

DFT-based inhibitor and promoter selection criteria for pentagonal dodecahedron methane hydrate cage

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Abstract. Density functional theory (DFT)-based simulations have been performed to provide electronic structure property correlation based reasoning for conceptualizing the effect of encapsulated methane molecule on the formation of methane hydrate cages, the role of methanol and ethylene glycol as inhibitor and the role of tetra-hydro-furan (THF) and cyclopentane as promoter of methane hydrate. Geometry optimization of 5^{12} cage, $5^{12}6^2$ cage and $5^{12}6^4$ cage with and without encapsulated methane and the cluster of 5^{12} cage with ethylene glycol, methanol, cyclopentane have been performed by density functional theory using ω B97X-D/6-31++G(d,p) method. Methane hydrate formation inhibition by methanol and ethylene glycol as well as methane hydrate stabilization by cyclopentane and tetrahydrofuran are critically analysed based on the interaction energy, free energy change, dipole moment and infrared frequency calculation. Calculation of free energy change for formation of methane hydrate with/without reagents at various temperature and pressure using optimized structure is reported here. It is observed that hydrogen bond between water molecules of clathrate 5^{12} cages become stronger in the presence of cyclopentane and tetrahydrofuran but weaker/broken in the presence of ethylene glycol and methanol. Simulated results correspond well with experimental findings and can be useful for designing new inhibitor and promoter molecules for gas hydrate formation.

Keywords. Interaction energy; red shift; methane hydrate; inhibitor; promoter.

1. Introduction

Methane hydrates are non-stoichiometric clathrate made of hydrogen bonded network of water molecules encapsulating methane gas as guest. These complex crystalline structures are stable at high pressure and low temperature.^{1–3} Prolific deposits of gas hydrates in marine sediments and below permafrost regions are considered as future energy source.^{3–5} Methane hydrates are also identified as the source for atmospheric methane gas in Mars.⁶ Methane hydrates are found to have three common hydrate unit structures (i.e., structure-I, structure-II and structure-H).^{7,8} Unit cell of structure-I consist of two pentagonal dodecahedron (5^{12}) cages and six hexagonal truncated trapezohedron ($5^{12}6^2$) cages. Structure-II unit cell has sixteen 5^{12} cages and eight $5^{12}6^4$ cages and structure-H unit cell has three 5^{12} cages, two $4^35^66^3$ cages, and one $5^{12}6^8$ cage. The gas hydrate has become an important research topic worldwide and lot of experimental and theoretical studies have been performed in last two decades.

Laboratory scale gas hydrates preparation,^{9–13} thermodynamic stability analysis and phase diagram study of clathrate hydrate,^{14–18} structural and physical properties of gas hydrate^{7,8,19} and study of cage occupancy by guest molecules in clathrate cages²⁰ have been performed by several researchers. Theoretical study of methane hydrate cage structure,²¹ vibration of methane molecule in clathrate cage,²² diffusion and absorption of different guest molecules in various clathrate cages²³ and molecular dynamics study of nucleation of methane hydrate^{24–26} have been reported in the literature.

Promoter molecules increase the gas hydrate formation rate as well as stability, and consequently help in the storage and transportation of natural gas using hydrate technology. The experimental studies on evaluating the role of different gas hydrate promoters like, micellar surfactant solutions with cyclopentane,²⁷ sodium dodecyl sulphate,²⁸ various alkanes, alkenes, alkynes, cycloalkanes or cycloalkene,^{29,30} tetra-*n*-butylammonium bromide,³¹ potato starch,³² tetra-*n*-butyl ammonium chloride,³³ mixture of sodium dodecyl sulphate and tetrahydrofuran³⁴ have been carried out by various researchers. On the other hand, formation of clathrate hydrate in oil pipeline is of great concern

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for petroleum industry as it plugs the oil flow.³⁵ Elimination of hydrate plug formation problem can be achieved either by adjusting gas hydrate phase equilibrium boundary by thermodynamic inhibitors^{36,37} or by lingering of gas hydrate nucleation using kinetic inhibitors^{36,38} and anti-agglomerates.³⁶ The role of methanol, ethylene glycol and NaCl as a thermodynamic inhibitor for gas hydrate formation has been studied by Lee *et al.*³⁹ Quantum chemical calculation based investigation using density functional theory (DFT), has been applied effectively to analyse the role of gas hydrate inhibitors. A theoretical study of hydrogen bond formation in different polyethylene glycol + water complex, dipropylene glycol + water complex^{40,41} and trimethylene glycol + water complex⁴² using Hatree–Fock (HF) method, second order Møller–Plesset perturbation theory (MP2) and DFT using 6-31++G(d,p) basis set have been performed. Density functional theory-based studies of methane hydrate pentagonal dodecahedron (5^{12}) cage in the presence of methanol and chitosan have been performed to elucidate the role as methane hydrate inhibitors (methanol and chitosan).^{43,44} There it has been revealed that the presence of methanol distorts the 5^{12} methane hydrate cage and the presence of chitosan reduce the strength of the hydrogen bonded water network of 5^{12} cage nearest to them. Detail theoretical study of inhibitors + clathrate cage configuration and promoter + clathrate cage configuration considering calculated free energy change of cluster formation in various temperatures and pressures, using *ab initio* method has not been performed so far. The objective of this work is to study the effect of ethylene glycol (EG), methanol, cyclopentane and tetra-hydro furan (THF) on pentagonal dodecahedron methane hydrate cage formation and stability in terms of free energy change, interaction energy, dipole moment, red shift and intensity of IR spectra values. Based on optimized structures, calculation of change in free energy for formation of methane hydrate with/without reagents at various temperature and pressure reported here is first of its kind. We propose selection criteria to identify methane hydrate cage inhibitor and promoters based on DFT calculation. This work would be helpful in understanding the electronic structure-property correlation based insight on inhibition effect by ethylene glycol and methanol, and stabilization performance by cyclopentane and tetra-hydro furan of methane hydrate.

2. Computational details

Geometry optimization and frequency calculation of 5^{12} , $5^{12}6^2$ and $5^{12}6^4$ hydrate cages with and without

encapsulated methane and the cluster of 5^{12} cage with ethylene glycol, methanol, cyclopentane and solvated in tetra-hydro furan have been performed by density functional theory^{45,46} using ω B97X-D/6-31++G(d,p) method. ω B97X-D⁴⁷ is long range corrected hybrid density functional having empirical atom–atom dispersion correction term. ω B97X-D functional has been chosen for simulating hydrate clathrate system here as it is better suited for describing non-bonded interaction. All the DFT calculations have been carried out by using Gaussian 09 software package.⁴⁸ Visualization of molecules have been carried out in Discovery Studio v3.1 of Accelrys Software Inc. Calculated vibrational frequency is scaled using scaling factor 0.975.⁴⁹

Interaction energy (ΔE) for cluster formation has been determined using equation (1),

$$\Delta E = E_{Cluster} - \sum E_{Components}, \quad (1)$$

where, $E_{Cluster}$ and $E_{Components}$ are optimized energy of cluster and individual components, respectively. Basis set superposition error (BSSE) correction to the interaction energy has not been carried out as it is computationally prohibitive for the large system size studied here. Moreover, BSSE is expected to be very less for calculation using extended basis set including diffuse and polarization function like 6-31G++(d,p). With larger basis set, the BSSE corrected and uncorrected values of structural parameters are generally found to be almost same. A cluster is more stable if its interaction energy is more negative compared to other clusters. Free energy at various temperature and pressure is calculated using ‘freqcheck’ utility of Gaussian 09. Free energy changes for cluster formation with and without the presence of inhibitor and promoter molecule are calculated using equation (2),

$$\Delta G = G_{Cluster} - \sum G_{Components}, \quad (2)$$

where, $G_{Cluster}$ and $G_{Components}$ are free energy of cluster and individual components, respectively.

3. Result and discussion

Optimized structures and contours of calculated free energy change (ΔG , kcal/mol) of formation of $1CH_4@5^{12}$, $1CH_4@5^{12}6^2$ and $1CH_4@5^{12}6^4$ methane hydrate cage with respect to various temperature and pressure using ω B97X-D/6-31++G(d,p) have been shown in figure 1. It is observed that at 298 K, $1CH_4@5^{12}$ (figure 1a), $1CH_4@5^{12}6^2$ (figure 1b) and $1CH_4@5^{12}6^4$ (figure 1c) hydrate cage formation are favourable i.e., showing negative free energy change values at ≥ 8 atm., ≥ 9 atm. and ≥ 20 atm. pressure,

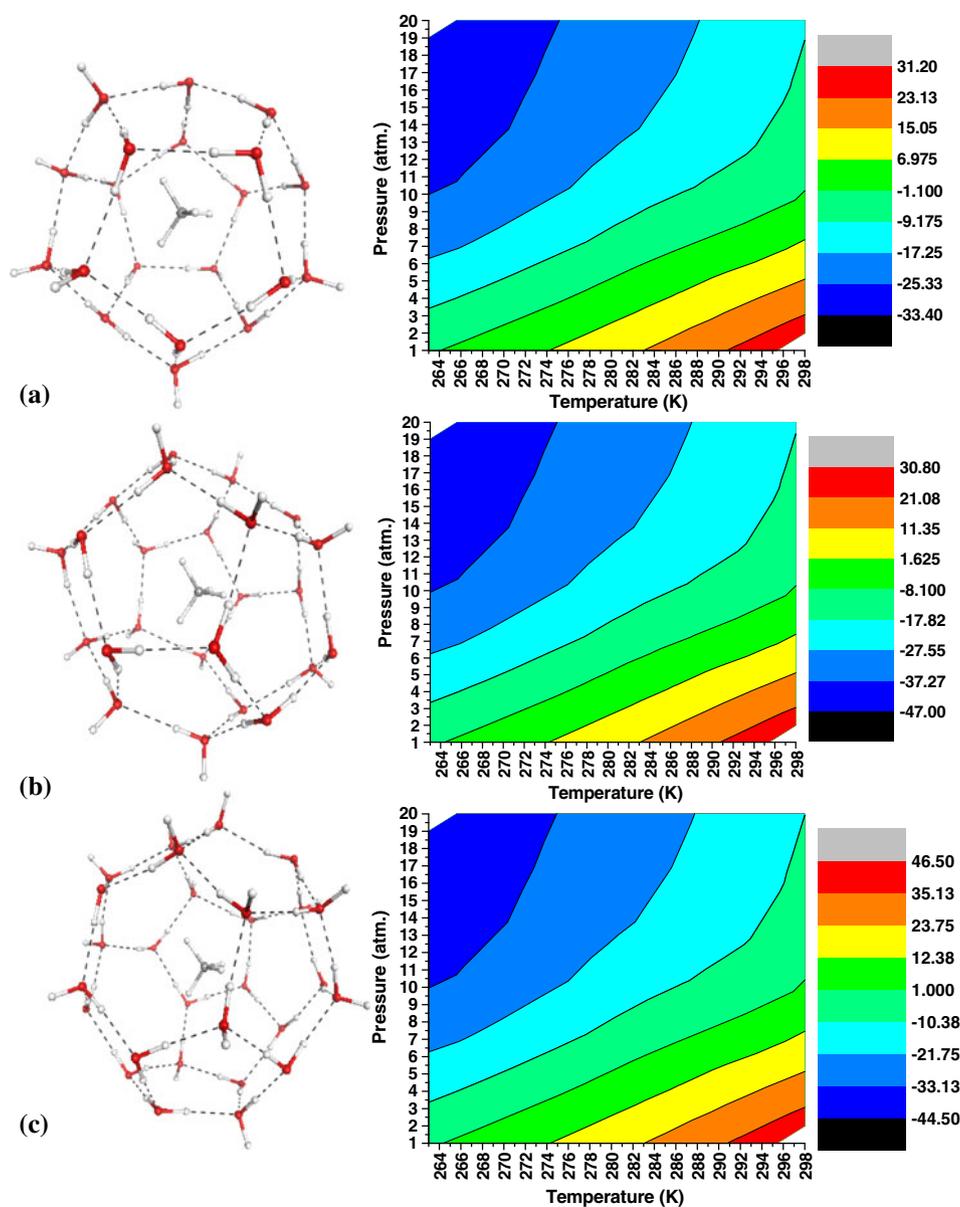


Figure 1. Optimized structures and contour of free energy change (ΔG , kcal/mol) of formation of (a) $1\text{CH}_4@5^{12}$ cage, (b) $1\text{CH}_4@5^{12}6^2$ cage and (c) $1\text{CH}_4@5^{12}6^4$ cage with respect to various temperature and pressure using $\omega\text{B97X-D/6-31++G}$ (d,p).

respectively. It is also observed that $1\text{CH}_4@5^{12}$ cage and $1\text{CH}_4@5^{12}6^2$ cage formations are favourable process at 265 K or lower temperature for one atmospheric pressure but the formation of $1\text{CH}_4@5^{12}6^4$ cage is only possible at 265 K for 3 atm. or higher pressure. The formation of $1\text{CH}_4@5^{12}$ and $1\text{CH}_4@5^{12}6^2$ hydrate cages are more favourable in comparison with $1\text{CH}_4@5^{12}6^4$ cage formation, therefore higher pressure is required to form $1\text{CH}_4@5^{12}6^4$ cage compared to form $1\text{CH}_4@5^{12}$ cage and $1\text{CH}_4@5^{12}6^2$ cage at same temperature.

Deformed $1\text{CH}_4@5^{12}$ cage structure in the presence of methanol and corresponding contours of calculated free energy change (ΔG , kcal/mol) at various

temperature and pressure using $\omega\text{B97X-D/6-31++G}$ (d,p) have been shown in figure 2a. At 298 K methanol found to hinder the formation of well built $1\text{CH}_4@5^{12}$ cage structure even at higher pressure (≥ 8 atm). It is also observed that $1\text{CH}_4@5^{12}$ cage structure is broken in the presence of methanol (figure 2a) even in the low temperature-high pressure region where well built $1\text{CH}_4@5^{12}$ cage formation is favourable without the presence of methanol as evident in figure 1a. Hydrogen bond formation between methanol and water molecules of $1\text{CH}_4@5^{12}$ cage and subsequent breaking of hydrogen bonded $1\text{CH}_4@5^{12}$ cage structure and negative free energy of formation of distorted $1\text{CH}_4@5^{12}$ cage

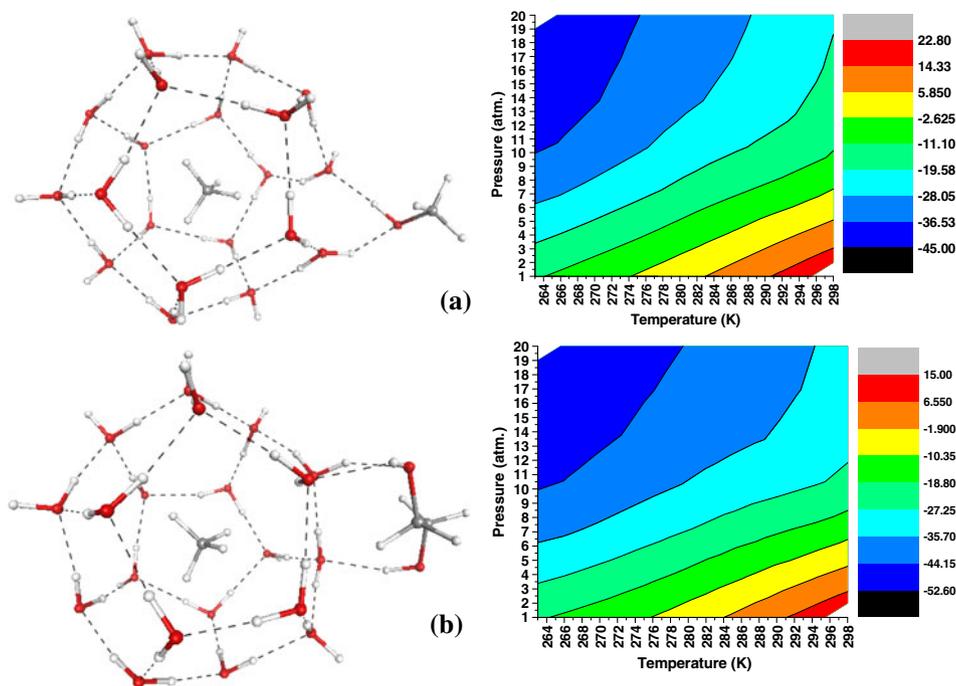


Figure 2. Optimized structures and contour of free energy change (ΔG , kcal/mol) of formation of (a) 1CH₄@5¹² cage + methanol, (b) 1CH₄@5¹² cage + EG with respect to various temperature and pressure using ω B97X-D/6-31++G (d,p).

structure at high pressure and low temperature strongly indicate methanol should be thermodynamic inhibitor. It has also been experimentally found that methanol is an effective gas hydrate inhibitor.^{36,40}

It is found that ethylene glycol form hydrogen bonded cluster with 1CH₄@5¹² cage and thereby weaken the original hydrogen bonded 1CH₄@5¹² cage structure (evident from IR red shift values in table 1).

Table 1. Calculated vibrational frequency (cm⁻¹), red shift (cm⁻¹), IR intensity (km-mol⁻¹) and experimental values (in cm⁻¹) of O–H bond stretching using ω B97X-D/6-31++G(d,p).

Systems	O–H stretching of water			O–H stretching of methanol			Exp. vibrational frequency
	Scaled freq. (cm ⁻¹)	Red shift (cm ⁻¹)	IR intensity (km-mol ⁻¹)	Scaled freq. (cm ⁻¹)	Red shift (cm ⁻¹)	IR intensity (km-mol ⁻¹)	
Water	3802		8.2				3756 (ref: ⁵⁰)
Water dimer	3587	215	344.4				3601 (ref: ⁵⁰)
1CH ₄ @5 ¹² cage	3550	252	1286.62				3300 (ref: ⁵¹)
1CH ₄ @5 ¹² 6 ² cage	3333	469	1144.27				
1CH ₄ @5 ¹² 6 ⁴ cage	3358	444	1377.24				
Methanol				3840		33.34	
1CH ₄ @5 ¹² cage in THF sol.	3443	359	1725.69				
1CH ₄ @5 ¹² cage in water sol.	3422	380	3522.03				
1CH ₄ @5 ¹² cage + methanol	3559	243	807.5	3587	253	3559	
1CH ₄ @5 ¹² cage + cyclopentane	3241	561	1151.34				
Systems	O–H stretching of water			O–H stretching of ethylene glycol			
	Scaled freq. (cm ⁻¹)	Red shift (cm ⁻¹)	IR intensity (km-mol ⁻¹)	Scaled freq. (cm ⁻¹)	Red shift (cm ⁻¹)	IR intensity (km-mol ⁻¹)	
EG				3829		51.04	
1CH ₄ @5 ¹² cage + EG	3595	207	696.91	3670	159	498.54	

This weakened $1\text{CH}_4@5^{12}$ cage structure in the presence of EG is also found to be stable at high pressure and low temperature region from free energy change diagram (figure 2b). These suggest that EG should act as an effective inhibitor for $1\text{CH}_4@5^{12}$ hydrate formation and the same has been observed experimentally.^{36,37,40} Optimized structures of $1\text{CH}_4@5^{12}$ cage solvated by THF taking polarizable continuum model using the integral equation formalism variant (IEFPCM) with $\omega\text{B97X-D/6-31++G(d,p)}$ and the contour of ΔG of formation at various temperature and pressure have been presented in figure 3a. THF solvation does not distort the $1\text{CH}_4@5^{12}$ cage structure and the formation of $1\text{CH}_4@5^{12}$ cage, solvated with THF, is more favourable than the formation of $1\text{CH}_4@5^{12}$ cage in vacuum as evident from ΔG values in figure 1a and figure 3a. ΔG values of the formation of $1\text{CH}_4@5^{12}$ cage in THF solution are found to be negative at all the pressure and temperature combinations studies (1–20 atm. and 263–298 K). These findings indicate the role of THF as methane hydrate promoter as supported by experimental and thermodynamic studies.³⁴

Optimized structure and contour of free energy change (ΔG , kcal/mol) of formation of $1\text{CH}_4@5^{12}$ cage in the presence cyclopentane at various temperature and pressure using $\omega\text{B97X-D/6-31++G(d,p)}$ are shown in figure 3b. It is observed that cyclopentane, unlike methanol/EG, does not disturb $1\text{CH}_4@5^{12}$ cage

structure and ΔG values of formation of unperturbed $1\text{CH}_4@5^{12}$ cage structure in the presence cyclopentane are found to be negative at high pressure and low temperature regions denoted by blue and sky blue colour in figure 3b. These outcome also suggest cyclopentane should be an effective promoter for gas hydrate formation and the same has been reported in literature.^{27,29}

Calculated interaction energies and dipole moments of $1\text{CH}_4@5^{12}$ cage, $1\text{CH}_4@5^{12}6^2$ cage, $1\text{CH}_4@5^{12}$ cage in THF solution, $1\text{CH}_4@5^{12}$ cage in water solution, $1\text{CH}_4@5^{12}$ cage + methanol, $1\text{CH}_4@5^{12}$ cage + cyclopentane and $1\text{CH}_4@5^{12}$ cage + EG using $\omega\text{B97X-D/6-31G++(d,p)}$ have been plotted in figure 4. The dipole moment value of $1\text{CH}_4@5^{12}6^2$ cage is found to be lesser than that of $1\text{CH}_4@5^{12}$ and $1\text{CH}_4@5^{12}6^4$ cages. This can be attributed to the more symmetrical structure of $1\text{CH}_4@5^{12}6^2$ cage compared to other two methane hydrate cages. It has been found that CH_4 molecule remains closed to one side of the optimized $1\text{CH}_4@5^{12}6^2$ cage with minimum $\text{O}-\text{H}_\text{M}$ (H_M being H of CH_4) distance of 2.83 Å, where as $1\text{CH}_4@5^{12}$ and $1\text{CH}_4@5^{12}6^4$ cages are found to be optimized with CH_4 molecule at the centre, with minimum $\text{O}-\text{H}_\text{M}$ distance of 3.63 Å and 3.76 Å, respectively. Consequently attractive van-der Waals interaction is more in $1\text{CH}_4@5^{12}6^2$ cage compared to $1\text{CH}_4@5^{12}$ and $1\text{CH}_4@5^{12}6^4$ cages. Thus, the interaction energy value of $1\text{CH}_4@5^{12}6^2$ cage is also found to be more negative in comparison

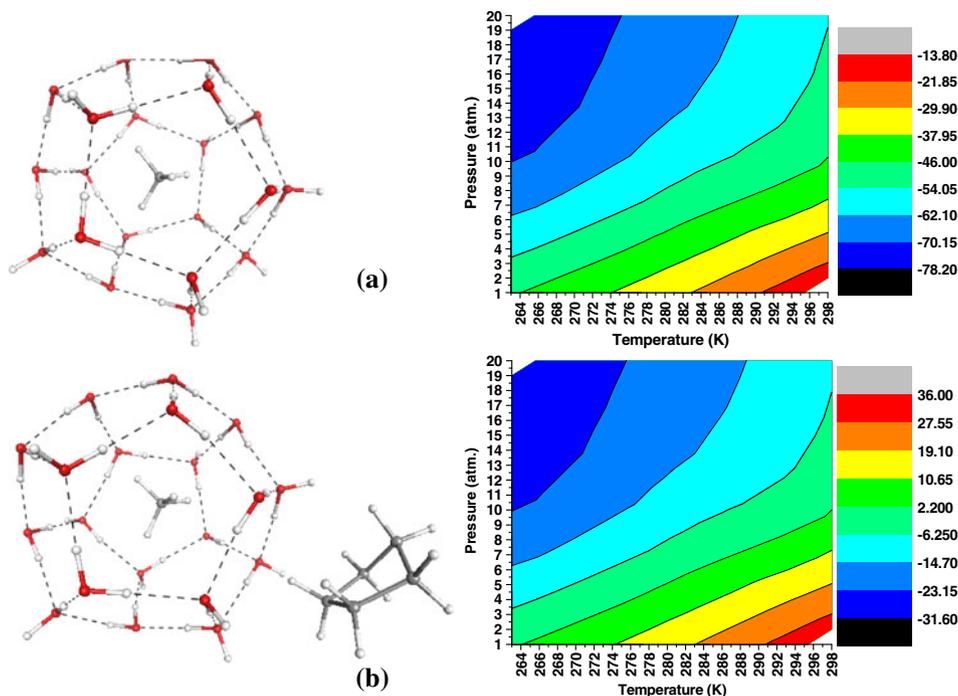


Figure 3. Optimized structures and contour of free energy change (ΔG , kcal/mol) of formation of (a) $1\text{CH}_4@5^{12}$ cage solvated by THF and (b) $1\text{CH}_4@5^{12}$ cage + Cyclopentane with respect to various temperature and pressure using $\omega\text{B97X-D/6-31++G(d,p)}$.

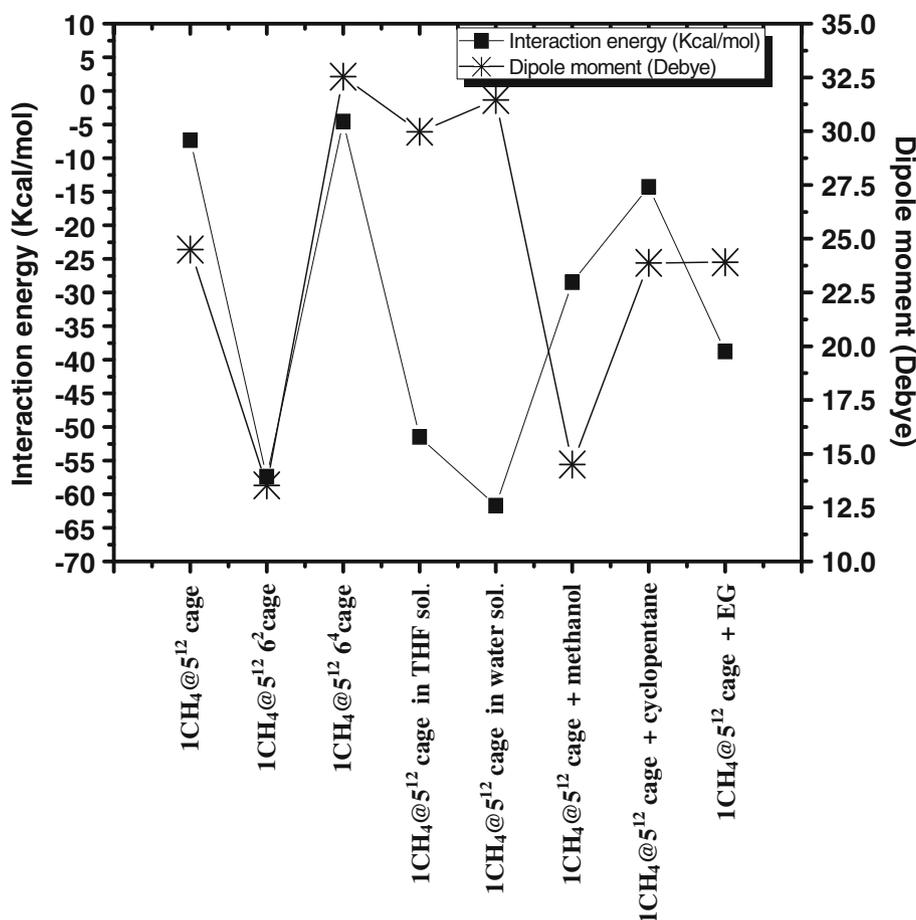


Figure 4. Plots of calculated interaction energy and dipole moments of different complexes using ω B97X-D/6-31G++(d,p).

with that of 1CH₄@5¹² cage and 1CH₄@5¹²6⁴ cage. It implies that 1CH₄@5¹²6² cage is more stable compared to 1CH₄@5¹² and 1CH₄@5¹²6⁴ cages. Presence of THF solution increases stability of 1CH₄@5¹² cage as the interaction energy for 1CH₄@5¹² cage formation in THF solution is found to be more negative compared to 1CH₄@5¹² cage formation in vacuum. As the dipole moment value of 1CH₄@5¹² cage is also found to be increased in THF solution, the directionality and consequently strength of hydrogen bonds of 1CH₄@5¹² cage structure increase in THF solution. In the presence of cyclopentane, the 1CH₄@5¹² cage structure remain intact and the interaction energy of 1CH₄@5¹² cage formation (in the presence of cyclopentane) is found to be more negative compared 1CH₄@5¹² cage formation in vacuum. Thus it can be further inferred from the interaction energy and dipole moment that THF and cyclopentane are effective promoters for methane hydrate. 1CH₄@5¹² cage also become stable and have stronger hydrogen bonded network in water solution as evident in figure 4. The negative interaction energy value of the distorted 1CH₄@5¹² cage and

methanol cluster ensures the feasibility of distortion of 1CH₄@5¹² cage in the presence of methanol. The presence of methanol also lowers the dipole moment of 1CH₄@5¹² cage structure and consequently reduces the strength of hydrogen bonded network of 1CH₄@5¹² cage. The interaction energy of hydrogen bonded cluster of 1CH₄@5¹² cage and ethylene glycol is found to be negative but the presence of ethylene glycol does not alter the dipole moment value of 1CH₄@5¹² cage in vacuum. These results suggest that methanol would be much more effective methane hydrate inhibitor compared to ethylene glycol.

Calculated vibrational frequencies (infra red) of O–H stretching in water, methanol, water dimer, 1CH₄@5¹² cage, 1CH₄@5¹²6² cage, 1CH₄@5¹²6⁴ cage, 1CH₄@5¹² cage in THF solution, 1CH₄@5¹² cage in water solution, 1CH₄@5¹² + methanol and 1CH₄@5¹² cage + EG clusters are summarized along with some experimental values in table 1. The calculated scaled vibrational frequency values of O–H stretching of water molecule, water dimer and 1CH₄@5¹² cage corresponds well with experimental values.^{50,52} The red shifts of O–H

vibrational frequency are the result of hyper-conjugation interaction for conventional hydrogen bond formation and higher red shift values indicate stronger hydrogen bonding tendency. The calculated red shift of O–H stretching of water molecule for different methane hydrate cages are of following order: water dimer < $1\text{CH}_4@5^{12}$ cage < $1\text{CH}_4@5^{12}6^2$ cage < $1\text{CH}_4@5^{12}6^4$ cage, as the increasing number of water molecules in a cluster increases hydrogen bond cooperativity effect. It is observed that the red shifts of O–H stretching of water molecule in $1\text{CH}_4@5^{12}$ cage in THF solution, $1\text{CH}_4@5^{12}$ cage in water solution, $1\text{CH}_4@5^{12}$ cage + cyclopentane cluster are higher than that of $1\text{CH}_4@5^{12}$ cage. It is also found that the red shifts of O–H stretching of water molecule in $1\text{CH}_4@5^{12}$ cage + methanol and $1\text{CH}_4@5^{12}$ cage + EG clusters are less than that of $1\text{CH}_4@5^{12}$ cage. Calculated IR intensities of O–H stretching of water molecule are in order of $1\text{CH}_4@5^{12}$ cage + EG ($696.91\text{ km}\cdot\text{mol}^{-1}$) < $1\text{CH}_4@5^{12}$ cage + methanol cluster ($807.5\text{ km}\cdot\text{mol}^{-1}$) < $1\text{CH}_4@5^{12}$ cage ($1286.6\text{ km}\cdot\text{mol}^{-1}$) < $1\text{CH}_4@5^{12}$ cage in THF sol ($1725.69\text{ km}\cdot\text{mol}^{-1}$) < $1\text{CH}_4@5^{12}$ cage in water sol ($3522.03\text{ km}\cdot\text{mol}^{-1}$) as evident in table 1. The rise in IR intensity of O–H stretching of water molecule in $1\text{CH}_4@5^{12}$ cage in THF and water solution can be for the increased ionic character of O–H normal mode according to the view point of the proposition of Barrow.⁵¹ Calculated higher red shift and intensity of O–H stretching of water molecule of $1\text{CH}_4@5^{12}$ hydrate cage in the presence of THF and cyclopentane indicate higher tendency of hydrogen bonded $1\text{CH}_4@5^{12}$ hydrate cage formation. On the contrary, lower values of calculated red shift and intensity of O–H stretching of water molecule of $1\text{CH}_4@5^{12}$ hydrate cage in the presence of methanol and EG demonstrate lower tendency of hydrogen bonded $1\text{CH}_4@5^{12}$ hydrate cage formation. These findings also further illustrate the roles of methanol and ethylene glycol as inhibitor, THF and cyclopentane as promoter for methane hydrate formation.

4. Conclusions

Density functional theory-based calculation using $\omega\text{B97X-D/6-31++G}$ (d,p) have been performed to explain the effect of encapsulated methane molecule on the formation of methane hydrate cages, the role of methanol and ethylene glycol as inhibitor and the role of tetra-hydro-furan (THF) and cyclopentane as promoter for methane hydrate formation. Methane molecule provide better stability for 5^{12} cage and $5^{12}6^2$ cage in comparison with $5^{12}6^4$ cage therefore higher

pressure is required to form $1\text{CH}_4@5^{12}6^4$ cage compared to $1\text{CH}_4@5^{12}$ cage and $1\text{CH}_4@5^{12}6^2$ cage at same temperature. The distortion of $1\text{CH}_4@5^{12}$ cage structure in the presence of methanol and the weakening of $1\text{CH}_4@5^{12}$ cage structure in the presence of ethylene glycol have been favourable according to calculated ΔG contour, dipole moment and interaction energy values. The formation of $1\text{CH}_4@5^{12}$ cage is found to be more favourable in THF solution compared to the formation of $1\text{CH}_4@5^{12}$ cage in vacuum as per calculated ΔG values. IR red shift values and intensities have been identified as important parameters for understanding the reason behind the role methanol and ethylene glycol as inhibitor and the role of tetra-hydro-furan (THF) and cyclopentane as promoter of methane hydrate. This study clearly demonstrates the structure-property correlation for methane hydrate formation in the presence of promoter and inhibitor molecules and the same can be used for designing better promoter and inhibitor molecules.

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