

Experimental Measurement of Methane and Ethane Mole Fractions During Gas Hydrate Formation

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ABSTRACT: *The Super-saturation condition has to be provided to form gas hydrates. Consequently, the prediction of the guest molecule fraction in the aqueous phase is crucial in the study of the gas hydrate kinetics. In the present work, several experiments were carried out in a semi-batch reactor in order to determine the mole fraction of methane and ethane during gas hydrates formation (growth stage). The temperature ranged from 274.15 to 284.15 K. The experiment pressure ranges were 3100 to 7765 kPa and 950 to 2635 kPa for methane and ethane, respectively. The mole fraction is proportional to pressure while it is not affected by temperature to a great extent. Furthermore, the amount of guest dissolved in the liquid water was observed in the aqueous phase which was fairly constant during hydrates formation.*

KEYWORDS: *Gas hydrate; Methane; Ethane; Mole fraction; Growth stage.*

INTRODUCTION

Clathrate hydrates are very complex crystalline molecules that are formed by mixture of water as the host with gas molecules as the guest at the low temperature and high pressure. Due to the hydrogen bonding, water molecules as host molecules form lattice or cage-like structure consisted of large and small cavities. These cavities are occupied by the guest gas molecules with smaller molecular diameters rather than cavities. Consequently, the framework, unstable in terms of thermodynamic, becomes stable, and thus the gas hydrates are made [1]. This phenomenon of gas hydration was first observed experimentally by *Sir Humphrey Davy* in 1810 [2]. According to *Hammer Schmidt's* observation in 1939, gas hydrates may lead to the blockage of natural-gas pipeline. Hence, hydrates formation has been considered as one of the most fundamental drawbacks of oil and gas

transmission pipelines. This incidence causes problems such as devastating the process equipment and disturbing the production. Despite these problems, gas hydrates have some advantages such as carbon dioxide sequestration, separation of greenhouse gases, hydrogen separation, gas storage, and desalination process [3].

Driving force selection is an important stage in studying hydrate kinetics. Numerous researchers have introduced different driving forces such as concentration, fugacity, pressure, degree of sub cooling, and total Gibbs energy. *Vysniauskas & Bishnoi* used degree of sub cooling as the driving force [4]. Later, *Englezos et al.* assumed the fugacity as the driving force [5,6]. They assumed the difference between fugacity of liquid bulk and that of surface of particles. *Skovborg & Rasmussen* [7], *Hashemi & Macchi* [8], *Bergeron & Servio* [9] and

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Mohebbi *et al.* [10] used concentration (mole fraction) as the driving force in their models. Moreover, the difference between Gibbs free energy was regarded as a driving force by Sarshar *et al.* [11] in 2010. Varaminian & Abbasi Nia used chemical affinity for modeling the hydrate formation of methane [12].

In all the above mentioned models, the driving force difference was estimated between the interface of gas and liquid (at operating conditions) and hydrate conditions in the aqueous phase (at operating temperature and corresponding equilibrium pressure). Thus, the prediction of the mole fractions of dissolved gases in water is directly affected by the accuracy of measurements and prediction.

There are a number of studies carried out on the solubility of methane and ethane at equilibrium hydrate formation. Yang *et al.* [13], Servio & Englezos [14] and Seo & Lee [15], measured the solubility of methane at equilibrium hydrate formation. They concluded that the mole fraction increases with rise in temperature. They also stated that the mole fraction of methane does not change considerably with pressure. The measurement of methane, ethane, propane, and their mixture solubility was conducted by Kim *et al.* Based on their observations; the concentration was not a function of pressure [16]. Lang & Servio have recently studied the solubility of methane and ethane in water under hydrate-liquid-vapor equilibrium conditions [17]. As it was cited, several authors have measured the solubility of guest gases in the liquid phase (in equilibrium conditions). To the best of our knowledge, there are only two published experiments regarding the mole fraction of gas hydrate former in the liquid bulk at the onset of hydrate growth and thereafter [18,19].

Bergeron & Servio found out that the mole fraction of methane and carbon dioxide did not change with respect to time in the growth step of hydrate formation [18]. A similar research has been conducted by Najafi & Mohebbi. They investigated the mole fraction of carbon dioxide in water during hydrate growth. They finally, concluded that the fugacity would not change significantly after the turbidity point [19].

In the present study, the mole fraction of methane and ethane in water was measured at different temperatures and pressures (after the turbidity point). Three types of experiments have been conducted. The first series were carried out at non-hydrate conditions to ensure the reliability of results of the experimental apparatus.

The second and the third series were carried out 10 minutes after hydrate the growth and through the time respectively. The results from this study can simplify the hydrate kinetics modeling and help better understand the concentration change in the growth stage.

EXPERIMENTAL SECTION

Materials

Both gases were provided from Persian Gas Cooperation with 99.95% purity. Furthermore, the de-ionized water was provided from Ramin power plant (Khusestan-Iran) with the conductivity of less than 0.1 $\mu\text{S/m}$.

Procedure

The apparatus used for this study is similar to that of the previous study by Najafi & Mohebbi [19] which conceptually originated from the work by Bergeron & Servio [18] - see Fig. 1. Prior to each experiment, 150 mL of double distilled water with the conductivity of less than 0.1 $\mu\text{S/m}$ was injected into the cell. The cell was pressurized with the experiment gas three times and evacuated by a Speedivac vacuum pump each time.

As all runs are at the constant temperatures, the experiment gases were injected in two stages. In the first stage, the gas was injected into the cell close to hydrate formation pressure (P_{eq}). As the temperature reached the experiment temperature (T_{exp}), the system pressure increased as the pressure reached the experiment pressure (P_{exp}). When the system pressure and the temperature were constant for 30 minutes, the mixing and data-acquisition started. The hydrate growth stage was identified as the cell pressure started to decrease rapidly.

In each experiment, a few aqueous phases were extracted from the cell, passed a micro-filter and metering valve, and was flashed in Erlenmeyer flask. The average diameter of micro filter was 2 μm to ensure that all the hydrate crystals had been trapped. The major part of the dissolved gas in water at experiment pressure was released in Erlenmeyer while some of it remained in water. The released gas was directed to an inversed filled-water burette. The volume of the replaced gas (V_{gas}) was used to calculate the released gas via to Eq. (1).

$$n_i^G = \frac{(P - P_{\text{H}_2\text{O}})V_{\text{gas}}}{RT_{\text{amb}}} \quad i = \text{methane, ethane} \quad (1)$$

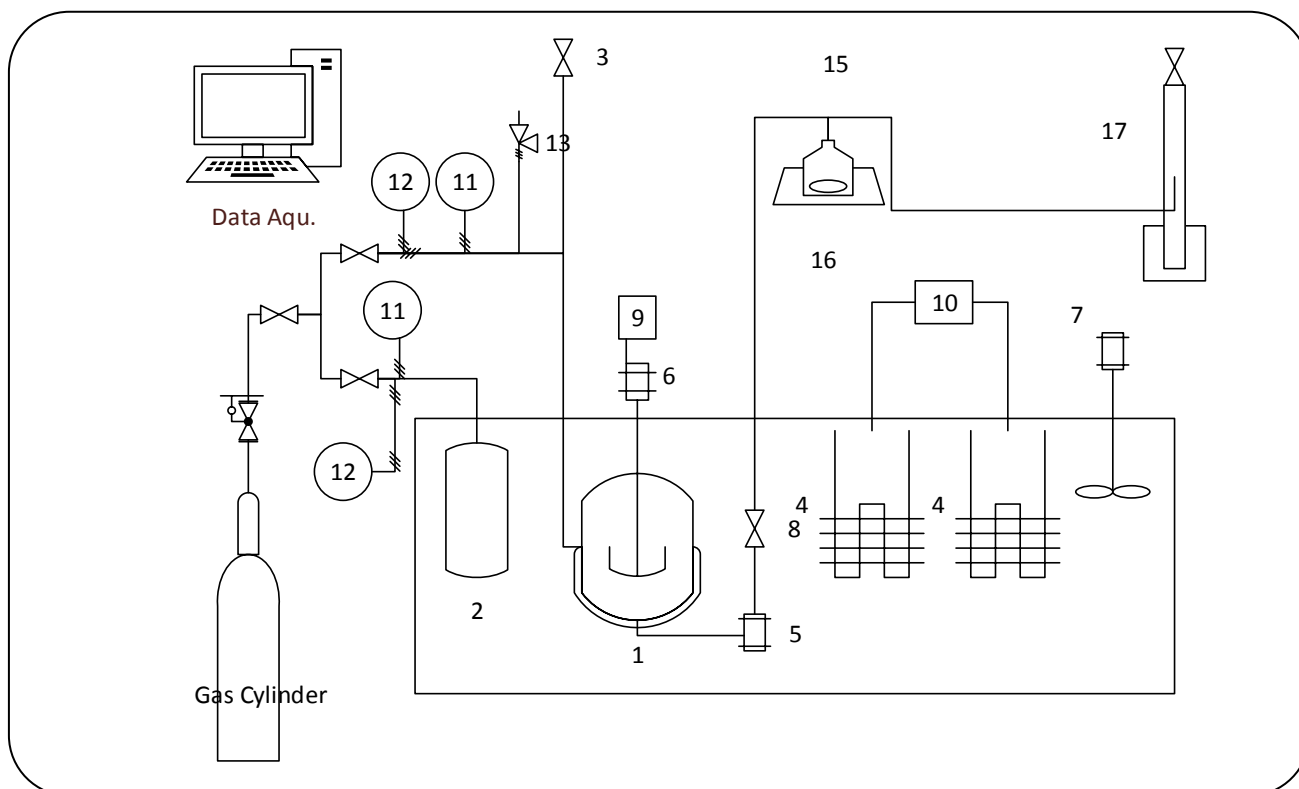


Fig. 1: Schematic of the experimental set-up: (1) main cell; (2) auxiliary cell; (3) vacuum pump; (4) heater and refrigerator for control temperature of system; (5) micro filter (metering valve); (6) electromotor; (7) mixer; (8) metering valve; (9) Programmable switch to control the rotation speed of motor; (10) programmable controller to control the temperature of the bath; (11) pressure gauge; (12) temperature indicator; (13) safety valve; (14) pressure transducer; (15) Erlenmeyer; (16) magnetic stirrer; (17) inversed burette filled with water.

The elements of P , R , T , and P_{H_2O} in Eq. (1) are the atmospheric pressure, universal gas constant, ambient temperature, and partial pressure of water at room temperature, respectively. The values of P_{H_2O} are obtained from Perry's Handbook [20].

Accordingly, the mole fraction (x) of gas components can be calculated via to Eq. (2).

$$x = \frac{n_i^G + \frac{x_{amb} n_{H_2O}}{1 - x_{amb}}}{n_i^G + \frac{x_{amb} n_{H_2O}}{1 - x_{amb}} + n_{H_2O}} \quad i = \text{methane, ethane} \quad (2)$$

x_{amb} denotes the mole fraction of gases dissolved in water in ambient conditions. Henry's law can be used to estimate solubility in atmospheric conditions [21]. In Eq. (2), n_{H_2O} denotes the mole of water in the Erlenmeyer flask.

RESULTS AND DISCUSSION

Three types of experiments were performed in this study. To verify the reliability of the measurements, several tests have been performed on the non-hydrate region (the first type). The mole fraction of methane and ethane was measured 10 minutes after the hydrate formation (the second types). Finally, the dependency of the mole fraction on time was studied (the third series). To determine the equilibrium conditions of the hydrate formation, the equilibrium data were used in the literature [1].

Non-Hydrate Conditions

In order to show the validity of the setup and the procedure, the equilibrium solubility of methane and ethane was measured (Tables 1 and 2) in non-hydrate conditions. Subsequently, the measured data were compared with the available experimental data [21,22]. The ranges of temperature and pressure for methane used in the present research were 274.15 to 282.15 K and

Table 1: Comparing the experimental solubility of methane in this work and calculated solubility from the work by Mohebbi et al. [21].

Temperature(K)	Pressure(kPa)	$x_{\text{exp}} (\times 10^{-3})$	Uncertainty %	$x_{\text{cal}} (\times 10^{-3})$	Error%
274.15	1983	0.765	3.40	0.753	1.6
274.15	2550	1.057	3.23	0.954	9.7
276.15	2430	0.931	3.27	0.873	6.2
276.15	3125	1.22	3.09	1.1	9.8
278.15	2970	1.18	4.16	1	15.2
278.15	3819	1.39	3.15	1.27	8.6
280.15	3641	1.24	3.17	1.17	5.6
280.15	4682	1.51	3.14	1.47	2.6
282.15	4484	1.49	3.25	1.36	8.7
282.15	5765	1.80	3.45	1.69	6.1

Table 2: Comparing the experimental solubility of ethane in this work and calculated solubility from the work by Mohammadi and Richon [22].

Temperature(K)	Pressure(kPa)	$x_{\text{exp}} (\times 10^{-4})$	Uncertainty %	$x_{\text{cal}} (\times 10^{-4})$	Error%
276.15	671	3.66	4.91	3.47	5.2
278.15	786	4.27	4.18	4.13	3.3
280.15	1013	5.2	3.87	4.97	4.4
282.15	1335	6.33	3.57	6.07	4.1

1983 to 5765 kPa respectively. Additionally, the ranges of temperature and pressure for ethane were 276.15 to 282.15 K and 671 to 1335 kPa respectively. To calculate the solubility of methane and ethane in water, the constants of Henry's law were predicted in the studies done by Mohebbi et al. and Mohammadi & Richon [21,22]. Furthermore, SRK equation of state was used to estimate the fugacity of the gas phase [23]. Tables 1 and 2 shows close results for this work comparing to other works in the literature.

Mole Fraction in the Growth Stage

Several studies have been carried out to measure the solubility of gas hydrate formers in equilibrium conditions in liquid water [13, 14, 16, 24-26]. Servio & Englezos stated that the solubility is a function of temperature but was not a strong function of pressure [14]. In this study, the mole fraction of methane and ethane has been determined in five temperatures (274.15, 276.15, 278.15, 280.15 and 282.15K) 10 minutes after

the hydrate formation. The pressure varied from 3100 to 7765 kPa and 950 to 2635 kPa for methane and ethane respectively. Tables 3 and 4 show the measured values for different temperatures and pressures for methane and ethane, respectively. Figs. 2 and 3 illustrate the mole fraction of methane and ethane. As it can be observed, the mole fraction is a function of pressure and to a minor extent temperature. This observation is in controversy with the results of Servio & Englezos [14]. One explanation to this fact is that the range of temperature in the current study is limited to the temperatures between 274.15 and 282.15 K (narrow temperature change). Thus, temperature may have no major effect of the mole fraction.

Mole Fraction through Time

In this study, the mole fraction of methane and ethane in water in two temperatures, 274.15 and 280.15 K, was measured through the time (10, 20, 25, 30 and 40 minutes after the hydrate growth). Figs. 4-7 illustrated the gas

Table 3: The mole fraction of methane at different temperatures (10 min after hydrate growth).

Temperature(K)	Pressure(kPa)	$x_{\text{exp}} (\times 10^{-3})$	Uncertainty %
274.15	3100	1.05	3.21
274.15	3300	1.19	3.10
274.15	3500	1.30	3.10
274.15	3783	1.34	3.17
276.15	3975	1.33	3.13
276.15	4000	1.36	3.38
276.15	4350	1.44	3.09
276.15	4750	1.52	3.13
278.15	4730	1.51	3.09
278.15	4800	1.58	3.06
278.15	5192	1.62	3.04
278.15	5800	1.79	3.10
280.15	5830	1.70	3.53
280.15	6100	1.79	3.12
280.15	6600	1.90	3.15
282.15	7055	1.96	3.16
282.15*	7055	1.98	3.33
282.15	7425	2.01	3.78
282.15	7765	2.10	3.71
282.15*	7765	2.12	3.89

*Repeated

Table 4: The mole fraction of ethane at different temperatures (10 min after hydrate growth).

Temperature(K)	Pressure(kPa)	$x_{\text{exp}} (\times 10^{-4})$	Uncertainty %
274.15	950	4.99	4.65
274.15	1116	5.90	4.28
274.15	1476	7.38	3.74
276.15	1465	6.97	3.74
276.15	1614	7.60	3.40
278.15	1465	6.58	3.47
278.15	1535	6.93	3.46
278.15	1828	7.93	3.42
278.15	2217	9.42	3.31
280.15	2286	9.31	3.21
280.15	2419	9.71	3.26
282.15	2286	9.12	3.26
282.15	2419	9.45	3.52
282.15	2635	9.93	3.22

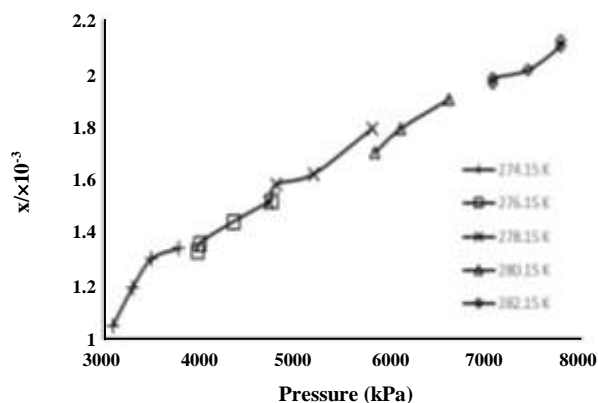


Fig. 2: Measured mole fraction of methane in different temperatures.

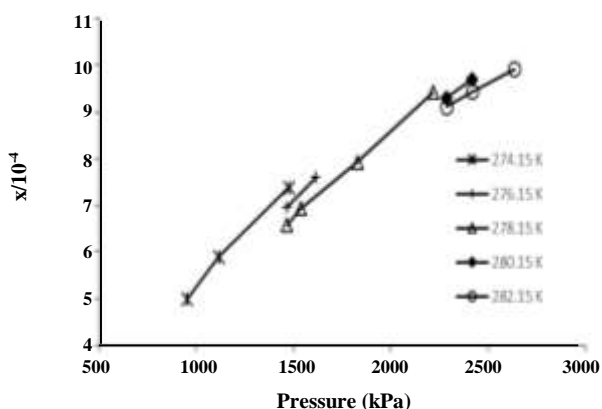


Fig. 3: Measured mole fraction of ethane in different temperatures.

content gradient in the aqueous phase. The initial point for the hydrate growth can be detected as the gas consumption rate starts.

As it was shown in Figs. 4-7, the mole fraction of CH_4 and C_2H_6 during hydrate formation does not change considerably with time. Several researchers assumed the change in the fugacity (or concentration) in the solution corresponding with time in their modeling [5,27,28]. In their modeling, the mass transfer resistance and the gas hydrate reaction around the solid particles were considered. Therefore, the change in the bulk fugacity or concentration should be considered in their modeling (df_b/dt).

Owing to the direct relationship between concentration (mole fraction) and fugacity, the fugacity also did not change considerably along with time. These results are in agreement with those found previously

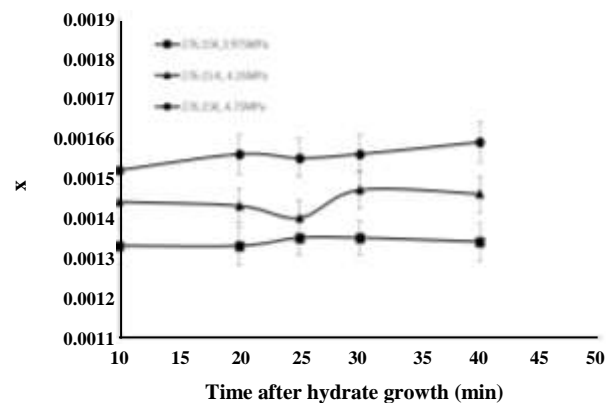


Fig. 4: Mole fraction of methane in water during hydrate growth in various pressure ($T= 276.15 \text{ K}$).

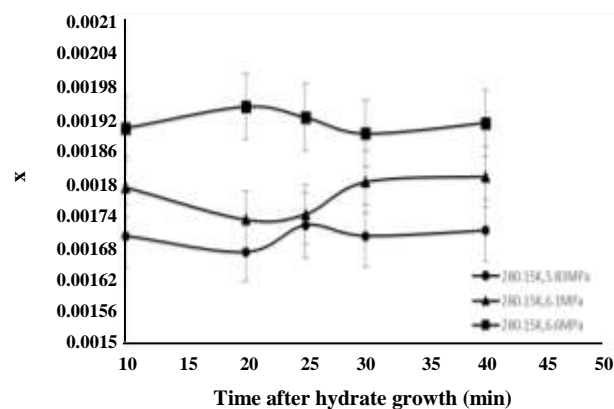


Fig. 5: Mole fraction of methane in water during hydrate growth in various pressure ($T= 280.15 \text{ K}$).

by Najafi & Mohebbi [19]. Several studies on the kinetics of hydrate formation have confirmed that the fugacity or the mole fraction changes with time in the aqueous phase [5,7,29]. For example, Skovborg & Rasmussen [7] used the difference in gas mole fraction at the gas-liquid interface and in the bulk-liquid phase as the driving force and assumed it varies with time. But this work indicates that the mole fraction of methane and ethane in aqueous phase tends to remain constant, which can be used for modeling of gas composition in the aqueous phase during the hydrate growth and simplifying the complex calculations of kinetic modeling significantly [30,31].

CONCLUSIONS

In this study, several tests were carried out to determine experimentally the mole fraction of methane and ethane during hydrate formation in a semi-batch reactor.

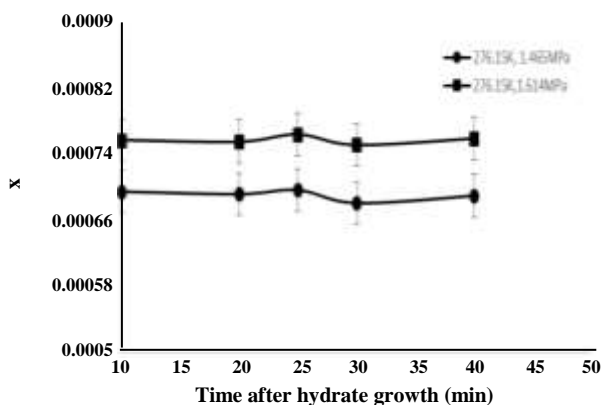


Fig. 6: Mole Fraction of ethane in water during hydrate growth in various pressure (T= 276.15 K).

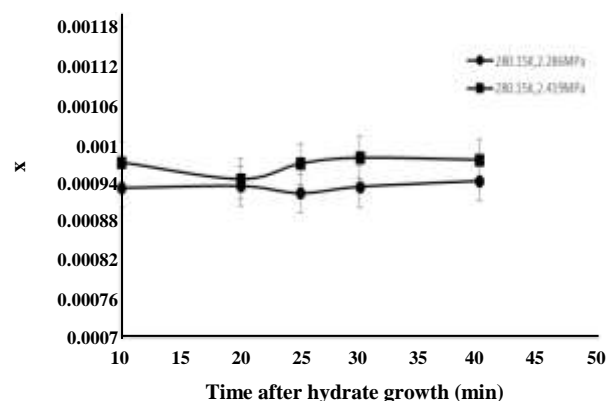


Fig. 7: Mole Fraction of ethane in water during hydrate growth in various pressure (T= 280.15 K).

The pressure and temperature were kept constant using a Ruska pump and external cooling system. A small amount of water phase was extracted from the cell and flashed in each experiment. The volume of the released gas was then determined. It was found out that the methane and ethane content in aqueous phase is strongly a function of pressure and, to a lesser degree, temperature. Furthermore, several experiments were conducted to observe the mole fraction change with time. It was observed that the mole fraction of gaseous guest molecules in water does not significantly change with time. The results from this work, showed that the driving force and the bulk fugacity are approximately constant during the hydrate formation.

Nomenclature

F	Fugacity
H	Hydrate
L	Liquid
n	Moles
PC	Personal computer
P	Pressure, kPa
R	Universal gas constant, J/K mol
T	Temperature, K
V	Volume, m ³
x	Mole fraction

Subscripts and superscripts

amb	Ambient
cal	Calculated
exp	Experiment

i	Component
G	Gas
V	Vapor
W	Water

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