also limited since any major incidents such as leakage or spillage of chemicals may lead to more pollution and interrupt the marine ecosystem. Degradable biomolecules are one of the solutions for hydrate mitigation where it may provide less toxicological and eco-toxicological effects to the environment [5-6]. Biomolecules have an advantage in terms of their ability to reproduce from natural products, which could reduce the excessive cost suffered by the major oil and gas companies to purchase hydrate inhibitors during exploration and extraction.

Biomolecules are polysaccharides, constructed with natural polymer units that are joined together to form large molecules. The molecules can be a long form of a polymer chain that contains a high number of hydroxyl groups and can make a network with H_2O via HB [7]. Therefore, these interactions of biomolecules with H_2O have shown high potential to mitigate the hydrate formation [8-9]. Lee et al. [10] determined the performance of cationic Starch to inhibit hydrates of gas mixtures. It was found that Starches can increase the induction time of methane hydrate by involving their parent chain hydroxyl groups in hydrogen bonding with H_2O molecules. Srungavarapu et al. [11] mentioned that during drilling operations, the formation of hydrate is hindered by using Xanthan gum and CMC. Xu et al. [12] suggested that Pectin with 75% biodegradability and 73% of cost reduction as compared to commercial kinetic inhibitors has important application in gas hydrate mitigation. Pectin is made up of α-D-galacturonic methyl ester acid (monomer), contributing a high amount of oxygen and hydrogen atoms in the structure. These polymers offer high capacity for capturing the H_2O molecules due to its huge size [13], and each monomer contains active groups that could form HBs with H_2O molecules [12, 14].

The presence of amino acid can disrupt the activity of the bulk H_2O and decrease the activity of hydrate crystallization via HB with H_2O molecules [15-16]. Studies have shown that based on basic chemical and physical properties amino acids are suitable to be used both as thermodynamic and kinetic inhibitors. Chemical properties of amino acids is related to the hydrophilic character of the species due to combination of carboxylic acid and amine groups, causing the high potential of interaction with H_2O, leading to less formation of hydrate cages [17]. Recent studies claim that like other kinetic inhibitors such as polymers, ionic liquids, Pectin, Starch, and antifreeze proteins [2-3, 5, 10, 12, 18-22] amino acids are also able to delay the hydrate nucleation and efficiently reduce hydrate growth.

However, the lengthy and tedious nature of gas hydrate kinetic experiments suggests the need for simulators, which can find unknown fundamental and potential properties of hydrate inhibitors in a short time. In this regard, Klamt [23] has introduced the COSMO-RS software. Based on quantum chemistry concept of density functional theory (DFT) in COSMO-RS the thermodynamic properties of any molecule can be determined. By manipulating the surface charge distribution (σ-surface, as the basis of all function) other properties such as sigma profile, sigma potential, HB, gas solubility and activity coefficient of the targeted molecules can be easily predicted [23].

Sulaimon and Tajuddin [24] proposed COSMO-RS based study for predicting hydrate inhibition potential of ILs and recommended that hydrogen bonding energy (E_{HB}) is the main energy that affects IL-H_2O interactions, resulting in changing the inhibition capability of ILs. Therefore, by increasing the anion E_{HB} inhibition ability is increased while by increasing the cation E_{HB} the inhibition ability is decreased [25].

To date, no COSMO-RS based study has been performed for predicting the fundamental properties of biomolecules that could provide an estimation about potential of biomolecules as gas hydrate inhibitor and facilitate hydrate experiments. Therefore, in this work, the fundamental properties (sigma surface, sigma profile/sigma potential and hydrogen bonding energy) of biomolecules such as Pectin, Na-CMC, Starch, Dextran and Glycine is simulated using COSMO-RS software.

2.0 METHODOLOGY

The main materials used in the present study are listed in Table 1. In this study, COSMOthermX, Version C2.1 is used for COSMO-RS predictions. The sigma charge distribution, chemical potential or sigma potential, HB and sigma profiles are generated and predicted by building monomer structure of biomolecules in the software. The structure of H_2O molecule is selected from the compound list with the parameter file BP_TZVP_C21_0111.ctd. Initially an input which is a molecular structure is imported in COSMO-RS then in a virtual conductor the charge density of a segment on respective molecule surface is calculated [26]. The E_{HB} was predicted by inducing a polarization charge density on the interface of the biopolymer and the conductor [27]. Sigma profile and the E_{HB} of biopolymers is determined using Equations (1) and (2).

$$ps(\sigma) = \frac{\sum_i x_i p^{x_i(\sigma)}}{\sum_i x_i} \quad (1)$$

The $ps(\sigma)$ of the solvent is defined as the mole fraction (x_i) weighted sum of the σ -profiles of its compounds x_i, p^{x_i} respectively, while E_{HB} is defined in the following equation [28-29]:

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

where, (σ_{donor} and $\sigma_{acceptor}$) are the function of the polarization charges of the two interacting segments, c_{HB} is the threshold for HB; a_{eff} is the active contact area between two surface segments.

Table 1: List of materials used for prediction in COSMO-RS software

Components name	Symbol
Water	H_2O
Methane	CH_4
Carbon dioxide	CO_2
Pectin	PC
Soidum-Carboxymethyl Cellulose	Na-CMC
Tapioca Starch	TS
Dextran	DX
Glycine	-

3.0 RESULTS AND DISCUSSION

3.1 Surface Charge Distribution (σ-Surface)

Figure 1 shows the overall surface charge distribution of biomolecule monomers and H_2O that is generated through a simulation from COSMO-RS. Results show that Na-CMC and Dextran have higher electropositive distribution as compared to electronegative distribution. This indicates that these molecules have a high tendency to work as a hydrogen bond donor during reaction with H_2O due to the presence of higher hydrogen groups as compared to the hydroxyl group on its chain. On the other hand, Pectin, Glycine and Starch shows an almost equal distribution of electropositive and electronegative charges on their surfaces due to a similar number of hydroxyl and hydrogen groups present on their chains. Therefore it can be concluded that to inhibit the hydrate formation the biomolecules can work both as HB donor and HB acceptor when reacting with H_2O. H_2O molecules exhibit a higher tendency to form hydrogen bonding via hydrogen donor mechanism due to a higher distribution of electropositive charges compared to electronegative charges.

The high distribution of electropositive charge is driven by the presence of two hydrogen atom in H_2O structure that are positively charged while only one oxygen atom presents the negative charge. The sigma surface of Pectin is subjugated by strong blue electropositive region and strong red electronegative region. The red region in Pectin shows the electronegativity of a carboxylic group and a hydroxyl group. While the sigma surface of Starch in Figure 1f is predominantly covered by green color showing its non-polarity. This non-polarity of

Starch shows its non-solvation with H_2O. Red color regions in sigma surface of all biomolecules indicate hydroxyl groups and their electronegativity, which is responsible for their strong interaction with the H_2O molecules, ensuing better hydrate inhibition.

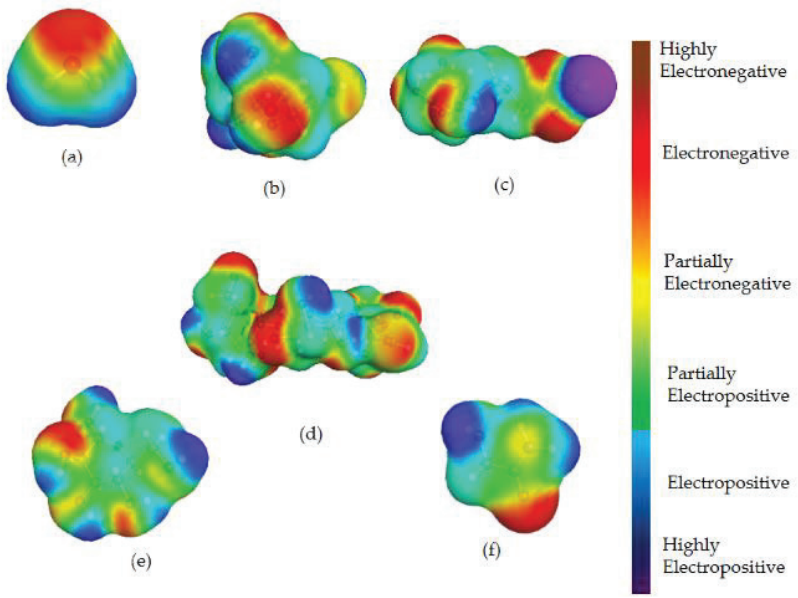

Figure 1: Charge distribution generated via COSMO-RS: (a) H_2O, (b) Pectin, (c) Na-CMC, (d) Dextran, (e) Starch and (f) Glycine

3.2 Sigma Profile (σ-Profile)

Sigma profile is the simplest way to represent and understand the electropositivity and electronegativity of compounds. Depending upon the molecular structure of conformers, every compound has its different sigma profile. The lowest energy conformers are used in this study.

Typically, a sigma profile is comprised of three regions: central non-polar region, a polar region with HB donor and polar with HB acceptor distribution. The peak length indicates the strength for every type of biomolecule in their regions which depends on the molecular distribution. H_2O mainly has a broad peak in hydrogen bond acceptor and donor region with very less peak in non-polar region (Figure 2). Reflecting on that, molecules having broad and similar length of sigma peaks like H_2O can effectually interact with H_2O via HB exchange. Glycine has the lowest peak distributions for polar hydrogen donor region followed by Starch, Pectin, Na-CMC, and Dextran in increasing order of peak distribution.

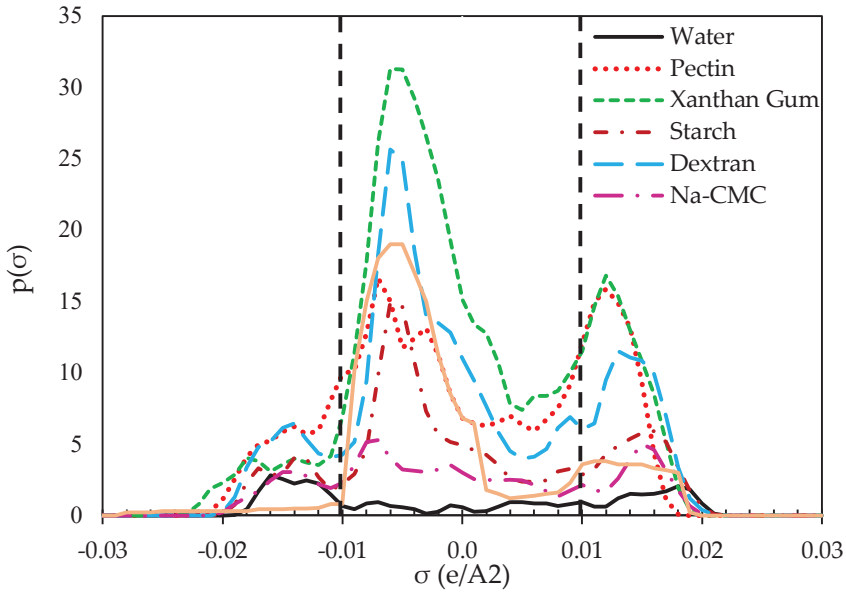

Figure 2: Sigma profile (σ-profile) of biomolecules and H_2O generated via COSMO-RS

Glycine also has the lowest peak distribution of polar hydrogen acceptor region, followed by Starch, Pectin, Na-CMC and Dextran in increasing order of peak distribution. For the non-polar region, Glycine has the lowest peak distribution as compared to Pectin, Starch, Na-CMC and Dextran with increasing order of peak distribution.

The broadness and peak length of chemicals is important to determine as it indicates the solvation level and miscibility of the biomolecules with H_2O. By using trapezoidal rule the total area underneath each sigma profile is calculated which quantitatively analyze the effect of biomolecules (Figure 3). Thus, monomers with a smaller area under the curve are most likely to miscible in H_2O due to the even charge distribution as required by H_2O. The area under the curve of methanol and H_2O is used for reference purposes where methanol is a well-known thermodynamic hydrate inhibitor. Glycine, Starch and Pectin are showing lower value for the area under the curves as compared to Dextran and Na-CMC.

Figure 3, shows that Glycine, Starch, and Pectin have a higher tendency to form hydrogen bonding with H_2O and can have almost similar performance to methanol in hydrate inhibition. CMC and Dextran also have the potential to inhibit the hydrate formation; however, it is expected that Glycine, Starch and Pectin can work better as compared to other biomolecules. However, as the sigma profile is concentration

independent, therefore, the effect of increasing biomolecule concentrations on the hydrate inhibition is still unclear.

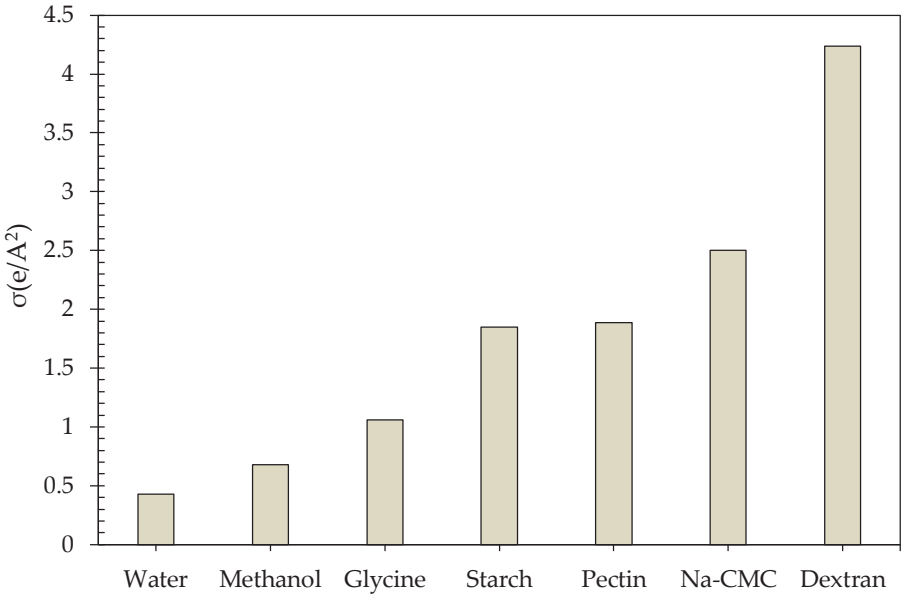

Figure 3: Sigma profile area under the curve for each additive

3.3 Hydrogen Bonding Energy (EHB)

The hydrogen-bonding energy of biomolecules is determined to predict their effect on the thermodynamic phase boundary of methane and carbon dioxide hydrate. Table 2 shows the predicted values of the hydrogen-bonding energy determined from the software. It is found that excessive E_{HB} is required for shifting the thermodynamic phase boundary toward lower temperature and higher pressure conditions so that the formation of gas hydrates can be prevented.

When comparing the E_{HB} of biomolecules with other prominent gas hydrate inhibitors like ionic liquids [24, 30], it is found that biomolecules owned less affinity to disturb water activity. Therefore possess less or no thermodynamic inhibition effect but due to their high viscosity they can delay hydrate growth and nucleation. The high viscosity of biomolecules limits the mass transfer which in results can delay the hydrate nucleation [31]. Among all studied biomolecules, Pectin and glycine showed maximum hydrogen bonding energies. However, previous studies supported that glycine is a potential THI [32] whereas, Pectin is a potential KHI [12].

Table 2: Hydrogen bonding energy of different concentrations of biomolecules in CH_4 and CO_2 system

Biomolecules	CH_4 Hydrogen bonding Energy		CO_2 Hydrogen bonding Energy	
	5wt%	10wt%	5wt%	10wt%
Pectin	-20	-19.78	-18.11	-18.17
Na-CMC	-18.5	-16.43	-17.52	-15.76
Starch	-15.5	-15.31	-13.29	-13.99
Dextran	-15.2	-15.0	-12.90	-12.00
Glycine	-22.7	-20.26	-18.42	-18.14

4.0 CONCLUSION

In this study, Pectin, Glycine and Starch shows better surface charge distribution and even polar arrangement between electropositive and electronegative charges on the surface. However, during the interaction with H_2O Dextran and Na-CMC, shows higher tendency to become hydrogen bond donors. Additionally, Glycine, Pectin and Starch reflects higher miscibility in H_2O due to lower peak area distribution from the sigma profile plots, followed by Dextran and Na-CMC. Additionally, Pectin, Glycine and Na-CMC can be good hydrate inhibitors because of their sufficient hydrogen-bonding energy. Starch and Dextran, on the other hands, shows weak hydrogen-bonding energy with H_2O molecules. Hydrogen bonding result reveals that at higher and lower concentrations, Pectin and Glycine can perform as potential gas hydrate inhibitor while, Na-CMC, Starch and Dextran need higher concentrations to have a similar performance as Pectin and Glycine.

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