

# **Density Functional Theory Based Investigation of 1-Butyl-3-Methylidazolium as a Potential Methane Hydrate Inhibitor**

A Thesis Submitted In Partial Fulfilment of the Requirements for the Degree Of

**Bachelor of Technology**

**In**

**Metallurgical & Materials Engineering**

**By**

**Satyam Choudhury**

**Roll No – 111MM0094**

**Under the supervision of**

**Dr. S. Pal**



**Department of Metallurgical and Materials Engineering**

**National Institute of Technology, Rourkela**

## National Institute of Technology, Rourkela



### CERTIFICATE

This is to certify that the job in this thesis report entitled “DENSITY FUNCTIONAL THEORY BASED INVESTIGATION OF 1-BUTYL-3-METHYLIDAZOLIUM AS A POTENTIAL METHANE HYDRATE INHIBITOR” which is being submitted by **Mr Satyam Choudhury**(Roll no: 111MM0094) of Bachelor of Technology, National Institute of Technology, Rourkela has been carried out under my guidance and supervision in partial fulfilment of the requirements for the degree of Bachelor of Technology (Res.) in Metallurgical and Material Engineering and is bonafide record of work.

To the best of my knowledge, the subject embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

**Dr. S. Pal**

Dept. of Metallurgical and Material  
Engineering. NIT, Raurkela.  
Rourkela - 769008

Date

## **ACKNOWLEDGEMENT**

With very deep regards and respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to Dr S. Pal, Assistant Professor, Department of Metallurgical and Materials Engineering for introducing the present research topic and for his inspiring guidance, valuable suggestion and constructive criticism throughout in this project work. It would have impossible for me to bring out this thesis without his help and constant support.

I am highly thankful to all staff members of Department of Metallurgical and Materials Engineering, NIT Rourkela, for their help during the execution of experiments and also thank to my well-wishers and friends for their kind support.

**SATYAM CHOUDHURY**

**111MM0094**

## **Density functional theory based investigation of 1-butyl-3-methylidazolium as a potential methane hydrate inhibitor.**

### **ABSTRACT**

Basically methane hydrate is solid crystal same as ice in which methane are trapped inside the cages of H-bonded water molecules. Low temperature and high pressure conditions are good for methane hydrates formation. Such type of condition prevails in gas or oil pipelines. The formation of these stable methane hydrates inside transmission pipelines and gas and oil production can lead to huge economic losses as blockage as well as rupture of pipeline may occur. Due to this problem the gas and oil industry triggers the research for preventing hydrates and its mitigation and this also benefits the recovery of methane from natural hydrates. Therefore in-order to minimize the loss we inhibits the growth of methane hydrate molecule by adding 1-butyl-3-methylidazolium which acts as potential inhibitor for methane hydrate molecule. In this paper we carried out few first principal based tests to show how 1-butyl-3-methylidazolium acts as inhibitor for methane hydrate ( $1\text{CH}_4@5^{12}$ ).

## CONTENT

1) CERTIFICATE.....	2
2) ACKNOWLEDGEMENT.....	3
3) ABSTRACT.....	4
4) INTRODUCTION.....	6- 12
4.1) INHIBITION OF GAS HYDRATE FORMATION	
4.2) GAS HYDRATE INHIBITORS	
4.3) THERMODYNAMIC INHIBITORS	
4.4) KINETIC INHIBITORS	
4.5) QUANTUM CHEMICAL STUDY OF INTERACTION OF WATER MOLECULE WITH GAS HYDRATE INHIBITOR MOLECULES	
5) THEORITICAL BACKGROUD .....	13- 18
5.1) THEORY OF QUANTUM CHEMICAL CALCULATIONS	
5.2) DENSITY FUNCTIONAL THEORY (DFT)	
5.3) $\omega$ B97X-D FUNCTIONAL	
5.4) BASIS SETS	
5.5) FRONTIER ORBITALS AND CHEMICAL PROPERTIES OF ATOMS	
5.6) HYDROGEN BOND	
5.7) COMPUTATIONAL METHODS	
6) RESULT AND DISCUSSION .....	19-23
6.1) PENTAGONAL DODECAHEDRON METHANE HYDRATE CAGE (1 CH <sub>4</sub> @5 <sup>12</sup> )	
6.2) HOMO AND LUMO STURCTURE OF METHANE HYDRATE AND 1-BUTYL-3- METHYLIDAZOLIUM COMPOUND.	
6.3) TWO DIMENSIONAL STRUCTURES OF HOMO AND LUMO	
6.4) MULLIKAN CHARGE DISTRIBUTION BETWEEN INHIBITOR MOLECULE AND PENTAGONAL DODECAHEDRON METAHNE HYDRATE CAGE (1 CH <sub>4</sub> @5 <sup>12</sup> )	
7. CONCLUSION .....	25
8. REFERENCES .....	26-29

## **4. INTRODUCTION**

Basically methane hydrate is solid crystal same as ice in which methane are trapped inside the cages of H-bonded water molecules. Low temperature and high pressure conditions favours the stability of methane hydrates under such condition the formation of these stable methane hydrates inside transmission pipelines and gas and oil production can lead to huge economic losses blockage or rupture of pipeline may occurs. Due to this problem the gas industry triggers the research for preventing hydrates & its mitigation and this also benefits the recovery of methane from natural hydrates.

At present four methods can be used to mitigate the hydrate formation. Under many situations the hydrate inhibition by adding inhibitors is the only effective choice. In order to delay the formation of hydrate the inhibitors gets attracted to water or hydrates which as a result can prevent the formation of H-bonded water cage. Hydrated inhibition aims at thermodynamics inhibitors for example – methanol, sodium chloride & ethylene glycol & kinetic inhibitors like Luvicap (40 wt% PVCap in EG), Poly (N-vinylpyrrolidone) (PVP), poly(N-vinylcaprolactam) (PVCap). These inhibitors forms hydrogen bond with water or have strong electrostatic charges.

### **4.1. INHIBITION OF GAS HYDRATE FORMATION**

Development of snow like gas hydrate and their subsequent agglomeration to form plugs can lead to obstructing of oil and gas pipelines (Hammerschmidt, 1934). Oil and gas industry perspectives hydrates as irritation as it hinder flow confirmation as well as badly affect oil and gas production establishments, operation and upkeep. Along these lines aversion of gas hydrate arrangement is essential. As indicated by thermodynamic and chemical perspective

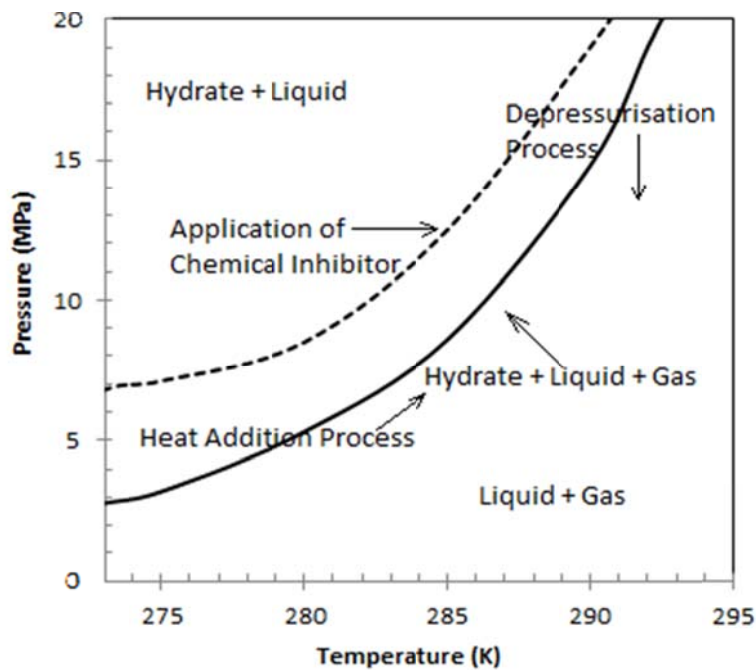
petroleum industries use following steps to inhibit gas hydrate formation (Englezos, 1993) as represented in Fig. 1.1.

Dehydration of natural gas

Heating the gas over the hydrate balance temperature at the operating pressure

Depressurization underneath the balance pressure at the working temperature

Application of chemical inhibitors



(Pal, 2013)

Fig. 1.1 Phase outline of gas hydrates indicating gas hydrate disintegration

In the event that the temperature increments for a given pressure such that it crosses hydrate + liquid and liquid + gas phase boundary, the gas hydrate get to be unstable and change to water and gas mixture as demonstrated in Fig. 1.1. Thus, for a given temperature the gas hydrate is not steady for pressure below hydrate + liquid and liquid + gas phase limit. The gas hydrate rich area can be diminished or reduced by utilization of a few gas hydrate inhibitors.

## **4.2. GAS HYDRATE INHIBITORS**

Gas hydrate inhibitors work either by inhibiting gas hydrate development thermodynamically unfavourable or by averting/ postponing the nucleation of gas hydrate and agglomeration of gas hydrate cores (nuclei). Likewise, they are classified as thermodynamic inhibitor and low dose kinetic inhibitor. Usually utilized chemical inhibitors, for example, methanol, ethylene glycol and triethylene glycol are thermodynamic inhibitors as their vicinity limits down the gas hydrate stability locale, with the goal that gas hydrate can't form in the working pressure and temperature condition. Thermodynamic inhibitors are needed in high concentration (up to 50 wt %) which are expensive reagents. Methanol, basically utilized thermodynamic inhibitor, is not ecologically benevolent. Low measurements hydrate inhibitors are of two sorts to be specific kinetic inhibitors and anti-agglomerates. Kinetic inhibitors impede the gas hydrate arrangement and against anti-agglomerates avoid aggregation of small gas hydrate nuclei. Non-poisonous water solvent polymers with small cyclic amide groups, for example, pyrrolidone and caprolactam as the dynamic units are motor gas hydrates inhibitors (Storr et al., 2004; Koh et al., 2002). Anti-agglomerates are by and large surfactants in which the polar head is pulled in to the hydrate and the hydrophobic tail is scattered in the liquid hydrocarbon phase.

## **4.3. THERMODYNAMIC INHIBITORS**

Thermodynamic inhibitors adjust the hydrate phase boundary limit in such a path, to the point that the hydrate development temperature gets to be lower and the hydrate arrangement pressure gets to be higher by changing the thermodynamic properties of the framework (Igboanusi et al., 2011) as demonstrated in Fig. 1.1.



Addition of thermodynamic inhibitors makes liquid water more stable than hydrate water as inhibitor particles mixed(dissolve) down in the free water phase and thereby lessening the chemical potential/fugacity of aqueous water (Parmar, 2009; Koh et al., 2002; Igboanusi et al., 2011). Lee et al. (2011) evaluated the phase equilibria of natural gas hydrates in the vicinity of methanol, ethylene glycol, and NaCl aqueous solution. Masoudi et al. (2010) have created thermodynamic model to get better comprehension of gas hydrate inhibitor, impacts of combination of salts (e.g., NaCl, KCl, CaCl<sub>2</sub>) and organic inhibitors (e.g., mono ethylene glycol and methanol) utilized for gas hydrate inhibition process in gas and oil industry. Thermodynamic inhibitors can shape intermolecular bonds with water thus confining the water atoms from building hydrogen bonded system among themselves (Lugo et al., 2010). The depression in solidifying temperature ( $\Delta T$ ) because of thermodynamic inhibitors can be evaluated utilizing Hammerschmidt mathematical statement as given underneath (Fink, 2012; Hammerschmidt, 1934).

Where 
$$\Delta T = K \frac{I}{100 - I} \quad (1.1)$$

Clath rate hydrate development temperature wretchedness in vicinity of inhibitors can likewise be figured by Pieroen mathematical statement (Wu, 2007), i.e.

$$\Delta T = \frac{nRT_0^2}{\Delta H} X \quad (1.2)$$

Where  $X$ ,  $T_0$ ,  $\Delta H$  and  $R$  are the mole portion of weaken non-electrolyte arrangement, the gas hydrate development temperature without inhibitors (K), the warmth of arrangement (J/mole) of one mole hydrate from n mole water at  $T_0$  and universal gas constant (1.987 cal/mol/K) respectively. Equation (1.1) is appropriate for tried inhibitors though mathematical statement (1.2) is relevant for non-electrolyte inhibitors just. A comparison got from thermodynamic

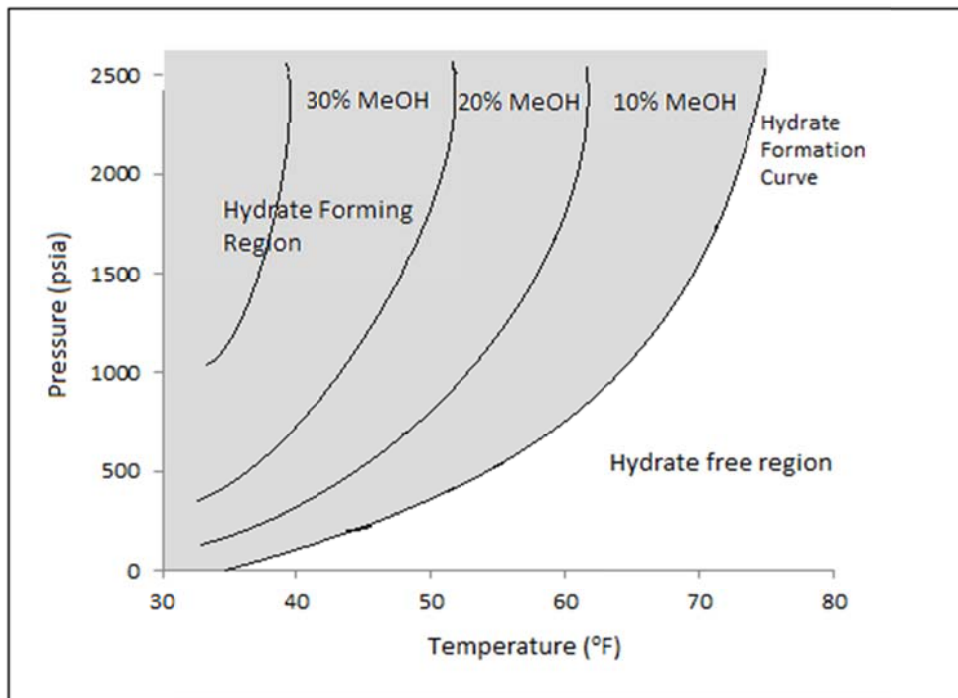
displaying, appropriate for all inhibitors, is (Wu, 2007):

$$\Delta T = \frac{n\lambda'}{\lambda''} \left( \frac{T_0'}{T_0''} \right)^2 \Delta T' \quad (1.3)$$

Where,  $T_0'$ ,  $\lambda'$ ,  $\lambda''$ ,  $T_0''$  and  $\Delta T'$  are freezing point of pure water (K), latent heat of pure water solidification (Kcal/Kg), latent heat of pure inhibitor solidification (Kcal/Kg), freezing point of inhibitor (K) and lowering of freezing point of inhibitor (K) respectively.

Methanol, broadly utilized thermodynamic inhibitor, brings down the activity of the water and shifts the equilibrium lines for hydrate development to lower temperatures (Gordienko, 2009; Sloan et al., 2011). Lower surface tension and viscosity of methanol make it appropriate for the application contrasted with other solvents (McIntyre et al., 2004). The hydrate forming zone or hydrate stability zone diminished dynamically as methanol substance increments as indicated in Fig. 1.2 (Sloan et al., 2011). Methanol has a few disadvantages as it has high vapour pressure (bringing about possibly high losses) which is flammable and poisonous (McIntyre et al., 2004). Bullin et al. (2004) have proposed ideal

utilization of methanol for hydrate hindrance in a gas gathering system.



**Fig-1.2** - Hydrate arrangement weights and temperatures (dark district) as a component of methanol focus in free water for a given gas mixture (Sloan et al., 2011).

#### 4.4. KINETIC INHIBITORS

Hydrate formation takes place in two stages, for example, development of stable nuclei (nucleation) and growth of cores (nuclei). Kinetic inhibitors hinder and inhibit nucleation of gas hydrate crystal (Fink, 2012; River et al., 2011). Nucleation hindrance and development restraint mechanisms by kinetic inhibitors have been resolved utilizing ultrasonic by Yang et al. (2011). Nucleation inhibitors like polyethylene oxide expands the gas hydrate nucleation induction time and check the memory impact (Kannan et al., 2009). Precious stone development inhibitor like alkylated ammonium, phosphonium, or sulfonium mixes confine further development of gas hydrate gems after nucleation (Klomp, 2005).

#### 4.5. QUANTUM CHEMICAL STUDY OF INTERACTION OF WATER MOLECULE WITH GAS HYDRATE INHIBITOR MOLECULES

Ab initio computing is a standout method amongst the most vital approaches to acquire criteria of stability. Geometry enhancement, vibrational frequencies, characteristic bond orbital, atom in molecule (AIM), and diminished vibrational space disintegration investigation have been performed to study water-methanol conformers utilizing Ab initio simulation by Bakkas et al. (1993). It is found by them that both CH<sub>3</sub>OH... OH<sub>2</sub> and CH<sub>3</sub>HO... HOH structures have practically same stability and computed (utilizing MP2/6-311++G (d, p)) vibrational frequencies compare well with trial results. Conformational and numerous body investigation of ethylene glycol – (water)<sub>n</sub> (n = 1 – 3) mind boggling using B3LYP/6-311++G\* have been performed by Chaudhary et al. (2004) and cyclic structures with water particles crossing over between two hydroxyl mixture of ethylene glycol is discovered to be the most stable conformer. The impact of the hydrogen bond development on the atomic attractive reverberation concoction shifts (isotropic and anisotropic) for all of methanol-water cluster utilizing HF, MP2 and thickness useful (B3LYP) theory with 6-311++G(2d,2p) premise set has been accounted for by Fileti et al. (2005).

Structure streamlining, tying energies, vibrational spectra, and electron thickness topological highlights of methanol (M) - water (W) edifices (M<sub>m</sub>W<sub>n</sub>, where  $m + n \leq 4$ ,  $m = 0 - 4$  and  $n = 0 - 4$ ) have been figured utilizing HF, MP2 and thickness useful (B3LYP) theory utilizing 6-31+G (d) and 6-311++G (d, p) by Mandal et al. (2010). Ab initio and thickness practical theory based estimations has been connected to study the structure, security, and vibrational spectra of different ethylene glycol (EG)<sub>m</sub> and ethylene glycol + water (EG<sub>m</sub>W<sub>n</sub>) ( $m = 1 - 3$ ,  $n = 1 - 4$ ) groups by Kumar et al. (2012).

## **5. THEORITICAL BACKGROUND**

### **5.1. THEORY OF QUANTUM CHEMICAL CALCULATIONS**

The primary targets of quantum chemical computation are to portray the structure and elements of numerous electron systems regarding wave function characterized over the configuration of particles using Schrödinger mathematical statement. In quantum chemical simulation molecules, clusters or condense phases are considered as accumulations of nuclei and electrons, with no reference of chemical bonds. Quantum chemical estimation strategies vary in their characteristics assumptions, range of applicability in terms of their ability, exactness, dependability and related computational expense.

### **5.2. DENSITY FUNCTIONAL THEORY (DFT)**

Density Functional Theory (Kohn et al., 1965) is the most prominent and flexible techniques utilized as a part of computational physics and computational chemistry since 1990s, when the estimates utilized as a part of the theory were enormously refined to model the exchange and correlation interactions precisely. In DFT technique, the energy of a molecule is found by working a functional on the electron likelihood density capacity (quantifiable physical amount). Electron density is a component of position just and depends just on three spatial variables however wave function of a N electron particle is an element of  $4N$  variables (3 spatial and 1 twist for every electron). This makes DFT profitable over Hartree-Fock method as DFT based count require less computational time. DFT based results agree well with experimental values contrasted with Hartree-Fock technique (Engel et al., 2011) as it considers electron pair-correlation effect.

DFT is taking into account two hypotheses proposed by Kohn and Hohenberg. Their first hypothesis expresses that the properties at ground state are a functional of the electron density at ground state. The second hypothesis is an analogous to the variation hypothesis. It expresses that the true ground state energy is always lower than or equivalent to energy given by the trial electron density function. Taking these two hypotheses Kohn-Sham concocted a way to deal with discover an expression for energy in terms of electron density. Consequently as indicated by the Kohn-Sham formalism, the ground-state electronic energy ( $E$ ) is represented as a sum of the kinetic energy ( $E_T$ ), the electron-nuclear attraction energy ( $E_V$ ), the electron-electron repulsion energy ( $E_J$ ), and the exchange/correlation energy ( $E_{xc}$ ).

$$E = E_T + E_V + E_J + E_{xc} \quad (1)$$

They recommended that the aggregate of electron active vitality, potential vitality of electron made out of repugnance in the middle of electrons and fascination in the middle of electron and the core (termed as outside potential) is a function of ground state electron density.

In DFT formalism, other than  $E_T$ , all segments of ground-state electronic vitality terms in the above mathematical statement rely on upon the aggregate electron density ( $\rho$ )

$$\rho(r) = 2 \sum_i^{\text{orbitals}} |\psi_i(r)|^2 \quad (2)$$

Where,  $\psi_i$  are termed as Kohn-Sham orbitals and the summation is carried out over pairs of electrons. The energy components within a finite basis set can be expressed as,

$$E_T = \sum_{\mu}^{\text{basis functions}} \sum_{\nu} \int \phi_{\mu}(r) \left[ -\frac{1}{2} \nabla^2 \right] \phi_{\nu}(r) dr \quad (3)$$

$$E_V = \sum_{\mu}^{\text{basis functions}} \sum_{\nu} P_{\mu\nu} \sum_A^{\text{nuclei}} \int \phi_{\mu}(r) \left| \frac{Z_A}{|r - R_A|} \right| \phi_{\nu}(r) dr \quad (4)$$

$$E_J = \frac{1}{2} \sum_{\mu}^{\text{basis}} \sum_{\nu}^{\text{functions}} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \quad (5)$$

$$E_{XC} = \int f(\rho(r), \nabla\rho(r), \dots) dr \quad (6)$$

In the above equations,  $Z$  is the nuclear charge,  $R - r$  is the distance between the nucleus, the electron,  $P$  is the density matrix,  $(\mu\nu|\lambda\sigma)$  are two-electron integrals and  $f$  is an exchange/correlation functions which relies on upon the electron density function and in addition the slope of the density. Energy Minimization regarding the strange (unknown) orbital coefficients delivers an arrangement of matrix mathematical statements in particular the "Kohn-Sham equations", which is analogous from the Roothaan-Hall comparisons.

$$Fc = \epsilon Sc \quad (7)$$

Now the elements of the Fock matrix are given below.

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + J_{\mu\nu} - F_{\mu\nu}^{\text{XC}} \quad (8)$$

Where,  $H_{\mu\nu}^{\text{core}}$ ,  $J_{\mu\nu}$  are core Hamiltonian and coulomb interaction respectively similar to equation (5 and 6) and  $F_{\mu\nu}^{\text{XC}}$  is the exchange/correlation term solely a functional of charge density and its form depends on the particular exchange/correlation functional applied.

Currently, two types of exchange/correlation functional are applied such as local density approximation (LDA) models and non-local or generalized gradient approximation (GGA) models.

### 5.3. $\omega$ B97X-D FUNCTIONAL

This functional was advanced by Chai et al. (2008). This is a change over the long-range remedied (LC) hybrid density. It incorporates experimental atom-atom scattering adjustments by utilizing the following comparison for  $f_{dmp}(R_{ij})$ .

$$f_{dmp}(R_{ij}) = \frac{1}{1 + a \left( \frac{R_{ij}}{R_r} \right)^{-12}} \quad (1)$$

Where,  $a$  is the non-linear parameter which controls the strength of dispersion corrections.

It is an improvised change over functional methodologies that record for dispersion interactions. It can define long-run interactions but can't define short-range interactions precisely.  $\omega$ B97X-D functional is discovered to be one of the best functional for depicting the non-covalent associations, for example, hydrogen bonds, van der Waals force, and  $\pi - \pi$  interactions from the investigation of the distance dependence of interactions energies in the model prototype complexes like formic corrosive, formamide, and formamidine (Thanthiriwatte et al. 2010).

### 5.4. BASIS SETS

A basis set (Jensen, 1969) is a collection/set of functions that are utilized to portray mathematically the electron distribution in an atom (atomic orbital) approximately. Molecular orbitals (linear mixture of atomic orbitals) are utilized to portray the structure of the molecule. In practical Hartree-Fock, density functional, Moller-Plesset computations Basis sets make utilization of Gaussian-sort functions called Gaussian type orbitals (GTOs). Gaussian functions are nearly related with the Slater functions (exponential functions acquired from exact solutions for the one-electron hydrogen atom Schrödinger equation) and involve a polynomial in the Cartesian coordinates (x, y, z) followed by an exponential in  $-r^2$ .



Smallest basis function (minimal basis set) is STO-3G where three Gaussians are utilized to portray a structure closer to the Slater type orbital. There is no fixed procedure to build up a basis set however more often than not a linear blend of Gaussian functions are utilized as best fits to Slater-type functions where the estimations of the Gaussian exponents and the linear coefficients are determined by least squares principle. Split-valence basis sets and polarization basis sets have been formulated to address these two inadequacies of STO-3G. A split-valence basis set applies one arrangement of functions to represent core atomic orbitals and a few arrangements of functions to represent to valence nuclear orbitals. 6-31G basis set is one of the split-valence basis set in which the core shell is portrayed by 6 Gaussians and the valence shell is partitioned into two sections i.e. the inner shell (characterized by 3 Gaussians) and the outer shell (characterized by 1 Gaussian). Relating polarization basis sets, 6-31G\*, is built by including a set of d-type polarization functions represented by a solitary Gaussian for every heavy (non-hydrogen) atom. The 6-31G\*\* basis set is identical to 6-31G\*, with the exception that it gives p-type polarization functions spoke to by a solitary Gaussian for hydrogen. Counts including anions frequently confront issues because of the loosely related additional electrons with particular atoms (or pair of atoms). To beat these disadvantages, basis sets require to be supplemented by diffuse (far away from the nucleus) s and p-sort functions for valence shells on heavy (non-hydrogen) atoms (designed by "+" as in 6-31+G\*\*). Correspondingly 6-31++G\*\* is split valence diffuse polarization basis set as diffuse functions are added to hydrogen atom system also.

## **5.5. FRONTIER ORBITALS AND CHEMICAL PROPERTIES OF ATOMS**

Stability and Reactivity of molecules can be defined by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (frontier orbitals) (Anh 2007). HOMO and LUMO energy gap corresponds to the minimum excitation energy. If the energy

difference between the HOMO of one interacting molecule and the LUMO of another interacting molecule is less, there can be powerful interaction between the frontier orbitals of these two interacting molecules.

Some fundamental chemical properties like, ionization energy (I), electron affinity (A), electro-negativity, chemical hardness and electrophilicity can be estimated using HOMO and LUMO energies ( $\varepsilon_{HOMO}$ ,  $\varepsilon_{LUMO}$ ) using the following equations (Pearson *et al.*, 2005).

$$I = -\varepsilon_{HOMO} \quad (1)$$

$$A = -\varepsilon_{LUMO} \quad (2)$$

$$\chi = \frac{I + A}{2} \quad (3)$$

$$\eta = I - A \quad (4)$$

$$\omega = \frac{\chi^2}{2\eta} \quad (5)$$

Electron affinity (A) is the amount of energy released when an electron is added to a neutral atom to form a negative ion. It is known that element having high ionization energy and high electron affinity is highly electronegative.

Ionization energy (I) is the amount of energy required to remove an electron from an atom. Electronegativity ( $\chi$ ) is defined as the ability of an atom to attract an electron towards itself during bonding. Chemical hardness ( $\eta$ ) can be represented by the energy gap between the two frontier orbitals. Thus, a hard molecule has a large HOMO–LUMO energy gap and a soft molecule has a small HOMO–LUMO energy gap. Chemical hardness helps to determine the stability of a product formed after interaction of different reactant molecules. Electrophilicity ( $\omega$ ) is the tendency of a positively charged species to attract electrons towards it.

## 5.6. HYDROGEN BOND

Hydrogen bond is not a genuine chemical bond but rather a solid dipole-dipole attractive force. Numerous biological and chemical phenomena happen because of the presence of hydrogen bonds. As per Pauling in 1939, under specific conditions a hydrogen atom is pulled in by rather strong forces by two atoms instead of only one, so that it might be considered to be acting as a bond between them termed as hydrogen bond. Another definition is that a hydrogen bond is an attractive donor-acceptor connection where the donors atoms are electronegative contrasted with hydrogen and acceptor atoms have lone pair electrons (Schuster et al., 1999; Jeffery, 1997). In 2005 an IUPAC council was situated up for complete meaning of hydrogen bond. As indicated by an essay composed by Desiraju (2011), hydrogen bond can be denoted as X-H...Y where X and Y are the electronegative species and H is the hydrogen atom.

Gas hydrates are hydrogen bonded network of water molecules encapsulating some visitor molecule. Accordingly hydrogen bonds play a vital part in the formation of gas hydrate structures. One approach to obstruct hydrogen bonds formation between water molecules (i.e., gas hydrate development) is to utilize chemical inhibitors. These inhibitors ought to frame stronger hydrogen bond with water molecules so to disrupt the hydrogen bond network of the clathrate structure. Accordingly understanding of the hydrogen bond interaction between inhibitor molecules and gas hydrate structures is important for identification and proposition of an efficient gas hydrate inhibitor.

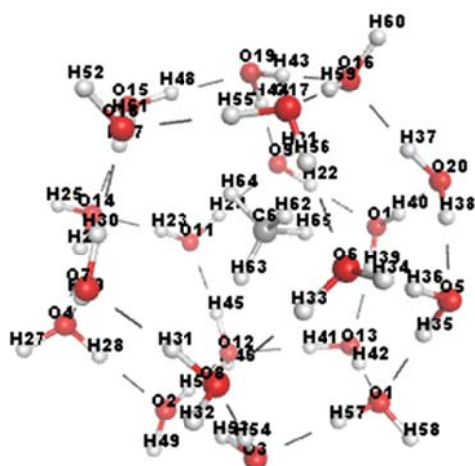
## 5.7. COMPUTATIONAL METHODS

Optimization of  $5^{12}$  methane hydrate cage and 1-butyl-3-methylidazolium complex using Density function theory (Kohn et al., 1965).

For this first principle based calculation B3LYP functional with additional DFT-D term and 6-31G++ (d, p) are used.

## 6. RESULT AND DISCUSSION

### 6.1. PENTAGONAL DODECAHEDRON METHANE HYDRATE CAGE (1 CH<sub>4</sub>@5<sup>12</sup>)



**Figure 1 – Optimized structure of Pentagonal dodecahedron methyl hydrate cage.**

Methane hydrate (1 CH<sub>4</sub>@5<sup>12</sup>) is a non-stoichiometric compound belongs to clathrate family and made up of by H-bonded water molecules (host) lattice trapping methane gas (guest) inside the lattice. There is huge trace of methane hydrate inside sea bed in the vicinity of continental margin and bottom of permafrost region of arctic and this methane hydrate considered to be potential future energy source (collet, 2002). Hence methane hydrate has being a vital concern among global research topics.

### 6.2. 1-BUTYL-3-METHYLIDAZOLIUM

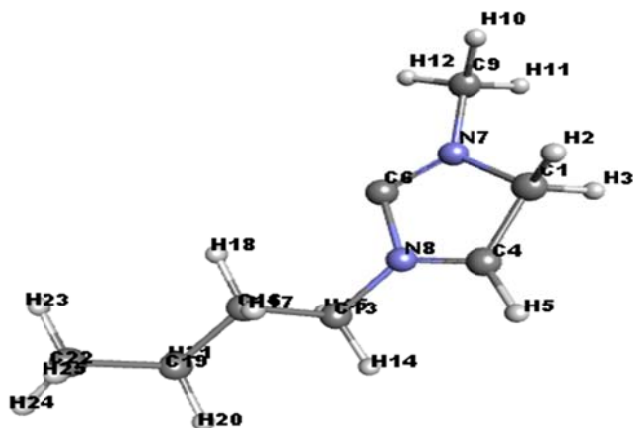


Figure – 2 - Optimized structure of 1-BUTYL-3-METHYLIDAZOLIUM

1-BUTYL-3-METHYLIDAZOLIUM act as potential inhibitor molecule for pentagonal dodecahedron methane hydrate cage.

### 6.3. HYDROGEN BOND FORMATION BETWEEN INHIBITOR MOLECULE AND PENTAGONAL DODECAHEDRON METHANE HYDRATE CAGE

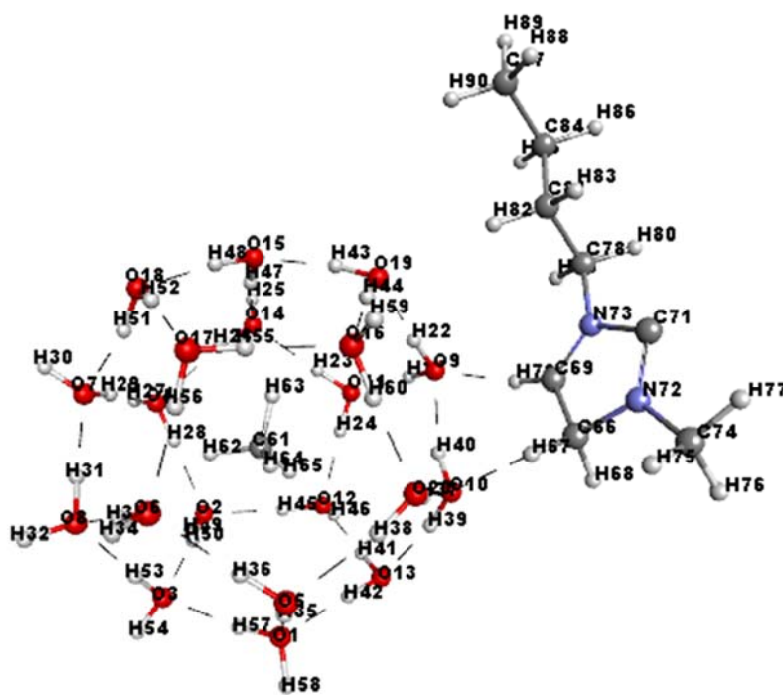


Figure – 3 - Optimized structure of 1-BUTYL-3-METHYLIDAZOLIUM and 1 CH<sub>4</sub>@5<sup>12</sup> methane hydrate cage complex

Here when pentagonal dodecahedron methane hydrate come in contact of inhibitor molecule 1-butyl-3-methylidazolium then hydrogen bond formation takes place between the hydrogen atom of inhibitor molecule and the oxygen atom of methane hydrate molecule. Therefore the H-bond in methane hydrate gets weakens. As a result of this hydrogen bond internal distortion (strain) in pentagonal dodecahedron methane hydrate cage (1 CH<sub>4</sub>@5<sup>12</sup>) occurs and hence molecules gets unstable. Hence therefore we can say 1-butyl-3-methylidazolium acts as inhibitor for pentagonal dodecahedron methane hydrate cage.

#### 6.4. HOMO AND LUMO STRUCTURE OF METHANE HYDRATE AND 1-BUTYL-3-METHYLIDAZOLIUM COMPOUND.

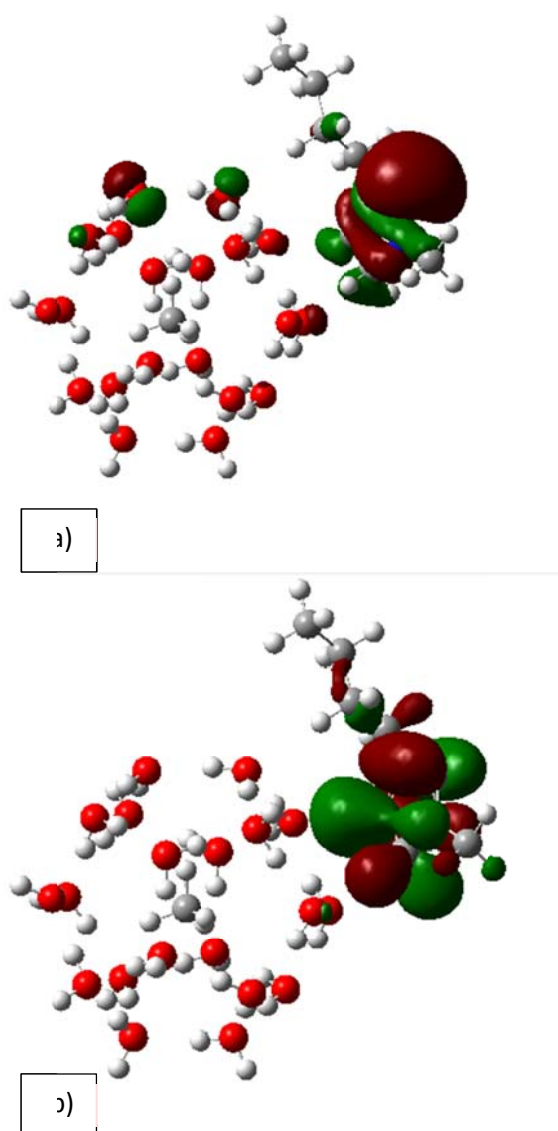
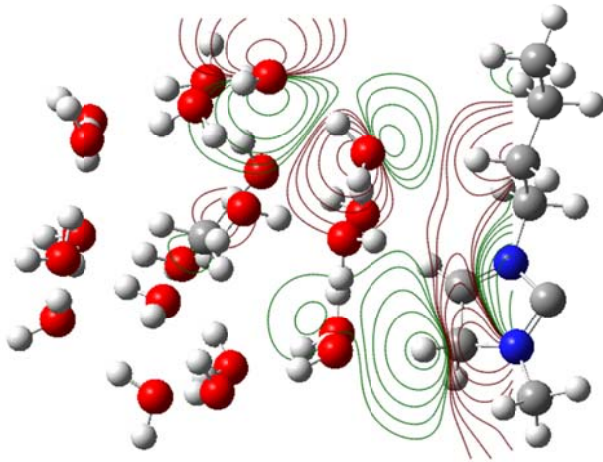


Figure – 4 – (a) HOMO structure and (b) LUMO structure of 1-BUTYL-3-METHYLIDAZOLIUM and 1  $\text{CH}_4@5^{12}$  methane hydrate cage complex

Stability and Reactivity of molecules can be interpreted by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (frontier orbitals) (Anh, 2007). HOMO and LUMO energy gap corresponds to the minimum excitation energy. If the energy difference between the HOMO of one interacting molecule and the LUMO of another

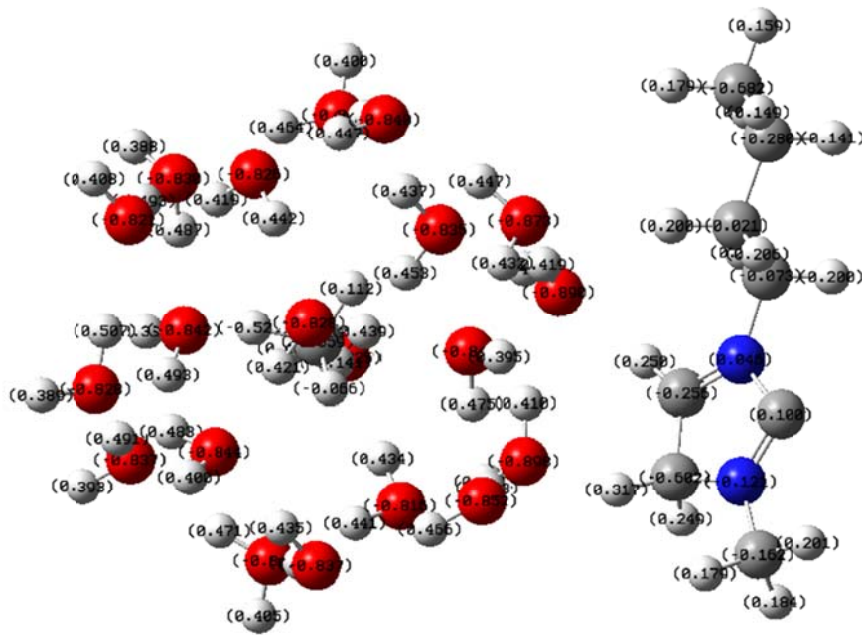
interacting molecule is less, there can be strong interaction between the frontier orbitals of these two interacting molecules.

### 6.5. TWO DIMENSIONAL STRUCTURES OF HOMO AND LUMO



**MULLIKAN CHARGE DISTRIBUTION BETWEEN INHIBITOR MOLECULE AND PENTAGONAL DODECAHEDRON METHANE HYDRATE CAGE (1 CH<sub>4</sub>@5<sup>12</sup>)**





Here we can see the charge distribution on each and every atom of both molecules the charge difference between the oxygen atom of methane hydrate and its nearest hydrogen atom is  $(0.898 - 0.410 = 0.488)$  whereas, the charge difference between the oxygen atoms of methane hydrate molecule and that of hydrogen atom of inhibitor molecule is  $(0.890 - 0.250 = 0.640)$ .

So as far as coulomb's law is concern the force of attraction between the hydrogen atom of inhibitor molecule with that of oxygen atom of methane hydrate is higher than the force of attraction between the oxygen and nearest hydrogen atom methane hydrate hence therefore both molecule link through H-bond as a result the methane hydrate molecule is unstable due to absence of intra-molecular H-bond hence we can say 1-butyl-3-methylidazolium acts as potential inhibitor molecule for pentagonal dodecahedron methane hydrate molecule.

## 7. CONCLUSION

First principle based calculation has been done to explain scientifically the action of “1-BUTYL-3-METHYLIDAZOLIUM” as inhibitor of methane hydrate. After Computation geometrical parameters states that 1-BUTYL-3-METHYLIDAZOLIUM decreases the stability of pentagonal dodecahedron methane hydrate cage ( $1\text{CH}_4@5^{12}$ ). The presence of 1-BUTYL-3-METHYLIDAZOLIUM decreases the hydrogen bond strength and consequently stability of  $1\text{CH}_4@5^{12}$  cage. This work could help to conceptualize the role of 1-BUTYL-3-METHYLIDAZOLIUM inhibitor for methane hydrate and the compendium of this work can be extended to bring insight into electronic structure property correlation based understanding of different methane hydrate inhibitors.

## REFERENCES

- Anh, N. T. (2007), *Frontier Orbitals*, John Wiley and Sons, West Sussex, England.
- Bakkas, N., Bouteiller, Y., Loutellier, A., Perchard, J. P. and Racine S. (1993), The Water-Methanol Complexes: A Matrix Isolation Study and an ab Initio Calculation on the 1-1 Species, *Journal Chemical Physics*, Vol. 99, No. 5, pp. 3335-3342.
- Collet T S 2002 AAPG Bulletin 86 1971.
- Chaudhary, A. and Lee, S. (2004), A Computational Study of Microsolvation Effect on Ethylene Glycol by Density Functional Method, *The Journal Of Chemical Physics*, vol. 120, no. 16, pp. 7464-7469.
- Chai, J., and Gordon, M. H. (2008), Long-Range Corrected Hybrid Density Functional With Damped Atom-Atom Dispersion Corrections, *Physical Chemistry Chemical Physics*, Vol. 10, pp. 6615-6620.
- Englezos, P. (1993), Clathrate Hydrates, *Industrial and Engineering Chemistry Research*, Vol. 32, No. 7, pp. 1251-1274.
- Engel, E. and Dreizler, R. M. (2011), *Density Functional Theory, an Advanced Course*, Springer, Heidelberg.
- Fink, J. K. (2012), *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*, Elsevier, Oxford.
- Fileti, E. E. and Canuto, S. (2005), ab initio NMR Study of the Isomeric Hydrogen-Bonded Methanol–Water Complexes, *International Journal of Quantum Chemistry*, Vol. 102, pp. 554–564.
- Gordienko, R. (2009), *Imaging Biologically-Based Clathrate Hydrates Inhibitors*, Thesis, Queen's University.
- Gupta, K., Ghanty T. K. and Ghosh S. K. (2012), Polarizability, Ionization Potential, and Softness of Water and Methanol Clusters: an Interrelation, *The Journal of Physical Chemistry A*, Vol. 116, pp. 6831–6836.
- Hammerschmidt, E. G. (1934), Formation of Gas Hydrates in Natural Gas Transmission Lines, *Industrial and Engineering Chemistry*, Vol. 26, No. 8, pp. 851-855.

Igboanusi, U. P. and Opara, A. C. (2011), 'The Advancement from Thermodynamic Inhibitors to Kinetic Inhibitors and Anti-Agglomerants in Natural Gas Flow Assurance', *International Journal of Chemical and Environmental Engineering*, Vol. 2, No. 2, pp. 131-134.

Jensen, J.H. (1969), *Molecular Modeling Basics*, CRC Press, Boca Raton.

Jeffery, G.A. (1997), *An Introduction to Hydrogen Bonding*, Oxford University Press, New York.

Kannan, K. and Punase, A. (2009), 'Low Dosage, High Efficiency, and Environment Friendly Inhibitors: a New Horizon in Gas Hydrates Mitigation in Production Systems', EUROPEC/EAGE Conference and Exhibition, Amsterdam, Netherlands.

Koh, C. A., Westacott, R. E., Zhang, W., Hirachand, K., Creek, J. L. and Soper, A. K. (2002), 'Mechanisms of Gas Hydrate Formation and Inhibition', *Fluid Phase Equilibria*, Vol. 194–197, pp. 143–151.

Klomp, U. C. (2005), 'Method for Inhibiting the Plugging of Conduits by Gas Hydrates', patent no. US 6,905,605 B2.

Lee, J. and Kang, S. (2011), 'Phase Equilibria of Natural Gas Hydrates in the Presence of Methanol, Ethylene Glycol, and NaCl Aqueous Solutions', *Industrial and Engineering Chemistry Research*, Vol. 50, pp. 8750–8755.

Lugo, R., Dalmazzone, C., Audibert, A. and Seine C. (2010), 'Method and Thermodynamic Inhibitors of Gas Hydrates in Water Based Fluids', patent no. US 7,709,419, B2.

Masoudi, R. and Tohidi, B. (2010), 'On Modelling Gas Hydrate Inhibition by Salts and Organic Inhibitors', *Journal of Petroleum Science and Engineering*, Vol. 74, pp. 132–137.

McIntyre, G., Hlavinka, M. and Hernandez, V. (2004), 'Hydrate Inhibition with Methanol – a Review and New Concerns over Experimental Data Presentation', Presented at the 83rd Annual Gas Processors Association Convention, Texas Houston.

Mandal, A., Prakash, M., Kumar, R. M., Parthasarathi, R. and Subramanian, V. (2010), 'ab initio and DFT Studies on Methanol-Water Clusters', *The Journal of Physical Chemistry, A*, Vol. 114, pp. 2250–2258.

Pal, S. and Kundu T. K. "Atomistic Simulations of Methane Hydrates and Inhibitor Design" Indian Institute of Technology Kharagpur September 2013.

Parmar, A. (2009), 'PV Cap as Kinetic Hydrate Inhibitor in Gas-Water Systems', thesis, University of Bergen.

Pearson, R. G. (2005), 'Chemical Hardness and Density Functional Theory', *Journal of Chemical Science*, Vol. 117, No. 5, pp. 369-377.

S. Grimme, "Accurate description of van der Waals complexes by density functional theory including empirical corrections," *Journal of Computational Chemistry*, vol. 25, no.12,pp.1463–1473,2004.

Schuster, P. and Wolschann, P. (1999), *Hydrogen Bonding: from Small Clusters to Biopolymers*, *Monatshefte fur Chemie*, Vol. 130, No. 8, pp. 947-960.

Storr, M. T., Taylor, P. C., Monfort, J. and Rodger, P. M. (2004), Kinetic Inhibitor of Hydrate Crystallization, *Journal of the American Chemical Society*, Vol. 126, pp. 1569-1576.

Sloan, D., Koh, C., Sum, A. K., Ballard, A. L., Creek, J., Eaton, M., Lachance, J., Cullen, N., Palermo, T., Shoup, G. and Talley, L. (2011), *Natural Gas Hydrates in Flow*, Elsevier, Oxford.

Thanthiriwatte, K. S., Hohenstein, E. G., Burns, L. A., and Sherrill, C. D. (2010). Assessment of the performance of DFT and DFT-D methods for describing distance dependence of hydrogen-bonded interactions, *Journal of Chemical Theory and Computation*, Vol. 7, No. 1, pp.88-96.

Wu, M., Wang, S. and Liu, H. (2007), A Study on Inhibitors for the Prevention of Hydrate Formation in Gas Transmission Pipeline, *Journal of Natural Gas Chemistry*, Vol. 16, No. 1, pp. 81-85.

Xu, Y., Yang, M. and Yang, X. (2010), Chitosan as Green Kinetic Inhibitors for Gas Hydrate Formation, *Journal of Natural Gas Chemistry*, Vol. 19, No. 4, pp. 431–435.

Zeng, H., Moudrakovski, I. L. and Ripmeester, J. A. (2006), Effect of Antifreeze Protein on Nucleation, Growth and Memory of Gas Hydrates, *AIChE Journal*, Vol. 52, No. 9, pp. 3304-3309.