

The Investigation of Using Inhibitors to Prevent the Formation of Hydrate in Gas Pipelines

Amir Samimi¹ and Soroush Zarinabadi²

¹Department of Chemical Engineering, Shahreza Branch, Islamic Azad University, Shahreza, Iran

²Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

Abstract. Hydrate is a water network or with a set of holes with little space in between. If gas molecules are trapped into some of these holes, hydrate can be considered as a stable solid. In other words, gas hydrates are complicated crystal molecules which are formed by mixing water and proper gas molecules. Gas hydrates are ice-resembling crystals but they are structurally different from ice. The formation of gas hydrates in gas pipelines leads to blockage of pipelines. Therefore, the formation of them should be prevented since blockage costs are high and the process is time-consuming. To prevent the formation of gas hydrates in pipelines, chemical inhibitors are used which are divided into two groups of thermodynamic and kinetic inhibitors. These inhibitors are also different in kind and amount to be used in pipelines.

Keywords: Gas Hydrate, Ice, Gas Pipelines, Inhibitors

1 Introduction

Hydrate is a water network or with a set of holes with little space in between. If gas molecules are trapped into some of these holes, hydrate can be considered as a stable solid. In other words, gas hydrates are complicated crystal molecules which are formed by mixing water and proper gas molecules. Because of hydrogen bonds, water molecules form unstable networks gas molecules occupy the space between the gaps in the network. When even a few of these holes are filled, gas hydrate molecules become crystalized. It happens at even a temperature above the freezing point. The structure of the formed hydrate gas will be as follows: structure I, structure II and recently structure H.

2 New Methods of Gas Hydrates Formation

A two-stage mechanism for the production of gas hydrates has been proposed:

- (1) A semi-chemical reaction to produce alkaline hydrates
- (2) Absorption of small gas molecules from base alkaline hydrates chain rings.

This new concept is based on previous studies and the kind of equilibrium: In the first stage, semi-chemical equilibrium reaction and in the second stage, equilibrium physical adsorption. The results obtained by continuous experiments show that the new models can predict the way of formation of hydrates for pure gasses and a combination of gasses. Many existing thermodynamic models for predicting hydrate formation which are made by various changes by Plato and the Vandervals are available.

Scientists have recently suggested that intermittent static mechanisms are the base of hydrate formation. The base and objective model is the relative similarity between hydrate formation and Langmuir adsorption.

3. Thermodynamic root of of the model and evaluation of the parameters of pure hydrate gasses

Based on the two-stage mechanism of hydrate formation explained earlier, there are two kinds of equilibriums in the system: a semi-chemical reaction occurring in the first stage and equilibrium physical absorption that have saturated gas molecules around chain rings in the second stage.

$$\mu_B = \mu_w + \lambda_2 \mu_g$$

Where,

μ_B is alkaline hydrates chemical potential, and μ_w and μ_g are water and gas standard chemical potentials respectively. After absorption of gas molecules in chain rings, alkaline hydrates chemical potential will decrease. μ_B can be shown like this:

$$\mu_B = \mu_B^0 + \lambda_1 RT \ln(1-\theta)$$

Where,

θ Represents a fraction of chain rings surrounded by gas molecules, μ_B^0 represents unsaturated chemical potential of alkaline hydrates ($\theta = 0$) and λ_1 is the number of small rings on water molecules in the alkaline hydrates.

4 The method of predicting hydrate formation through solid-steam equilibrium constants

The best ways or methods used to predict or recognize hydrate phases in equilibrium state in water-hydrocarbon systems are based on the coordination of ratio or size of solid-steam equilibrium constant K_v s. Equilibrium constant tables for the kinds or components of known hydrates with normal butane as the heaviest material can be found in several articles and books.

In this proposed method, "k" of normal butane is considered as ethane with low concentration. "K" is considered free for nitrogen and heavier components because they are either in the form of hydrate in different states or they are not in this form at all.

5 Removing and preventing hydrate formation in gas pipelines theoretically

Glycol and alcohol may be used to reduce (or prevent) hydrate formation. This is one of the basic phenomena that the soluble compound may be lower than the freezing point of the solvent. The equation is as follows:

$$d = \frac{k_i \times X}{100M - X \times M}$$

d = depression of hydrate point

w = weight percent inhibitor in the liquid water phase

M = mol wt of inhibitor

$$K_i = \text{constant}$$

Pressure drop (d) must be reduced from the determined point of hydrate and by linear methods mentioned above. Ethylene glycol (DEG) is the most common glycol used for this purpose.

This is a proposed amount. Thus, fluid flow in pipeline contains between 50-60 percent by volume of DEG. The last suggestion was related to concentration. Solubility is usually less than 0.1 to 0.3 gallons DEG per 100 barrels of extracted hydrocarbons, which depends on the amount of aromatic.

Total losses include evaporation, overflow, leakage of the pump, solubility and so on and on average it is usually 1 gallon per 100 barrels transferred from one plant (or the condensed amount injected to a unit).

These graphs are designed based on low temperature of separator units. In a specific unit, there is the

possibility of activity in temperatures of 50-65 °F below hydrate point. The order of calculations is as follows:

- ❖ Determining the temperature of hydrate formation of a gas
- ❖ Specifying the minimum expected temperature in a system (in underground pipes 40°F is good provided that constant data are not available)
- ❖ Calculating the water existing in stage 2, and using dew point of water in that temperature
- ❖ Using an equation to obtain w
- ❖ If methanol is used, correction is necessary for the amounts wasted in steam phase.

6. Predicting hydrate formation based on thermodynamic closed model

Solid-steam equilibrium constant is defined in solid phase based on the same mole ratio of a compound in gas phase, both of which are without water.

$$K_{vs} = \frac{y_i}{x_i^s}$$

When K_{vs} is solid-steam equilibrium constant, y_i is a mole fraction of component in steam waterless-based phase and X_i^s is a mole fraction of component i in hydrate waterless-based phase. Calculating pressure and temperature when hydrates are from a gas phase is like calculating dew point for a saturated steam. So we will have:

$$\sum_{i=1}^n x_i^x = \sum_{i=1}^n \frac{y_i}{k_{vs}} = 1$$

The K_{vs} tables for ethane, methane, methane propane and iso-butane were prepared by Carson and Katz in 1942 and the tables for CO_2 and H_2S were prepared by Katz and Koworkerz. In previous years, it has been reported that the examples of hydrate structures are just in kinds of benzene cyclohexane and Cyclopentane which exist in structure II of hydrates and today they exist in considerable concentrations in gas and oil systems. In a new research study it has been proven that heavy structure II hydrate samples refer to free zone of true fluids. So heavy structure II hydrate samples cannot be ignored. Preparing a practical method developed from K_{vs} which includes heavy structure II hydrate samples requires tables for these compounds. Considering the information above, the method used in preparing K_{vs} tables for heavier structure II hydrate samples is very detailed. In addition, a corresponding equation has been suggested for each compound which simplifies using K_{vs} method in a computer program. Plus, prediction of released hydrate through K_{vs} method is consistent with laboratory data. Therefore, thermodynamic closed model is proved with satisfactory results.

The effect of inhibitors on hydrate formation process

Leatherhaus et.al studied the effects of a few kinetic inhibitors on natural gas hydrate formation process in a series of experiments and showed poly vinyl caprolactam (PVCAP) and salt can slow the formation of hydrate. Visual observations in these experiments showed the hydrate obtained in the presence of salt has bigger crystals than the hydrate obtained in the presence of PVCAP.

Long and Kwami model can explain why hydrate forms in low temperatures and high pressures. As temperature decreases, kinetic energy of liquid- phase molecules decreases and the number of hydrogen bonds between water molecules increases. As a result of these bonds, the number of molecular accumulations in surface increases. The increase in the number of these holes means the number of spots

into which gas molecule can be trapped and form hydrate has increased and therefore there is more chance of gas molecule being trapped in these holes accidentally. As pressure increases, the number of gas molecules in a unit of water surface increases and the chance of a gas molecule falling into an appropriate holes increases and as a result, the probability of hydrate formation increases.

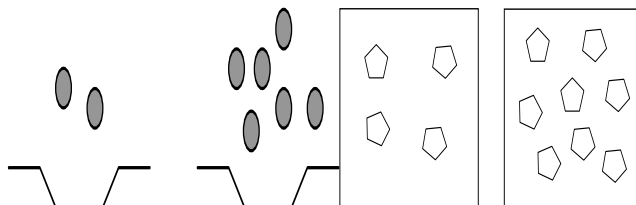
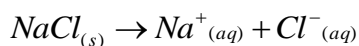


Figure 1: a) the effect of reducing temperature on the number of holes on gas-water interface b) the effect of pressure increase on the probability of gas molecules hitting water-gas interface

Based on Leatherhaushe et al's experiments, it can be concluded that inhibitors can slow the process of hydrate formation or prevent it either by decreasing the holes on the surface, like salt, or by blocking these holes. To justify inhibiting mechanism of salt in the process of hydrate formation, the similarity between this phenomenon and freezing of water can be used. Pure water starts freezing at zero temperature. To this end, first water molecules should make appropriate molecular accumulations by making hydrogen bonds. These accumulations are constructing units of ice crystal. Salt is quickly ionized by being dissolved in water and its positive and negative ions spread in liquid phase. These ions normally have high charge concentration and can make strong cohesion with polar molecules of water.



By making cohesion between water molecules and the cations and anions, each ion is rapidly surrounded by six water molecules. Therefore, the existence of cations and anions keeps water molecules out of reach of each other so they cannot have proper arrangements for the formation of ice crystals. On the other hand, hydration is a very pyrogenic process. The released energy breaks some of the hydrogen bonds between water molecules and destroys the molecular accumulations having formed earlier. The result of these two phenomena is reducing the speed and the amount of hydrate formation. This mechanism can be used to justify the effect of salt on the process of hydrate formation. As it was mentioned, for hydrate to form, it is necessary to have holes of water molecules in water-gas interface. In the presence of salt, water molecules are bonded by molecular forces of sodium and chlorine. This cohesion is stronger than hydrogen bonds between water molecules and therefore, it can break molecular accumulations.

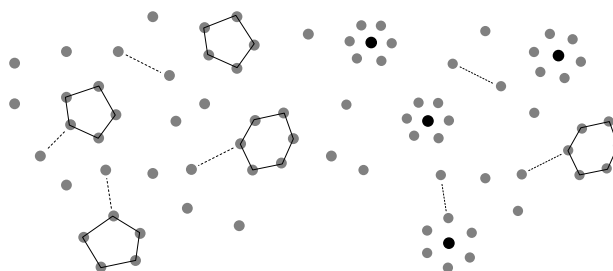


Figure 2: a) Formation of molecular accumulations in water b) Hydration of salt ions as a result of being dissolved in water

On the other hand, as hydration heat is released, the temperature of liquid phase increases locally and moves it away from phase diagram of hydrate formation. Therefore, the level of inhibition of salts depends on the load existing on ions as well as the radius of released ions. Since hydrogen bonds in accumulations with fewer water molecules are few, less energy is needed to break the bonds and being absorbed by existing positive and negative ions. Therefore, small holes are easily removed. But when the number of bonds in accumulations with more number of molecules is high, more energy is needed to break them. Makagon showed power of inhibition of salts is directly related to the number of released ions and has a reverse relationship with ion radius. Therefore, the best inhibitors are those which release maximum number of cations with minimum ion radius. The more a salt can decrease solubility of guest gas molecules (AP), the better inhibitor it is.

Table 1: the level of reduction of guest molecule solubility by different cations

Element	Electric load	Ion radius (A)	AP
Be	+2	0.34	0.67
Al	+3	0.57	0.20
Mg	+2	0.78	0.11
Ca	+2	1.06	0.05
Na	+1	0.98	0.04
K	+1	1.33	0.02

In addition to ion radius and electric load, the price and level of solubility of salt are important too. Among anions, chlorides, nitrates and sulfates have the most application. An important factor which should be considered in choosing salt is its corrosion. Another drawback of salts is that they become thicker when being heated and sediment at the bottom of pipe in colder areas. In other words, these inhibitors enter with less thickness exactly where the probability of hydrate formation is high. The experiments by Leatherhaus et.al in the presence of PVCAP showed the existence of only one weight percent of it in the solution can completely stop the process of hydrate formation. This polymer consists of big monomer molecules. Because of the existence of electron groups which absorb oxygen and nitrogen on benzene ring, electron cloud of the ring is pulled toward these atoms and some positive load is applied on the hydrogen of the ring. Having positive load, the molecules of this polymer can be absorbed by negative load of oxygen atoms of water molecules, enter surface holes and block them. As a result, the number of active points for nucleation in surface decreases and the chance of gas molecules being trapped into these holes becomes smaller. Due to their large size, these molecules can only be absorbed in bigger holes and therefore smaller holes are left for hydrate formation. It is why the hydrate formed in the presence of polymer inhibitors with big molecules has smaller crystals compared to pure solution. The figures below show the effect of different inhibitors with different thicknesses on hydrate formation.

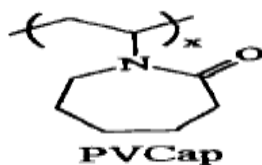


Figure 3: polymer molecule of PVCAP

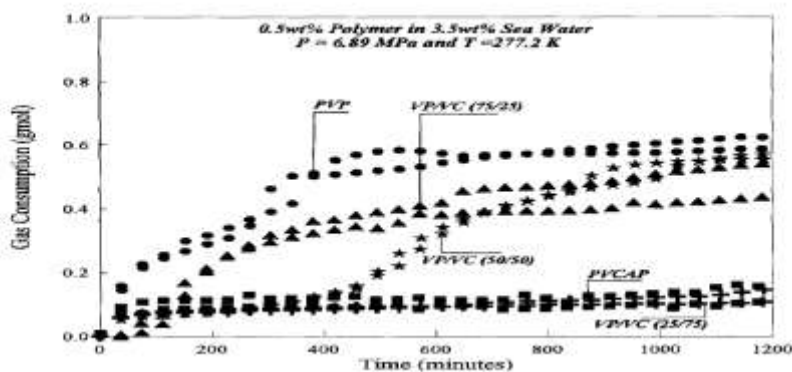


Figure 4: kinetic of the effect of inhibitors on the process of hydrate formation

Hamrashmit suggested the following equation for the effect of inhibitors on the process of hydrate formation:

$$\Delta T = \frac{K \cdot x}{M(100 - x)}$$

Where, ΔT is the fall of the tature of hydrate formation

K is constant value of inhibitor

M is molecular mass of inhibitor

And x is mass concentration of inhibitor.

Table 2: k constant values for some inhibitors

Inhibitor	K values
Methanol, ethanol, cymene, ammonia	1228
Sodium chloride	1220
Glycol, propyl	2195
Sulphonal	2425

Peargon suggested the following equation for temperature fall of hydrate formation as a result of the presence of inhibitors:

$$\Delta T = \frac{nRT_0^2}{\Delta H} X_3$$

Where, x_3 is the concentration of non-electrolyte solution, T_0 is the temperature of hydrate formation without inhibitors, ΔH is hydrate formation heat and R is global constant of gasses.

Chang and Goo, 1998, suggested the following equation for the effect of inhibitors:

$$f_i = x_i f_i^0 \left[1 - \sum_j \theta_j \right]^\alpha$$

$$\sum_i x_i = 1.0$$

$$\sum_j \theta_j = \frac{\sum_j f_j C_j}{1 + \sum_j f_j C_j}$$

Where, α is equal to 1.3 for one-hydrate structure and equal to 2 for two-hydrate structure

f_i is fugacity of the gas forming hydrate

X is concentration of the components involved in hydrate formation process

And θ is the number of holes joining each other as a result of the presence of i from gas into liquid phase.

The temperature of hydrate formation in the presence of inhibitors is calculated by obtaining C_j from the equation above and putting it in the equation below:

$$C_j = X_j \exp \left[\frac{Y_j}{T - Z_j} \right]$$

Where, x, y, z are constants of inhibitors.

Table 3: the results of Chang and Goo's model

Gas phase	Concentration of inhibitor in aqueous phase (wt.%)	P -range (MPa)	T -range (K)	AADT (1) ^a (%)	AADT (2) ^b (%)
CH ₄	10% CH ₃ OH	2.14-18.82	266.23-286.40	0.140	0.698
	20% CH ₃ OH	2.83-18.75	263.34-280.17	0.146	1.326
	35% CH ₃ OH	2.38-20.51	250.90-270.10	0.468	0.508
	15% C ₂ H ₅ OH	3.83-13.67	273.30-284.70	0.113	0.256
CH ₄ + C ₂ H ₆	10% CH ₃ OH	0.53-13.83	265.51-291.23	0.442	0.150
	20% CH ₃ OH	0.94-14.10	265.17-286.47	0.423	0.521
	35% CH ₃ OH	0.62-20.11	253.10-276.60	0.437	0.539
	50% CH ₃ OH	0.69-20.42	241.20-262.60	0.484	-
C ₂ H ₆	10% CH ₃ OH	0.42-2.82	268.28-281.89	0.085	0.474
	20% CH ₃ OH	0.55-2.06	263.53-274.07	0.094	1.322
	35% CH ₃ OH	0.50-1.47	252.6-262.2	0.588	0.386
	50% CH ₃ OH	0.42-1.01	237.5-249.8	1.281	-
C ₃ H ₈	5% CH ₃ OH	0.23-0.47	272.12-274.79	0.149	0.138
	10.39% CH ₃ OH	0.19-0.43	268.30-271.82	0.053	0.443
	35% CH ₃ OH	0.14-0.21	248.00-250.20	0.132	0.807
CO ₂	10% CH ₃ OH	1.59-3.48	269.49-274.92	0.414	1.264
	20.02% CH ₃ OH	1.59-2.94	263.96-268.86	0.465	2.039
	10.04% EG	1.15-3.20	270.90-278.30	0.146	0.278
	10% CH ₃ OH	1.74-2.35	271.60-273.80	0.060	0.272
H ₂ S	10% CH ₃ OH	0.07-1.08	265.69-291.77	0.255	0.604
	16.5% CH ₃ OH	0.28-1.50	273.20-290.10	0.625	1.810
	20% CH ₃ OH	0.22-0.59	271.79-281.15	0.115	1.218
	35% CH ₃ OH	0.22-0.58	263.20-274.20	0.410	0.670
	16.5% C ₂ H ₅ OH	0.39-1.48	280.70-291.80	0.890	0.745
CO ₂ + CH ₄	10% EG	1.14-3.22	268.70-278.00	0.384	0.646
	CO ₂ + C ₂ H ₆	0.85-2.31	269.10-276.40	0.173	0.199
	CO ₂ + N ₂	0.93-3.39	267.20-276.90	0.143	0.637
NG1	10% CH ₃ OH	1.04-19.03	268.27-288.34	0.653	1.550
	20% CH ₃ OH	1.41-19.15	264.41-280.97	1.062	2.617
NG2	42.9% TEG	2.31-8.59	275.15-285.25	0.201	0.209

Angloros and Jodang managed to improve the functionality of inhibitor by adding poly ethylene oxide. For instance by adding poly ethylene oxide, the delay in hydrate formation from methane increased from 29 to 150 hours. The figures and tables below depict the effect of adding poly ethylene oxide:

Table 4: the effect of adding poly ethylene oxide on the formation of methane hydrate

Methane hydrate experiments				
No.	System	P_{exp} (kPa)	T_{exp} (K)	Induction time (min)
1	No inhibitor	6000	273.7	0.5
4	INH1	6000	273.7	1253
5	INH1 + P	6000	273.7	9006
6	INH2	6000	273.7	40
7	INH2 + P	6000	273.7	27
8	INH3	6000	273.7	86
9	INH3 + P	6000	273.7	148
10	INH4	6000	273.7	8.6
11	INH4 + P	6000	273.7	15.6
12	INH5	6000	273.7	6.5
13	INH5 + P	6000	273.7	82.3
14	INH6	6000	273.7	1.3
15	INH6 + P	6000	273.7	16.6
16	INH7	6000	273.7	6.6
17	INH7 + P	6000	273.7	7.3
19	INH8	6000	273.7	30
20	INH8 + P	6000	273.7	21.3

Conclusion

Since sub-zero temperatures are rare in Iran, especially in the regions around Persian Gulf, appropriate conditions exist for the formation of thermodynamic inhibitors with kinetic inhibitors. The calculations related to equilibrium line of hydrate formation in Parse Jonoobi gas and natural gas condensate pipeline clearly prove this claim. Although it is probably possible to use different kinds of LDHIs (low-dosage –hydrate inhibitors) especially kinetic inhibitors in most areas in Iran, it is always necessary to investigate the limitations of these materials before using them. Anyway, using these materials can have economic and environmental benefits.

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