CHAPTER 3
LITERATURE REVIEW

The ever-increasing demand for fossil fuel resources and depletion of global energy reserves has necessitated exploring possible alternative sources. An alternative energy source that has caught considerable attention during the recent times is the gas hydrates. Gas hydrate deposits exist beneath certain parts of the ocean and under many regions of permafrost. Methane hydrate, a major constituent of natural gas hydrates, is formed in these places because it is stable only at high pressure and low temperature condition. In the ocean bottom, gas hydrates are formed in the form of nodules, mound etc, it mixes up with clay and other substances like natural surfactants, sands, salts etc. at subsea soil. Naturally its property gets changed during formation as well as dissociation. Therefore the nature of pure gas hydrate is different from that of hydrates in presence of additives. A review of gas hydrate formation and its dissociation in presence of various additives like surfactants, alcohols, glycols, salts, polymers and sediments is presented in this chapter. The objective of this chapter is to provide the insights to work on the proposed research title “Studies of Methane Hydrate Formation and Dissociation in Presence of Extraneous Materials”.

3.1 INTRODUCTION

Gas Hydrates are crystalline, non-stoichiometric, clathrate compounds. They are formed by certain gases under favorable conditions of temperature and pressure. The water molecules in the hydrates form a cage-like crystal structure through hydrogen bonding around the entrapped gas molecules (Fig 3.1). The water molecules are referred to as the “host” molecules and other compounds, which stabilize the crystal, are called the “guest” molecules. There is no chemical bonding between the guest and host molecules. The guest molecules are free to rotate inside the cages built up of the host molecules. The exact temperature and pressure of hydrate formation depends on the composition of gas. Hydrates can form in any place where water and gas coexist under the right combination of temperature and pressure conditions, including producing wells, oil and gas pipeline. Hydrates in gas wells are mostly
encountered at shallow depth having low bottomhole temperature or in offshore or arctic environments and where Joule-Thomson expansion cooling occurs.

The industrial interest in gas hydrates began with the discovery that hydrate formation could plug natural gas pipelines. Several theoretical and experimental works were focused on studying gas hydrates. The modern studies of hydrates are aimed at some goals. These are:

(a) Prevention of formation and removal of large hydrate accumulation in natural gas production, transportation and processing systems.
(b) Exploitation of natural gas reserves accumulated in the earth in hydrate state and studying the ecological aspects of gas hydrates.
(c) Creation of new technologies by utilizing properties of hydrates for storage and transportation of gas in hydrate state.

![Fig. 3.1: Gas molecule trapped in cage of water molecules](http://dusk.geo.orst.edu/oceans/deep_currents.html)

Study of gas hydrates is a very challenging job which got initiated from 1811, when Humphery Davy first produced chlorine clathrate hydrate by cooling an aqueous solution saturated with chlorine gas below 9°C. It was just a chemical curiosity. Within 200 years lot of work has been carried out on gas hydrates and it became such a vast subject that it has necessitated subdivisions and identification of various components in this, so that in-depth study in any area is possible for better understanding.

The process of formation of gas hydrates begins with appearance of crystallized nuclei on the gas water contact surface. The hydrate formation takes place when mutual orientation forces between the water molecules and the molecules of hydrate forming gases overcomes the disrupting forces of thermal motion of molecules. Actually, as the temperature drops or
pressure increases, first a moment comes when equilibrium is reached between the orienting and disrupting forces. Then at still lower temperature or higher pressure, a transition takes place from the point of equilibrium to a region in which the orienting forces of mutual molecular attraction overcomes the disrupting forces that hinder the mutual orientation. After the formation of nuclei of a critical size, the hydrate crystal grows depending on temperature, pressure and surface area of contact between water and gases.

Gas hydrate formation is strongly dependent on pressure, temperature and composition of gas. However it can be affected if the interfacial surface area of liquid-gas, gas-solid, liquid-solid surfaces change. The interface between water and gas phases is an ideal location for the formation of gas hydrates. Besides pressure, temperature and composition of gas mixture, the formation and dissociation of gas hydrates are affected by chemicals such as salts, alcohols, glycols, polymers, surfactants etc.; some of these act as gas hydrate inhibitors, and some act as promoters.

3.2 GAS HYDRATE IN PRESENCE OF SEDIMENTS

Methane hydrates, in arctic permafrost and deep ocean sediments, store vast amounts of methane, which is the primary constituent of natural gas. Understanding the formation-dissociation behavior of gas hydrates in sediments is important for seafloor platform and well stability. These sediments contain sands, silts, and clays. The sediment composition and texture may affect gas hydrate stability. Smaller pores typically inhibit hydrate formation (enhance dissociation) more than large pores; however pore spaces in some minerals may enhance hydrate formation under certain conditions. Most minerals studied do not directly affect stability, with the exception of some swelling clays, which under some conditions may enhance stability. For any assessment of natural gas hydrates in hydrate-bearing sediments, the determination of microstructure, composition and physical properties, as well as of the underlying formation and possible decomposition processes is essential. Gas hydrate nucleation, growth and dissociation also depend on sediment grain size, shape, and composition [Clennell et al., 1999]. The equilibrium condition of gas hydrates in sediments, which is referred to here as the decomposition temperature at a given pressure, is affected by the gas and water composition. Melnikov and Nesterov [1996] developed a model on gas hydrate formation showing the influence of porous media on equilibrium conditions of hydrate formation.
Blackwell [1998] found that mineral surfaces that more closely mimic the crystal structure of ice were effective hydrate nucleators, showing the greatest degree of kinetic promotion. Cha et al. [1988] observed a significant shift in the P-T stability curve of natural gas hydrate in bentonite suspensions, suggesting the bentonite surfaces exhibited a thermodynamic effect.

Chuvilin et al. [1999] studied the formation and decomposition kinetics of hydrate, and their P-T conditions, for natural gas-ice-rock systems in order to understand gas hydrate formation in permafrost. They reported that the presence of clay particles in sand strongly changed the character of hydrate accumulation which decreased water transfer during hydrate formation. A number of experiments on the influence of particle surface chemistry on hydrate formation have been reported in the literature.

Riestenberg et al. [2003] studied methane hydrate formation and effects of sediment surfaces on methane hydrate formation and dissociation. It was investigated using colloidal suspensions containing bentonite clay. Experimental results indicated that significantly decreased pressure is required for hydrate formation relative to formation in pure water. Dissociation conditions were also investigated in bentonite and silica suspensions with solids concentration of 34g/l and found that it did not differ significantly from that of water.

Uchida et al. [2004] studied decomposition conditions of methane hydrates in silica sand, sandstone, and clays (kaoline and bentonite), which are typical natural materials known as hydrate bearing sediments. With bentonite particles, the results indicated that methane hydrates formed not only between the particles but also in the interlayer. They found a thermodynamic promoting effect for dilute bentonite suspension.

Kamata et al. [2005] applied thermal recovery method to dissociate methane hydrate in hydrate sediment sample by hot-water injection from one side and gas production from another side. It was found that temperature and pressure in the sample fluctuated between stability region and decomposition region of methane hydrate sample when temperature of the hot water was high.

Li et al. [2008] investigated the influence of salinity and temperature on gas production of methane hydrate in porous sediment. The results indicated that the dissociation rate was fast with the increase of the salinity within a certain range. For hydrate samples
synthesized in different volume size beds. Linga et al. [2009] found that the rate of methane recovery depended on the bed size when dissociated by thermal stimulation.

In the gas production experiments by injecting brine scheme, Madden et al. [2009] conducted experiments to examine massive hydrate accumulation from methane gas bubbles within natural sediments in a large volume pressure vessel through temperature and pressure data, as well as visual observation. Observations of hydrate growth suggest that accumulation of gas bubbles within void spaces and at sediment interfaces likely results in the formation of massive hydrate deposits. Methane hydrate was first observed as a thin film forming at the gas/water interface of methane bubbles trapped within sediment void spaces. These experiments suggest that in systems containing free methane gas, bubble pathways and accumulation points may be controlling the location and habit of massive hydrate deposits.

Lee [2010] found that the permeability of rock is one of the important factors that influence production from gas hydrates by injecting brine. Numerical simulations were also used to investigate the hydrate dissociation.

### 3.3 EFFECTS OF ALCOHOLS, GLYCOLS AND GLYCEROL ON GAS HYDRATE FORMATION AND DISSOCIATION

The formation of gas hydrate is a serious problem in the oil and gas industry since it results in plugging of pipelines and other processing equipments. The petroleum industry would like to maintain their process streams outside the hydrate stability range. Fortunately, the hydrate stability temperature and pressure range is predictable to within experimental accuracy using modern thermodynamic programs usually based on a Gibbs energy extension of the van der Waals and Platteeuw method. Unfortunately, however, low temperatures (such as the deep-sea floor temperature of 277 K) and the mandates of high pressure for economic energy densities place many pipelines well within the hydrate-formation region. Therefore high pressure and low temperature conditions require hydrate-inhibition methods to be adopted. The addition of chemicals known as thermodynamic inhibitors in the water phase to prevent hydrate formation is a general method used in the oil and gas industry.

From an applied point of view, attention to the system under consideration is caused by the use of some alcohols in natural gas industry to inhibit hydrate formation. Alcohols form hydrogen bond with water through their hydroxyl group. The hydrocarbon end of the
alcohol molecule causes a clustering effect on water molecules. Therefore alcohols have duel effects which compete with dissolved non-polar molecules for clusters: the hydroxyl group hydrogen bonds the water molecules (major effect) and hydrocarbon end of the alcohol tends to organize the water into solvent clusters (the lesser effect), in direct competition with the hydrate for guest and host molecules.

Katz et al. [1959] indicated that the inhibition ability of alcohols decreases with volatility i.e. methanol > ethanol > isopropyl alcohol. Methanol is the most commonly used thermodynamic inhibitor in natural gas industry [Sloan and Koh, 2007]. Methanol is considered only as an inhibitor of hydrate formation, that is, a substance decreasing the chemical potential of water in water-methanol solution and thus reducing the temperature of decomposition of gas hydrates formed from these solutions [Davidson et al., 1981].

Recent works [Imai et al., 2007; Mohammadi and Richon, 2007; Chapoy et al., 2008; Maekawa, 2008] provide evidence that n-propanol and isopropyl alcohol form double clathrate hydrates with methane; the double hydrate with isopropanol is reported to be of cubic structure II type.

Zhukaro et al. [2010] presented the numerical data on the decomposition curves of gas hydrates formed by methane and aqueous solutions of ethanol, propan-1-ol, propan-2-ol and isobutanol. Experiments were performed within the pressure range 1-16 MPa. They reported that hydrate formation occurs in a specific manner for each of these systems and no general regularities were observed. Ethanol acts as an inhibitor of hydrate formation; however, for a given molar concentration the decrease in the temperature of hydrate formation is smaller for ethanol than for methanol. Isopropanol and n-propanol form double hydrates with methane; dissociation temperatures of these hydrates differ insignificantly from each other and from the dissociation temperature of the hydrate of pure methane. Dissociation temperatures of the hydrates formed by aqueous isobutanol solutions are lower in comparison with the hydrate formed by pure water.

Abay and Svartaas [2010] studied the effect of ultralow concentration of methanol on methane hydrate formation. Experimental results show that an ultra low concentration of
methanol exhibits dual effect, both as an inhibitor and as a promoter on methane hydrate formation.

Although methanol is one of the most effective inhibitors used in oil and gas industry; huge loss due to high volatility and toxicity may restrict its use. Now glycols being used instead. The glycols provide more hydrogen bonding opportunity with water than alcohols. The glycols have generally higher molecular weights with lower volatility so they may be recovered and recycled from processing/transmission equipments. This property of glycol may encourage its use. The knowledge of equilibrium hydrate-forming conditions is necessary for the rational and economic design of processes in the chemical, oil, and other industries where hydrate formation is encountered [Englezos, 1993]. Ross and Toczylkin [1992] had presented data on the effect Triethylene glycol (TEG) on methane and ethane hydrates.

Breland and Englezos [1996] measured the equilibrium hydrate formation data for carbon dioxide in aqueous glycerol solutions. They observed that inhibiting effects of TEG is comparable to glycerol at the same wt% basis but weaker than methanol. Servio and Englezos [1997] measured incipient equilibrium propane hydrates formation conditions in aqueous TEG solution. TEG was shown to have considerable inhibiting effect on propane hydrate formation.

Wu and Englezos [2006] studied the inhibiting effect of TEG and glycerol on hydrate formation for a mixture of methane + ethane and methane + propane. Both chemicals were found to have a significant inhibiting effect that is proportional to their concentration in the water. Glycerol was found to be a stronger inhibitor than TEG. The dissociation conditions of methane, ethane, propane, and carbon dioxide simple hydrates in presence of aqueous solution of glycerol was tried to predict and produce experimental data which was compared with experimental data reported in the literature. They report acceptable agreements between the experimental data obtained in their work and that reported in literature [Mohammadi et al., 2008b].

Mohammadi and Richon [2010] studied the phase equilibria of methane hydrates in presence of methanol and ethylene glycol (EG) aqueous solution and reported experimental
dissociation data for methane hydrates in the presence of aqueous solutions of methanol and EG of different concentrations and successfully compared with the predictions of a thermodynamic model to demonstrate its reliability for low concentrations of methanol or ethylene glycol in aqueous solution.

### 3.4 Influence of Electrolytes on Gas Hydrate Formation and Dissociation

Although methanol and glycol are well characterized, these inhibitors often require a large concentration which increases costs and have serious environmental impacts [Anderson et al., 1986]. Besides the organic inhibitors, inorganic electrolyte solution including those of sodium chloride, calcium chloride and lithium chloride can also be used. As far as effectiveness, non-poisonous nature and low cost are concerned, sodium chloride is frequently used. But corrosivity of its dilute electrolyte solution restricts its applications under many conditions. Among water soluble substances, electrolytes act as gas hydrate inhibitors as their presence shifts the equilibrium line at constant pressure to lower temperatures analogous to the colligative freezing point depression [Atik et al., 2006]. Thus an exact knowledge of the influence of individual electrolyte is very much important to correctly estimate the formation conditions of methane gas hydrates in the presence of electrolytes (for instance, deep sea conditions).

The enthalpy of decomposition of hydrate in presence of salts is an important parameter for developing the proper technology either to avoid formation of hydrate in pipelines or to develop proper technology for exploitation of natural gas hydrates. Significant work in the relevant field has been reported by different authors [Kamath et al., 1987; Moridis, 2003; Dill et al., 2005; Firoozabadi et al., 2009]. From their observations it can be stated that equilibrium phase behavior of gas hydrate is very complex in nature and it depends on pressure, temperature, type of salts, concentration of salts and finally the composition of guest gases.

Experimental dissociation data for methane, ethane, propane, and carbon dioxide in the presence aqueous solutions of NaCl, KCl, and CaCl₂ with different concentrations of single salt were reported by Mohammadi et al. [2008a]. Experimental hydrate dissociation
data was compared with some selected experimental data from literature and there was good agreement which is a proof for reliability of their experimental technique

Porz et al. [2010] investigated experimentally methane hydrate equilibrium conditions in the presence of KNO₃, MgSO₄, and CuSO₄. It was observed that there was inhibiting effect on hydrate formation, which is in contrast to a previous observation that found CuSO₄ has promoting effect on CO₂ hydrates.

Long et al. [2010] studied the phase equilibrium of ethane hydrate in aqueous solutions of MgCl₂. The MgCl₂ is reported to have an inhibiting effect on ethane hydrate formation. The inhibiting effect of MgCl₂ solution becomes stronger with increasing concentration.

Chen et al. [2010] reported the phase equilibrium and dissociation enthalpies for cyclopentane (CP) + methane hydrates in NaCl aqueous solution. The phase equilibrium pressure of CP + methane hydrates increased with the increase in temperature, and the increase was observed to be linear with increase in NaCl concentration in solution. The higher the temperature, the more remarkable the effect and salinity had on the phase equilibrium pressure. The dissociation enthalpy decreased with the increase in temperature and the NaCl concentration.

### 3.5 EFFECT OF POLYMERS ON GAS HYDRATE FORMATION

Methods to avoid hydrate plugs include raising the temperature insulation or hot water heating, lowering the pressure, removing the water and shifting the equilibrium for hydrate formation by adding anti-freeze chemicals. These techniques are often expensive. Hence there is need for cheaper technology. The thermodynamic inhibitors such as methanol and glycol or salts are required in large quantities (10 - 50 wt %) to prevent hydrate formation, resulting in sub-optimal economical and ecological prevention [Kelland, 2006; Koh et al., 2002; Urdahl et al., 1995].

Low dosage hydrate inhibitors (LDHIs) had been devolved which can be significantly cheaper to deploy than other methods. Kinetic hydrate inhibitors, instead of shifting the hydrate equilibrium to lower temperatures or higher pressures, affect the kinetics (nucleation
and growth rates) of hydrate formation. If the hydrate kinetics are known, and can be controlled, that is, by adding LDHIs, it may be then possible to operate the transmission lines at hydrate formation conditions. Polymeric compounds such as polyvinylcaprolactam (PVCap) or polyvinylpyrrolidone (PVP) have shown to be quite effective in retarding both nucleation and growth of gas hydrate at concentrations 10 - 100 times lower than for thermodynamic inhibitors. There are two classes of LDHI:

- Kinetic hydrate inhibitors (KHIs)
- Anti-Agglomerants (AAs)

Kinetic inhibitors were initially discovered in 1991. Since then, many chemical compounds have been tested for their ability to increase the induction time or hydrate growth period [Long et al., 1994]. Both KHI and AA are used in low concentration (0.1-1.0 wt %) to avoid hydrate formation. KHIs delay hydrate nucleation and also crystal growth so that there is enough time to transport the fluids to the process facilities before hydrates build up in the line. KHIs are special classes of water-soluble polymers. PVCap was shown to delay the average hydrate nucleation time and also to make hydrate nucleation to become more stochastic. Unlike AAs, KHIs can also be used in gas lines. AAs allow hydrates to form but they prevent them agglomerating and subsequently accumulating into large masses. An AA enables the hydrates to form as transportable non-sticky slurry of hydrate particles dispersed in the liquid phase [Kelland et al., 1994]. There are two mechanisms known for this process. The first mechanism discovered by researchers used special type of emulsifiers, usually polymeric [Behar et al., 1991]. The emulsifier creates not only water-in-oil emulsions but confines hydrate formation to the water droplets, preventing their agglomeration. The second mechanism involves the use of surfactants designed to attach to hydrate crystal surfaces [Klomp et al., 1995]. Attachment of the polar head group to the hydrate crystal surface disrupts the hydrate growth process slowing down crystal growth.

Kelland et al. [2009] discussed a new AA mechanism that relies on a chemical forming a third layer between the water and liquid hydrocarbon phases with good agitation in the system. Polypropoxylates and some demulsifiers were tested for this. The surfactant polypropoxylates form a separate layer between the two phases, which coat the dispersed water droplets as they are converted to gas hydrates, keeping them from agglomerating.
Demulsifier, Dowfax DM655, an alkylphenol formaldehyde resin alkoxylation gives good AA performance up to 16.5 °C subcooling when dosaged at 10,000 ppm in synthetic sea water. York and Firoozabadi [2008] carried out the experiments with a multiple screening-tube rocking apparatus and they found that rhamnolipids is an effective AA comparable to other chemical surfactants.

Villano et al. [2009] tested the kinetic hydrate inhibitor performance and sea water biodegradability of a series of poly (2-alkyl-2-oxazoline). The study also included hydrate crystal growth tests on structure II THF hydrate crystals as well as high pressure nucleation and crystal growth studies on a synthetic natural gas mixture giving structure II hydrates. The best polymer for gas hydrate nucleation inhibition was a random copolymer of MeOx and iBuOx consisting of methyl and isobutyl side chains. Its performance was close to the performance of a commercial KHI, Luvicap 55W containing vinylpyrrolidone / vinyl caprolactam copolymer as the active component. Seawater biodegradation studies on all the polymers indicated that they are poorly biodegradable (<20% in 28 days).

The flow assurance industry is progressively moving away from avoidance of hydrate formation, towards risk management. The risk management philosophy allows hydrates to form, but prevents hydrates from agglomerating and forming a plug, or delays hydrate formation within the timescale of the water residence in the hydrate prone section of the flow line [Sloan and Koh, 2007]. There is a particular interest in finding more environmentally friendly LDHIs. One such type could be antifreeze proteins (AFPs). AFPs are compounds that exist naturally in certain species of fishes, insects, and plants living at cold conditions. They cause freeze resistance of the plasma and cell material of these living species in a non colligative manner [Devries et al., 1977]. However further research of these proteins has identified that they possess three different properties that are specific to concentration and temperature, that is, re-crystallization inhibition, crystal habit modification, and thermal hysteresis freezing. They have an impact on ice crystals that are already formed and therefore may have an effect that is more than just antifreeze. Hence this class of proteins has also named ice structuring proteins (ISPs). ISPs have been shown to be able to retard the nucleation and growth of methane hydrates [Zeng et al., 2003; Zeng et al., 2006; Ai-Aden et al., 2008].
Jensen et al. [2010] also reported the inhibition of methane hydrate formation by ISPs. Experimental results indicate that ISP from Tenebrio Molitor is the most effective hydrate inhibitor. Thermal hysteresis ice formation experiments revealed that ISP from Tenebrio Molitor cause higher thermal hysteresis for ice formation compared to type III ISP identified in ocean pout while PVP did not cause thermal hysteresis. This indicates that there might be a direct relationship between ISP performance for ice and hydrate inhibition, and that thermal hysteresis experiments can be used to screen ISPs as kinetic inhibitors.

3.6 GAS HYDRATE STUDY IN PRESENCE OF SURFACTANTS

Gas hydrates have drawn much attention not only as a new natural energy resource but also as a new means for natural gas storage and transportation. The storage of natural gas hydrate is appealing for industrial utilization because of not only its high storage capacity, but also its high safety. Hydrates can store large quantities of natural gas e.g. 180 SM$^3$ per M$^3$ of hydrates [Makogon, 1997; Khokhar et al., 1998]. Gudmundsson et al. [1994] reported that hydrate could be stored at -15$^o$C under atmospheric pressure for 15 days, retaining almost all gas. Gudmundsson and Børrehaug [1996] showed a substantial cost saving (24%) for the transport of natural gas in hydrate form compared to liquefied natural gas from the North Sea to Central Europe.

Slow formation rate of natural gas hydrate has been considered to be a critical problem hindering the industrial application of gas hydrates for storage and transportation of natural gas, un-reacted interstitial water as a large percentage of the hydrate mass, reliability of hydrate storage capacity, and economy of process scale-up. Since the solubility of natural gas in water is very low, only a thin hydrate film is formed at the interface between the water and gas without stirring or other enhancing measures. To solve these problems, two approaches (mechanical and chemical means) are generally adopted. The mechanical method includes stirring [Iwasaki et al, 2005; Takaoki et al., 2005] spraying of liquid in continuous gas phase [Fukumoto et al., 2001; Ohmura et al., 2002] bubbling of gas in continuous liquid phase, micro-bubbling and icing. The chemical method consists of changing the properties of reactant system by adding low dose of surfactants to decrease gas/liquid interfacial tension and to increase the solubility of gas in liquid water. For example, surfactant such as SDS is used to reduce the formation time of hydrates and increase the gas storage efficiency.
Karaaslan and Parlaktuna, 2000; Sun et al., 2004]. In recent years, researchers have reported the promotion effect of some surfactants on gas hydrate formation and gas content. Not only high formation rate and gas content of natural gas hydrate are very important in commercializing the technology of storage and transportation of gas hydrates, but also the stability of the hydrate formed.

The importance of studying hydrate formation and dissociation in the presence of surfactants is due to the fact that some surfactants are naturally formed from the crude oil itself under suitable conditions in the reservoir [Yarranton et al., 2000; Gafonova and Yarranton, 2001; Moran and Czarnecki, 2007]. During the last two decades, several studies have been reported showing a significantly increased hydrate formation rate with the addition of surfactant molecules [Kalogerakis et al., 1993; Karaaslan et al., 2002; Sun et al., 2004]. The success of the potential applications based on hydrate is mainly hindered by some technological problems associated with hydrate formation, including slow formation rates, low conversions, and the economics of process scale-up [Ribeiro et al., 2008]. Some kinds of additives have been used to overcome such difficulties. The addition of THF reduces the induction time and the hydrate formation pressure. However, the rate of hydrate growth is reduced [Linga et al., 2008].

Surfactants are amphiphilic molecules which exhibit a dual affinity for polar and non-polar substances. The properties of surfactant molecules are determined by the balance effects produced by the type, size, and strength of the hydrophilic and hydrophobic groups. The surfactant molecules tend to be water soluble if the hydrophilic groups are more and if surfactant is ionized and the hydrophobic hydrocarbon chain is short (< 12 carbon atoms). A long hydrocarbon chain (> 16 carbon atoms) will make surfactant molecule oil soluble. The chemical structure of surfactant and other parameters depending on the different fluids, temperature and pressure can alter the affinity of surfactants with water and oil phases. Surfactant molecules present two fundamental properties: interfacial adsorption and self-association, which are the essential processes leading to surfactants forming structures enhancing solubilisation. The adsorption of surfactant molecules to interfaces is driven by its double affinity to polar and non-polar substances, where free energy of the system is the minimum. The surfactant can diffuse from bulk phase to an interface such as gas/liquid, liquid/liquid and liquid/solid, decreasing the interfacial tension, modifying the contact angle...
between the phases and wettability of solid surfaces and changing surface charge and surface viscosity [Shah, 1997].

When water soluble surfactants are added to an aqueous phase, surfactant molecules adsorb to any available interface until the interface is saturated. With increasing surfactant concentration, surfactant molecules start to associate, forming spherical aggregates called micelles. The surfactant concentration at which the first micelle is formed is known as the critical micelle concentration (CMC) and may be detected from a discontinuity in the change in several variables such as surface tension, viscosity, osmotic pressure, electrical conductivity and density [Preston, 1948]. The association of surfactant molecules in the form of micelles at concentration above the CMC accelerates gas hydrate formation and reduces the induction time in quiescent systems, which is of special interest for the application of gas hydrates in the storage and transportation of natural gas [Kalogerakis et al., 1993].

Zhong and Rogers [2000] studied the effect of sodium dodecyl sulfate (SDS) on the hydrate formation mechanism using ethane and natural gas as guest molecules. They suggested that micelles act as nucleation point by increasing the solubility of hydrocarbon gas in the aqueous phase and by inducing the formation of hydrate crystals around the micelle in the bulk water phase below the gas/water interface. Consequently, the hydrate formation rate was observed to increase by more than 700 times and the induction time for nucleation decreased significantly compared to systems without surfactants. Other studies have also obtained similar effects with different surfactants but invoked different mechanistic explanations, questioning the CMC requirement [Zhang et al.; 2004, Lee et al., 2010].

The morphology of the hydrate film that forms at hydrocarbon/water interfaces is affected by the adsorption of surfactant molecules at the interface. Luo et al. [2007] studied gas hydrate formation in methane bubble column without surfactants, observing the hydrate shell around gas bubbles, which hindered further formation of gas hydrates. The effect of SDS below the CMC on hydrate formation of gas bubbles using static mixture was studied by Tajima et al. [2010], who reported an increase in hydrate formation rate and a change in the morphology of the hydrate film with addition of SDS. The adsorption of surfactant at the bubble interface promoted the formation of a rougher hydrate film with a weaker structure that easily collapsed; the increase in hydrate formation rate was attributed to higher mass transfer through hydrate film and surface renewal by the film collapse. Kalogerakis et al.
[1993] compared the effect of anionic and non-ionic surfactants in a stirred cell, reporting a greater increase in methane hydrate formation rate with an anionic surfactant (SDS). From the experiments with anionic surfactant, aggregates of hydrate particles suspended in the liquid phase were observed, increasing the slurry viscosity. Hydrate growth on the reactor wall was attributed to a more water-wet wall due to the anionic surfactant solution. The effect of anionic surfactants seems to be detrimental for the transportability of hydrate slurries and should be avoided in pipelines, while non-ionic surfactants seem to prevent agglomeration of hydrate particles.

Karaaslan et al. [2002] studied the effect of linear alkyl benzene sulfonic acid on the formation rate of hydrates with structures I and II. The work revealed that this compound increases the rate of production of both types of hydrate, but its effect on structure I is more significant.

Sun et al. [2003] studied the effect of an anionic surfactant (SDS), a non-ionic surfactant (dodecyl polysaccharide glycoside) and cyclopentane on the gas content of the hydrate formed from natural gas containing 92 mol% methane. The effect of the anionic surfactant was more pronounced compared to the non-ionic surfactant. Cyclopentane reduced the induction time but could not improve the storage capacity. Gnanendran and Amin [2003] used various concentrations of para-toluene sulfonic acid as hydrate promoter and found that its optimum concentration for hydrate formation as 3.5 g/l. Link et al. [2003] observed that by addition of sodium dodecyle sulfate, the gas content of methane hydrate could reach 97% of the theoretical value.

Zhang et al. [2004] reported that alkylpolyglycoside, sodium dodecyl benzene sulfonate and potassium oxalate monohydrate increase the natural gas hydrate formation rate and its storage capacity.

Gayet et al. [2005] studied the methane hydrate equilibrium within the temperature range of 275-300K. This temperature range corresponds to equilibrium pressures of 3.15 - 55MPa. The hydrate formation-dissociation experiments were performed in a high pressure reactor under isochoric conditions and with no agitation. A small amount of SDS was added to water. It was found that SDS did not have any influence on the gas hydrate equilibrium, but
hydrate formation rate is increased drastically compared to the experiments without surfactant.

Ganji et al. [2007a] studied the effects of anionic surfactants sodium dodecyl sulphate (SDS) and linear alkyl benzene sulfonate (LABS), cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and non-ionic surfactant ethoxylated nonyphenol (ENP) on the formation, dissociation and storage capacity of methane hydrate. Each surfactant was tested with three different concentrations 300, 500 and 1000 ppm. SDS was found to accelerate the hydrate formation rate effectively with these concentrations. LABS increased the hydrate formation rate at 500 and 1000 ppm but decreased it at 300 ppm. CTAB and ENP showed promotion effect at 1000ppm while decreased the rate at 300 and 500 ppm. Hydrate stability tests have also been conducted at three temperatures, 268.2, 270.2 and 272.2 K, with and without surfactant. All three additives increase the dissociation rate of methane hydrate below the ice point. CTAB showed the minimum and LABS the maximum effect on the methane hydrate dissociation rate.

Ganji et al. [2007b] reported that by addition of minor amount xanthan or starch in SDS solution decreased the dissociation rate of methane hydrate effectively. The effect of surfactant carbon chain lengths (A series of surfactants with sodium sulfonic acid group in common C4, C12, and C18) on kinetics of hydrate formation was also studied. The surfactant with shortest chain length (C4, butanesulfonic acid sodium salt) showed the highest acceleration of about 2.5 times larger than pure water for methane hydrate formation [Daimaru et al., 2007].

Mandal and Laik [2008] investigated the effect of SDS on ethane hydrate formation and dissociation. They observed that hydrate formation rate increases with the surfactant concentration above the critical micelle concentration (CMC) and also found increased dissociation rate with surfactant concentration under similar operating condition of pressure and temperature.

Zhang et al. [2010] attempted to reduce the dosage of SDS for methane enclathration by adding a small amount of salt and cyclopentane(CP). The results showed that a small amount of CP reduces the SDS dosage. At a concentration of 20ppm or less, SDS cannot promote methane enclathration even with CP. Under the above condition, methane
enclathration is accelerated by adding salts. Among the two salts investigated, NaCl was more effective than NaClO₄ in promoting the enclathration.

3.7 SUMMARY

The detailed literature on gas hydrate formation and dissociation in presence of additives has been done in the present chapter. It may be summarized with the following important points:

- Natural gas hydrates in huge quantities are widely distributed in permafrost and offshore that will be significant future energy source.
- Requirement of high pressure for hydrate formation has been overcome by adding hydrate promoter.
- A new technology by utilizing properties of hydrates for storage and transportation of gas in hydrate state has to create.
- Hydrate formation is unavoidable faced by the oil and gas industry, which must be solved in an economically and environmentally appropriate manner. In order to prevent the agglomeration of hydrate particles in pipelines effectively, there is need to know the detail mechanisms of hydrate nucleation and growth.
- Thermodynamic inhibitors are required in large quantities to affect bulk-phase properties and inhibit hydrate formation. Hence low dosage inhibitors must be developed to work under more extreme conditions of temperature and pressure.
- Hydrate deposits in deep permafrost and marine sediments where the effects of sediment surfaces are largely unknown. Significant research work is still required to know the detailed mechanism of hydrate formation and dissociation under these conditions.

Although a lot of work has been done in area of gas hydrate there are many areas which are still unknown and hence a significant work is still required to know the mechanism of gas hydrate formation and dissociation. Our research focused on the formation and dissociation of methane hydrate which is the major component of natural gas hydrates in presence of extraneous materials. These include silica sand, bentonite clay, various salts, glycols, glycerol, and different surfactants.