

# Original Article: Investigating Clathrate-Like Hydrates in the Gas Phase

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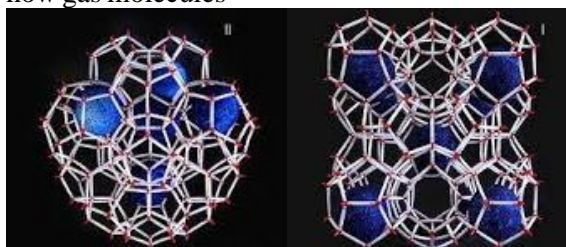
## ABSTRACT

This paper investigates clathrate-like hydrates in the gas phase. Natural gas hydrate is a solid crystalline compound formed from a combination of water and gas, at low temperatures and relatively high pressures. Hydrate is a member of the clathrate family. The guest gas molecules are trapped inside the cavities of the water network (host), formed by hydrogen bonding between the molecules of the water molecule. Carbon dioxide can be formed by pure gas or a gaseous mixture consisting of two or more components. Clathrate is considered to be a solid solution in which guest gas molecules and hydrate gases are in contact. They are located with the host lattice (water), so gaseous hydrate is known as a non-stoichiometric solid. They are held together by van der Waals forces.

## Introduction

The general formula for gas hydrates is  $M_n \cdot nH_2O$ , where M represents the guest molecule. An example of how gas molecules

is trapped inside hydrate cavities is shown in Figure 1 [1-3].



**Figure 1.** Trapping of guest gas molecules inside water cavities [4]

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## History of Gas Hydrates

The history of natural gas hydrate is divided into three main periods: Period 1 began with the discovery of Humphrey Davy in 1810 and continues until present day, and is related to the phenomenon of hydrate formation from a scientific point of view because the accumulation of water and gas in a solid phase (hydrate) is a scientifically significant phenomenon [5-7]

Period 2 dates back to almost 1934 after the discovery of Schmidt, stating that the formation of hydrates causes the closure of natural gas transmission lines to begin and continues to the present. Dayton and Frost were the first to perform experimental experiments on hydrate formation conditions and report the results. During this period, hydrate is mainly considered as a problem for natural gas producers and processors. In other words, in this part of the history of hydrate, it is dedicated to the construction of industries and the problems caused by it [8-11]

The third period began in the mid-1970s with the discovery that nature produced hydrates millions of years before the existence of humans and continues until today. These hydrates are found in glacial regions of the deep oceans as well as in the deep oceans as well as outside the Earth's atmosphere on other planets such as Mars. [12]

In 1950, the structure of the hydrate crystal lattice was examined by X-rays. This led to the development of the idea of using statistical thermodynamics to justify and interpret conditions of the emergence of these crystals. In the 1960s, it was discovered that large numbers of these molecules were present in the subterranean layers, also containing a large amount of natural gas. This huge volume of gas trapped in the hydrate crystal led many people to invent new methods or improve existing methods to extract these trapped gases. During the years 1960 to 1970, activities for desalination and desalination of seawater using hydrate formation were examined and the possibility of this work was shown in semi-industrial units, but at that time, due to lack of economic justification, it did not reach the design and production stage [13-15].

Since 1996, with the growing tendency to use hydrates in the separation and transfer of natural

gas, research on the use of thermodynamic and kinetic enhancers in the hydration process has remarkably emerged [16-18].

### *The process of separation from the gas mixture*

Separation by formation of gaseous hydrates is a new method. There are reasons for using hydrates in separation processes. Hydrate crystals are made up of only guest molecules and water. Each gas molecule as a guest molecule cannot be included in the structure of hydrate crystals and only certain molecules can participate in the structure of hydrate due to their chemical nature, shape and size [19-21]. When hydrate is formed in a gas mixture, the hydrate phase will be rich in gas, which is more inclined to form hydrate, and the remaining gas phase will be enriched with other gases. Based on this argument, the hydrate formation process can be used to separate gases, especially when the use of conventional separation processes such as distillation is not possible, such as systems that have close boiling points and have high separation rates at separation costs [22-24]. Other applications of hydrate in the separation process include: Separating CO<sub>2</sub> from combustible gaseous mixtures. Another process called hydrate separation (HBGS) involves tetrahydrofuran (THF), which is used as a precursor to hydrate formation. THF lowers the equilibrium pressure of hydrate formation and expands the hydrate stability zone. The HBGS process allows the recovery of 99 mol% of CO<sub>2</sub> from combustion gases at normal temperature K (283-273) [25-27]. Separation is ethylene from the mixture and ethylene in the presence (SDS) and without SDS [28-30]. It also concentrates solutions by forming hydrates [31].

### *Natural gas storage and transmission*

In recent years, the use of gas hydrates for storage and transmission of natural gas, especially for small and remote gas fields, has been proposed. About 3% of the world's natural gas fields are small and medium-sized fields, half of which are remote fields. The energy density of methane hydrate is equal to that of compressed gas but less than the energy density of liquefied petroleum gas (LNG) for which conventional methods such as LNG are not economically justified. Natural gas hydrate is a suitable option for gas transfer [32-35]. The self-

retaining properties of the hydrate allow the hydrate to remain stable at pressures below its formation pressure. Give. In this case, if it does not reach that heat, the hydrate will not decompose.

In fact, part of the surface of the hydrate decomposes and the resulting water freezes and covers it like a protective layer, preventing further decomposition. One of the advantages of the hydrate method is that it does not require very low temperatures such as the required temperature of LNG or very high pressures such as the required pressure of CNG and its production process is short. It can also be used in the sea and in the place of wells on the platform. There are between 150 and 180 volumes of gas in each volume of hydrates under standard conditions, and according to economic estimates, the cost of a gas-hydrate cycle is 25% less than that of LNG. The main problems of this process are low conversion rate, low speed and difficulty in separating excess water. It seems that in the not-too-distant future, the NGH process can be used as a method for gas storage and transport.

### Cooling Tanks

One of the applications of hydrate-containing slurries is to create a cold in the cooling cycle. These materials decompose by absorbing energy from the environment and cause it to cool. One of the positive points of this process is its compatibility with the environment.

#### *Effect of additives on hydrate formation*

In general, additives used in the formation of hydrates can be divided into two general categories: Inhibitors and enhancers [46-48] Inhibitors include methanol, ethanol, monoethylene glycol (MEG), diethylene glycol (DEG), Triethylene glycol (TEG), low injection inhibitors (LDHI), anti-cumulative (AA), kinetic (KI) [6], which is injected to prevent hydrate formation in gas transmission lines. One of the costliest steps in hydrate formation is the process of compressing gas to relatively high pressures, as well as the need for low temperatures to form hydrates. To solve this problem and facilitate the formation of hydrates, researchers have done a lot of research on thermodynamic facilitators. The use of thermodynamic facilitators results in the formation of dual hydrates. Thus, these additives, together with the main hydrating

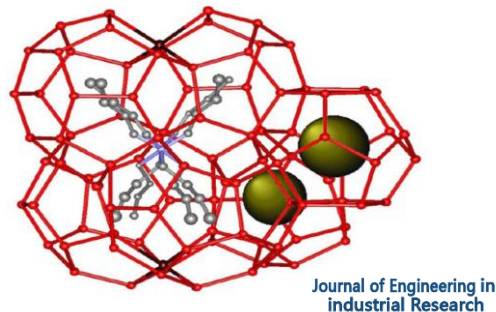
gas, occupy the cavities of the hydrate crystal lattice. One of the best of these substances, which greatly facilitates the formation of hydrates, is THF [49-51]. But the most serious problem with this substance is that it is volatile and toxic. Therefore, it is very important to use substances that can facilitate the formation of hydrates and also do not have problems such as toxicity, volatility and flammability.

In 1940, new structures of hydrates were first discovered by Fuller et al. The structural nature of the hydrates discovered differs from that of simple gaseous hydrates. In this type of hydrate, the guest molecules, in addition to being placed inside the hydrate cavities, also participate in the structure of the hydrate network. For this reason, these structures are called quasi-clarite, because tetraalkylammonium salts produce clathrate-like hydrates, called ionic hydrates.

### Hydrate Formation Clarite-Like

hydrates are composed of tetra-n-butyl or tetra-iso-amyl salts on the quaternary ammonium or phosphonium cation. The anions are attached to water molecules by hydrogen bonds to form part of the clathrate structure.

Figure 2 shows the structure of tetra-n-butyl ammonium bromide TBAB with hydrate number 38 reported by Shimada et al. Tetra n-butyl ammonium halide (TBAX) -like hydrate (TBAX) is stable at atmospheric pressure and temperature. Tetra-n-butyl ammonium bromide (TBAB), tetra-n-butyl ammonium chloride (TBAC) and tetra-n-butyl ammonium Fluoride (TBAF) are examples of these salts. Tetra-n-butyl ammonium bromide, part of the structure of which is shown with the hydrate number 38 in Figure 2, has two 14-sided cavities of Tetra Kai Deca Hadron (51262), two 15-sided cavities of Penta Kai Deca Hadron (51263). And the two 12-sided cavities are the two deca hedron (512). The 14- and 15-sided cavities are occupied by the tetra-n-butyl ammonium cation. Shimada et al. [30] addressed the unoccupied cavities This structure is capable of being occupied by small molecules such as methane. Hydrogen, nitrogen and hydrogen sulfide are identified. The small 12-sided cavities (512) can be filled with water or gas molecules of the right size or left empty.



**Figure 2.** Structure [TBAB.38H<sub>2</sub>O<sub>32</sub>]. The most common structures of clathrite-like hydrates for tetra-butyl ammonium salts are Cube I (CSS-I), quadrilateral I (TS-I) and hexagonal I (HS-I)

Three structures have been reported for TBAC clathrite hydrate: TBAC.24H<sub>2</sub>O, TBAC.30H<sub>2</sub>O and TBAC.32H<sub>2</sub>O. The stability of each of these structures depends on the TBAC concentration, temperature and pressure used. TBAF-like clathrite hydrate has two known structures: the CSS-I structure (TBAF.29 / 7H<sub>2</sub>O) and the TS-I structure (TBAF.H<sub>2</sub>O)

## Conclusion

Thermodynamic improves the formation of gaseous hydrates towards formation at low pressures and high temperatures (optimal thermodynamic conditions). Kinetic improvers can be classified into two groups: Surfactants and hydrotropic. Surfactants are the most important kinetic enhancers. Surfactants are divided into several categories based on hydrophilic groups: Anionic surfactants (sodium dodecyl sulfate is an example of anionic surfactants), cationic surfactants, nonionic surfactants and dual ionic surfactants (Amino acids (nanoparticles) are another category of kinetic enhancers. Thermodynamic enhancers are divided into two general categories: The first category of water-soluble materials and the second category of materials, which are insoluble in water. The first class of these substances, which are easily soluble in water, are divided into two categories, saline compounds and non-saline compounds.

Non-saline compounds usually form structure II. The most important of these compounds are tetrahydrofuran, 1 and 4-dioxane, acetone and furan. When gaseous hydrates are formed in the presence of such improvers, due to the large size of these compounds, they are placed in large cavities and the gas molecules occupy small particles. In this case, structure II hydrates are formed, which

changes the thermodynamic conditions. Water-insoluble improvers, depending on their molecular size, form two types of hydrate structures. Materials, cyclopentane, cyclohexane, etc. form structure II.

Compounds such as methylcyclohexane, etc., which have a larger molecular size, form the H structure. The structure of hydrates formed in the presence of water-soluble salt compounds differs from conventional hydrate structures. In addition to being located inside the cavities, these materials also participate in the structure of the hydrate network, which is why the hydrates formed in the presence of these materials are called quasi-clathrite. These compounds significantly facilitate the formation of hydrates and are able to form hydrates in environmental conditions.

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