Phase Stability and Kinetics of CH 4 + CO 2 + N 2 Hydrates in Synthetic Seawater and Aqueous Electrolyte Solutions of NaCl and CaCl 2

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Phase Stability and Kinetics of CH_4 + CO_2 + N_2 Hydrates in Synthetic Seawater and Aqueous Electrolyte Solutions of NaCl and $CaCl_2$

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ABSTRACT: The hydrate formation and dissociation in aqueous electrolyte (NaCl and $CaCl_2$) solution of different concentrations and in synthetic seawater with CH_4 + CO_2 + N_2 mixture have been studied. Experiments were performed in saltwater of 2 % (w/v) and 3 % (w/v) NaCl and $CaCl_2$ and in synthetic seawater with salinity 3.27 % (w/v), 3.40 % (w/v), and 3.66 % (w/v). Phase-equilibrium conditions for multicomponent hydrocarbon-saline water mixture have been determined experimentally. Both the electrolyte, i.e., NaCl and $CaCl_2$ significantly inhibited the formation of hydrate. It has also been noticed that the increase in salinity shifts the phase equilibrium curve more toward the inhibited zone. The phase equilibrium of hydrate in synthetic seawater has also been investigated, and the enthalpy of dissociation of hydrates has been calculated using the Clausius−Clapeyron equation. The kinetics of hydrate formation have also been studied to measure the induction time and hydrate formation rate. Further the amount of gas consumes by water to form hydrate has been calculated using the real gas equation.
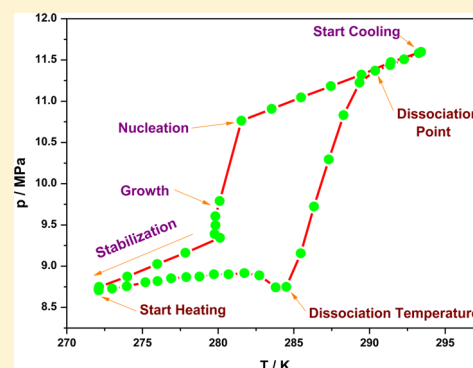
INTRODUCTION

Gas hydrates are nonstoichiometric crystalline compounds in which gas molecules are present inside cages formed by water molecules with the help of hydrogen bonds and stabilized due to van der Waal's forces.[1] Many gas molecules, i.e., CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, CO_2, H_2, N_2, H_2S, He, etc. can form hydrates under favorable condition.[2−5] The favorable conditions for formation of hydrate are generally high-pressure and low-temperature.[6] All known common hydrates form three crystal structures depending upon the type and number of cavities formed by water and the molecular size of the guest molecules. These are cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH).

There are lots of studies available on methane hydrate formation and dissociation. But knowledge of the hydrate-forming conditions of the $CH_4/CO_2/N_2$ mixture is also important for natural gas handling, processing, and transportation as natural gas contains these gases also besides methane. There are also few literature available on hydrate forming condition with carbon dioxide and nitrogen mixture.[7−14] Rajnauth et al. (2010) noticed that CO_2 reduces the pressure/temperature equilibrium line, while N_2 increases it.[15]

Many researchers have reported the thermodynamic inhibition of gas hydrate by methanol, monoethylene glycol, diethylene glycol, and some other electrolytes. But the problem with methanol and glycol is that they require in large concentration, which increases the costs and has serious environmental impacts.[16] Apart from those above-mentioned organic inhibitors, inorganic electrolyte solutions of NaCl, $CaCl_2$, etc. can also effectively inhibit hydrate formation. Thus, it is vital to know the influence of an individual electrolyte to accurately estimate the formation and dissociation conditions of hydrates in saline water.

Several researchers had studied the hydrate formation and dissociation in the aqueous electrolyte solution. Dholabhai et al. studied the equilibrium condition of CH_4 + CO_2 hydrate formation in aqueous electrolyte solutions of NaCl, KCl, $CaCl_2$, and their mixture. They found that inhibiting effect of electrolyte increases with a higher ionic strength.[17] Similar results were obtained by Mei et al. in their study.[18] They reported that the inhibiting effect of NaCl is more than $CaCl_2$. Sabil et al. reported that NaCl decreases the consumption of CO_2 during the hydrate formation process.[19] Mei et al. reported experimental data on the hydrate formation condition from water containing NaCl, $NaHCO_3$, and $MgCl_2$ with methane and nitrogen mixture.[20] Fan et al. studied the effect of $CH_4/C_2H_6/N_2$ in CO_2 rich gas mixtures on the formation conditions of hydrate in water and aqueous solution of NaCl.[21] Lee et al. studied the phase equilibria of natural gas hydrate in the presence of methanol and ethylene glycol at various concentrations and in the presence of salt.[22] Mohammadi et al. reported experimental data for CH_4, C_2H_6, C_3H_8, and CO_2 hydrate dissociation in the presence of NaCl, KCl, and $CaCl_2$ aqueous solutions at different salt concentrations.[23]

There is a large amount of natural gas trapped as hydrate in marine sediment. So it is important to know the hydrate phase behavior in saline seawater for the production of gases from those hydrate reservoirs. Rouher and Barduhn[24] studied desalination process of seawater analyzing equilibrium data of isobutane hydrates in seawater. Englezos and Bishnoi[25]
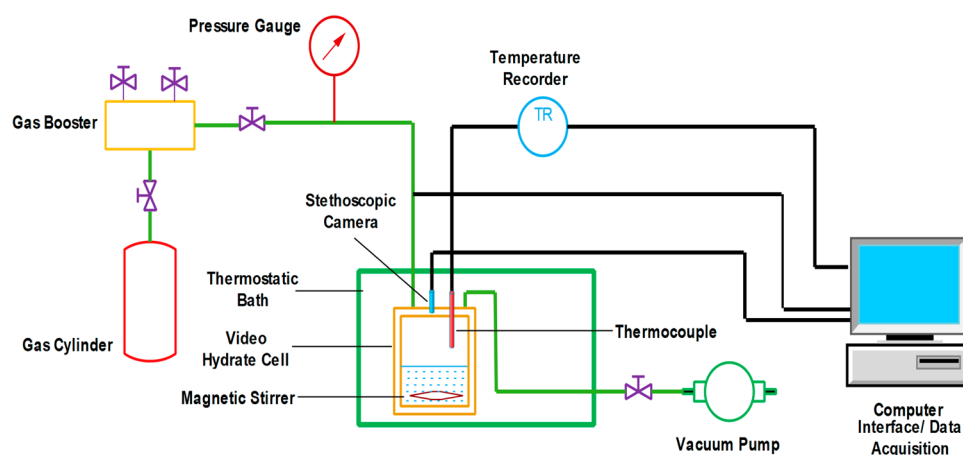
Figure 1. Schematic diagram of the gas hydrate setup.

developed a model for prediction of water activity and hydrate stability conditions for methane in artificial seawater. Dholabhai et al.[26] studied methane hydrate equilibrium conditions in varying concentrations of NaCl + KCl, NaCl + CaCl$_2$, and in synthetic seawater. Ohgaki et al.[27] studied phase equilibrium condition of CO$_2$ hydrate in pure water and synthetic seawater. Phase equilibrium data for CH$_4$ hydrate in natural seawaters were also determined by Dickens and Quinby-Hunt[28] and Maekawa and Imai.[29] Tishchenko et al.[30] developed a correlation for predicting CH$_4$ hydrate equilibrium condition in seawaters of various salinities. Atik et al.[31] studied the phase equilibrium condition of CH$_4$ hydrate in artificial seawater experimentally.

In this paper, we have studied the phase equilibrium of CH$_4$ + CO$_2$ + N$_2$ hydrates in the aqueous electrolyte solution of NaCl and CaCl$_2$ of different concentration and in synthetic seawater. The work is focused on how dissociation behaviors change with different salt and also with different concentrations. The kinetics of hydrate formation have also been studied to measure the induction time of hydrate formation. Gas consumption during hydrate formation and rate of hydrate formation have also been calculated.

■ EXPERIMENTAL SECTION

Apparatus. The schematic diagram of the gas hydrate autoclave apparatus is shown in Figure 1. The high-pressure hydrate autoclave was manufactured by Vinci Technology, France. The apparatus measures the pressure and temperature at which hydrate is stable. It can measure the induction time and pressure−temperature as a function of time during hydrate formation and can also take video pictures during the experiments. The system consists of a cell with a capacity of 250 cm^3. Maximum allowable working pressure is 20.68 MPa. The cell is a stainless-steel cylinder, where a stethoscopic camera, a thermocouple, and a pressure digital gauge are fitted to the top of the cell. The temperature in the cell is controlled by a thermostatic fluid (a mixture of 85% water and 15% glycol) with an operating temperature range from −10 to 60 °C. The bath size is about 225 × 370 × 429 mm. The temperature inside the cell is measured by a thermocouple with an accuracy of ±0.1 °C. The cell pressure is measured by a pressure transducer. Pressure uncertainty for the pressure transducer is ±0.005 MPa. The fluid inside the cell is agitated by a magnetic stirrer with adjustable rotation speed (up to 1000 rpm). In this present work all the experiments were performed

at constant rotational speed (1000 rpm) throughout the experiments. The autoclave setup is also attached with a gas booster to build up high pressure inside the hydrate cell, and a vacuum pump is used to evacuate air in the cell before inserting gas.

Materials. The gas mixture used in the present study were procured from Ultra Pure Gases (I) Pvt. Ltd. Gujrat, India. The composition of the gas mixture is listed in Table 1. All of the

Table 1. Composition of Gas Mixture

component	concentration (mole %)	accuracy (%)
methane	89.89	± 1
carbon dioxide	5.00	± 1
nitrogen	balance	

experiments were performed with deionized water from Millipore water system (Millipore SA, 67120 Molshein, France). The different salts (purity 98 % to 99.9 %) used for preparing saline water were supplied by Merck Specialties Pvt. Ltd., Mumbai, India. The compositions of synthetic seawaters used in this work are shown in Table 2 along with the reported composition in literature. Three samples of seawater were used with different salinity as reported in Table 2.

Procedure. Our previous work describes the experimental procedure in detail.[32] Briefly, 120 cm^3 of saline water was taken into the autoclave cell and then immersed the cell in the thermostatic bath containing water and glycol. Then the gas mixture was injected into the cell and attained the required pressure after removing the air from the cell through a vacuum pump. The initial starting temperature was 20 °C. The cell was then cooled stepwise to attain the hydrate formation environment. The gas mixture and the saline solution were agitated by a magnetic stirrer. The formation of hydrate was detected by a sudden drop in pressure. After hydrate formation, the entire cell was heated at a rate of 1 K·h^{-1} to decompose the hydrates until the heating curve meets the cooling curve.

■ RESULTS AND DISCUSSION

Experiments were started with formation methane hydrate in water to know the reliability of our setup. The phase equilibrium data for the CH$_4$ hydrate in pure water were obtained and compared with the data available in the literature.[33,34] The results shown in Figure 2 indicate that our apparatus are in good agreement with the literature values.

Table 2. Overview of Seawater Compositions

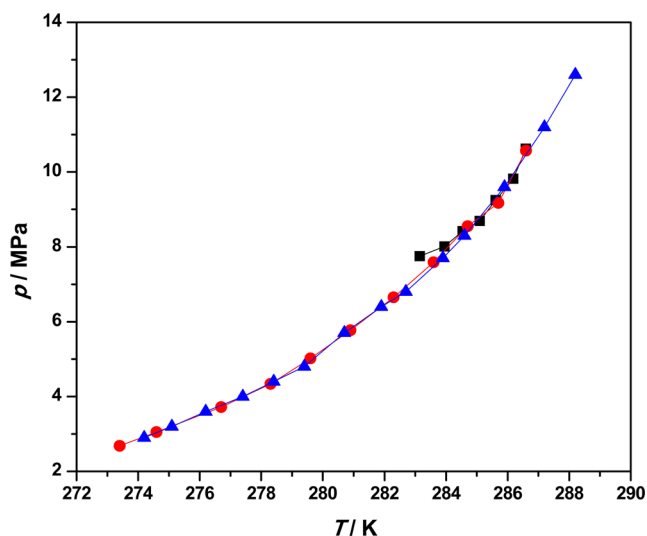| compound and purity (mass %)	reported composition[28,31] (g·L⁻¹)	present study		
		composition of synthetic seawater I (g·L⁻¹)	composition of synthetic seawater II (g·L⁻¹)	composition of synthetic seawater III (g·L⁻¹)
$NaCl$ (≥ 99.99 %)	22.0–26.44	23.0	23.5	24.66
KCl (≥ 98 %)	0.65–0.76	0.65	0.70	0.76
$CaCl_2$ (≥ 98 %)	0.71–1.16	0.71	1.00	1.15
$MgCl_2$ (≥ 98 %)	2.56–9.70	4.56	5.00	5.56
Na_2SO_4 (≥ 98 %)	3.31–4.07	3.31	3.35	4.07
$SrCl_2$ (≥ 97 %)	0–0.02	0.02	0.02	0.02
KBr (≥ 99 %)	0–0.11	0.10	0.10	0.10
NaF (≥ 97 %)	0–0.09	0.09	0.09	0.09
$NaHCO_3$ (≥ 99.8 %)	0.20	0.20	0.20	0.20
H_3BO_3 (≥ 99.5 %)	0.03	0.03	0.03	0.03
salinity (g·L⁻¹)	32.5–36.6	32.67	33.99	36.64

Figure 2. Phase equilibrium of CH_4 hydrate in pure water: ■, this work; ●, Adisasmito et al.;[34] ▲, Maekawa.[33]

Phase Equilibrium Stability of Hydrates. In this study the equilibrium pressure and temperature plots for hydrate of $CH_4 + CO_2 + N_2$ for various concentrations of NaCl (2, 3 (w/v) %); $CaCl_2$ (2, 3 (w/v) %), and synthetic seawater (3.27, 3.40, 3.66 (w/v) %) in an aqueous system have been determined experimentally. Figure 3 shows the $CH_4 + CO_2 +$
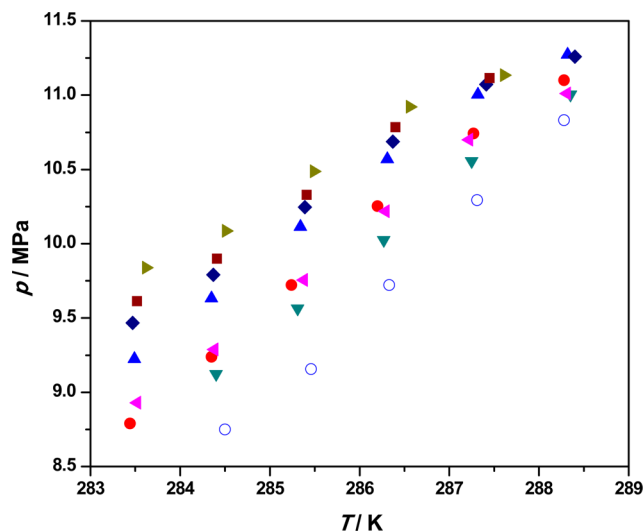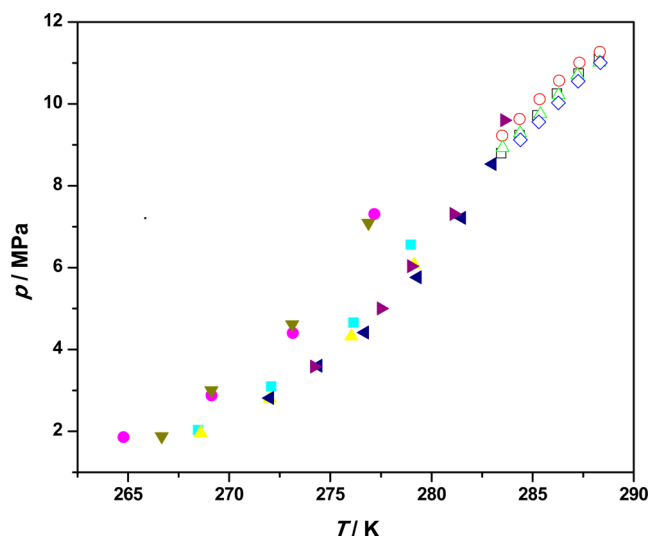

Figure 3. Phase equilibrium of $CH_4 + CO_2 + N_2$ hydrates in NaCl, $CaCl_2$, and synthetic seawater: ○, pure water; ●, 2 % (w/v) NaCl; ▲, 3 % (w/v) NaCl; ▼, 2 % (w/v) $CaCl_2$; ◄, 3 % (w/v) $CaCl_2$; ►, 3.66 % (w/v) TDS; ♦, 3.27 % (w/v) TDS; ■, 3.40 % (w/v) TDS.

N_2 hydrate phase equilibrium plot in different concentration of NaCl and $CaCl_2$ along with synthetic seawater of different salinities. The phase equilibrium condition of $CH_4+CO_2+N_2$ hydrate in the presence of NaCl and $CaCl_2$ is also summarized in Table 3. Effect of NaCl and $CaCl_2$ on hydrate phase equilibrium from some selected literature data is shown along with our results in Figure 4. The phase equilibrium of mixture of $CH_4/CO_2/N_2$ hydrate is significantly influenced by the electrolytes present in the solution. The addition of these salts to pure water decreases the stability of gas hydrates.[26,35−37] Addition of 2 % (w/v) NaCl to the $CH_4 + CO_2 + N_2$ gas

Table 3. Experimental Data on Hydrate Equilibrium Conditions of Methane/Carbon Dioxide/Nitrogen Mixture in Aqueous Electrolyte Solution

sl. no.	salt	exp. no.	conc. (% w/v)	p/MPa	T/K
1	without salt	1		8.75	284.50
				9.16	285.46
				9.72	286.33
				10.29	287.31
				10.83	288.28
				11.23	289.34
2	NaCl	2	2	8.79	283.44
				9.24	284.35
				9.72	285.24
				10.25	286.20
				10.74	287.27
				11.10	288.28
				11.29	289.28
		3	3	9.23	283.49
				9.63	284.35
				10.12	285.34
				10.57	286.31
				11.00	287.32
				11.27	288.32
3	CaCl₂	4	2	9.12	284.40
				9.56	285.31
				10.03	286.27
				10.56	287.25
				11.00	288.35
				11.20	289.36
		5	3	8.93	283.52
				9.29	284.38
				9.76	285.38
				10.22	286.29
				10.70	287.22
				11.01	288.31

Figure 4. Comparison of experimental phase equilibrium data of this work with some previously reported experimental data: □, 2 % (w/v) NaCl (this work); ○, 3 % (w/v) NaCl (this work); △, 3 % (w/v) CaCl₂ (this work); ◇, 2 % (w/v) CaCl₂ (this work); ■, 10 % (w/v) NaCl (80 % CH₄ + 20 % CO₂) (Dholabhai et al.[17]); ●, 15 % (w/v) NaCl (80 % CH₄ + 20 % CO₂) (Dholabhai et al.[17]); ▲, 10 % (w/v) CaCl₂ (80 % CH₄ + 20 % CO₂) (Dholabhai et al.[17]); ▼, 15 % (w/v) CaCl₂ (80 % CH₄ + 20 % CO₂) (Dholabhai et al.[17]); ◀, 5 % (w/v) CaCl₂ (CH₄) (Mohammadi et al.[23]); ▶ 5 % (w/v) CaCl₂ (CH₄) (Mohammadi et al.[23]).

system suppress the hydrate formation temperature by about 1.98 K. Similarly, addition of 2 % (w/v) CaCl₂ suppress the formation temperature by about 1.02 K. This inhibiting effect of electrolytes can be seen from the pressure−temperature plot of CH₄ + CO₂ + N₂ hydrate dissociation in pure water and different concentration of NaCl and CaCl₂ in Figure 3. When an inhibitor is added to the system, the phase equilibrium curve moves to a relatively high pressure and low temperature zone. As the concentration of the inhibitor increases, the hydrate phase equilibrium curve moves further into the inhibited region, i.e., toward high pressure and low temperature zone. Addition of 3 % (w/v) NaCl shifts the equilibrium curve more toward left and suppress the hydrate formation temperature by 1.98 K, while 2 % (w/v) NaCl suppress only 1.09 K. A similar trend is shown by CaCl₂ also. It has been already known that the hydrate stability in saline solution decreases as the concentration of salt in solution increases.[38,39] As the concentration of salt in solution increases, the hydrate formation temperature decreases at a given pressure. Figure 3 shows that, as the concentration of salt in solution increases the phase equilibrium curve shifts toward higher pressure and lower temperature, thus showing more inhibiting effect. Comparing the inhibition effect of NaCl in CH₄ + CO₂ + N₂ gas mixture with that of CaCl₂, an addition of 3 % (w/v) NaCl to the pure water system causes a temperature suppression of about 1.98 K, while CaCl₂ of same concentration only suppress hydrate

formation by about 1.06 K. Thus, we can see that inhibiting effect of NaCl in the CH₄ + CO₂ + N₂ gas system is more than CaCl₂. Similar results were also reported in literature by researcher earlier. In 1994, Dholabhai et al. studied phase equilibrium conditions of CH₄ + CO₂ hydrates in aqueous electrolyte solutions of NaCl, CaCl₂, KCl, and their mixture at varying ionic strengths.[17] Their result shows that hydrate with NaCl solution forms at higher pressure and lower temperature. Mei et al. also reported that hydrates with NaCl forms at lower temperature than CaCl₂.[18]

The equilibrium pressure and temperature of CH₄ + CO₂ + N₂ hydrate formation in synthetic seawater of different salinity [3.27, 3.40, 3.66 (w/v) %] has also been studied. Figure 3 shows the phase equilibrium curve of CH₄ + CO₂ + N₂ hydrates in synthetic seawater of different salinity and it is summarized in Table 4. Addition of individual salts (e.g., NaCl, CaCl₂, etc.) to water depressed the equilibrium temperature by a constant amount with respect to pure water system for certain pressure ranges has already been shown in Figure 3. As seawater contains different salts of varying concentration, the net effect of all these dissolved ions in seawater also depressed the equilibrium temperature for CH₄ + CO₂ + N₂ hydrate stability by a constant amount (Figure 3). For seawater with salinity of 3.27% (w/v), the equilibrium temperature of CH₄ + CO₂ + N₂ hydrate is offset by approximately 1.96 K with respect to the pure water system (Figure 3). It has also been seen that as salinity of seawater increases, the hydrate equilibrium curve moves to high pressure and low temperature zone. Analyzing the CH₄ + CO₂ + N₂ hydrates in synthetic seawater, when the salinity of the seawater increases from 3.27 (w/v) % to 3.66 (w/v) % the temperature depression relative to pure water system increases from around 1.96 K to 2.71 K.

Dissociation Enthalpies of CH₄ + CO₂ + N₂ Hydrates in Aqueous Electrolyte Solutions and Synthetic Seawater.

Table 4. Experimental Data on Hydrate Equilibrium Conditions of Methane/Carbon Dioxide/Nitrogen Mixture in Synthetic Seawater

sl. no	exp. no.	seawater salinity (% w/v)	p/MPa	T/K
1	6	3.27	9.47	283.47
			9.79	284.37
			10.25	285.39
			10.69	286.37
			11.07	287.41
2	7	3.40	9.61	283.52
			9.90	284.41
			10.33	285.41
			10.79	286.40
			11.12	287.45
3	8	3.66	9.84	283.62
			10.09	284.51
			10.49	285.49
			10.92	286.56
			11.14	287.6

The dissociation enthalpy is the change in enthalpy during dissociation of gas hydrate. According to Sloan,[41] dissociation enthalpy depends on the following factors: the hydrogen bonds that forms the cages, the cavity occupation, and the size of guest gas molecule.

One can measure the heat of dissociation (ΔH_{diss}) of hydrate formation in a calorimetric experiment. The determination of enthalpy of dissociation by calorimetric method has been reported by many authors.[42−45] Handa[46] measured enthalpy of dissociation of two naturally occurring hydrate samples collected from the field by a calorimeter. He mentioned that calorimetric measurement of dissociation enthalpy for gas hydrate is difficult because hydrates are stable either at low temperature or high pressure. But the accuracy of calorimetric measurement is better than those calculated from the phase equilibrium data.

Sloan and Fleyfel[47] calculated dissociation enthalpy of hydrates by using the Clausius−Clapeyron equation, shown below:

$$\frac{d \ln p}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{diss}}{zR} \tag{1}$$

where p is pressure, T is temperature, z is compressibility factor for gas and is determined by Brill−Begs correlation for the compressibility factor,[48] R is universal gas constant ($R = 8.314$ J·mol^{-1}·K^{-1}), and ΔH_{diss} is the dissociation enthalpy of gas hydrates.

Figure 5 shows the plot between $\ln p$ versus $1000/T$ for NaCl and CaCl$_2$ salts and synthetic seawater. As seen from figures, $\ln p$ versus $1000/T$ exhibits a very good linear relation at all concentration of salts in water.

The dissociation enthalpies of CH$_4$ + CO$_2$ + N$_2$ hydrates in aqueous electrolyte solutions and synthetic seawater determined using Clausius−Clapeyron equation is shown in Table 5.

As the concentration of salt in solution increases the enthalpy of dissociation decreases. Chen et al.[49] reported in their study that the enthalpy of dissociation decreases with the increase in concentration of NaCl in solution. The same trend has been noticed in Table 5 for CH$_4$ + CO$_2$ + N$_2$ hydrates in NaCl and CaCl$_2$ aqueous electrolyte solution. Dissociation enthalpies of CH$_4$ + CO$_2$ + N$_2$ hydrates in synthetic seawater determined via
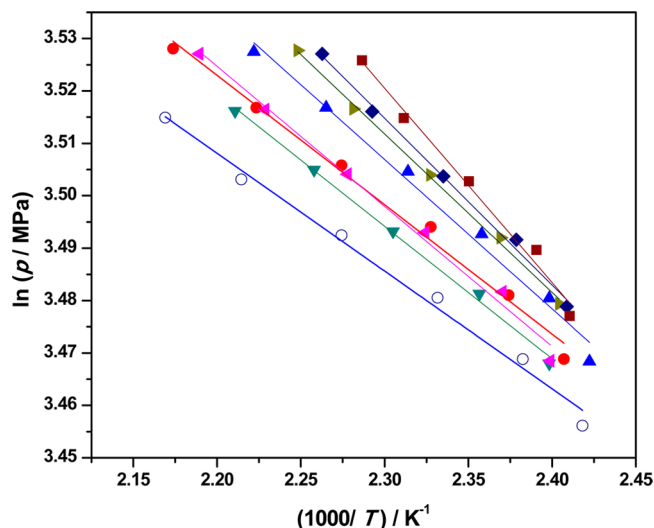
Figure 5. Semilogarithmic plots of pressure versus reciprocal temperature for NaCl and CaCl$_2$ salt solution and synthetic seawater: O, pure water; ●, 2 % (w/v) NaCl; ▲, 3 % (w/v) NaCl; ▼, 2 % (w/v) CaCl$_2$; ◄, 3 % (w/v) CaCl$_2$; ►, 3.27 % (w/v) TDS; ♦, 3.40 % (w/v) TDS; ■, 3.66 % (w/v) TDS.

Table 5. Dissociation Enthalpies of CH$_4$ + CO$_2$ + N$_2$ Hydrates in Aqueous Electrolyte Solutions and Synthetic Seawater

salt	exp. no.	conc./TDS % (w/v)	ΔH_{diss}/kJ·mol^{-1}
pure water	1		29.38
NaCl	2	2	24.06
	3	3	22.89
CaCl$_2$	4	2	23.34
	5	3	22.60
synthetic seawater	6	3.27	21.75
	7	3.40	20.57
	8	3.66	17.50

the Clausius−Clapeyron equation is reported in Table 5, and it shows a decrease of enthalpy with an increase in salinity of the seawater. A similar decrease of dissociation enthalpy with increasing salinity has also been observed by Saw et al.[40] in synthetic seawater but with methane hydrate system.

Induction Time and Gas Consumption during Hydrate Formation in Aqueous Electrolyte Solutions and Synthetic Seawater. Hydrate is not formed immediately, even though gas and water are placed in the suitable pressure and temperature region. A certain amount time is required to initiate hydrate nucleation. This time lapse is known as the induction time. Based on the individual measuring techniques different authors[50−52] have given different definitions of the induction time. In this work, we define the induction time as the time from the first contact between the gas molecule and water to the time of the appearance of first crystal of hydrate indicated by the spikes seen in the temperature profile.

To measure the induction time, the process sample (gas and aqueous electrolyte solution) is adjusted to the temperature and pressure where hydrate is completely dissociated, i.e., the dissociation point or equilibrium point of the hydrate and allows the process sample to achieve that temperature where hydrate begins to form, i.e., the nucleation temperature. The time taken during this process is the induction time or
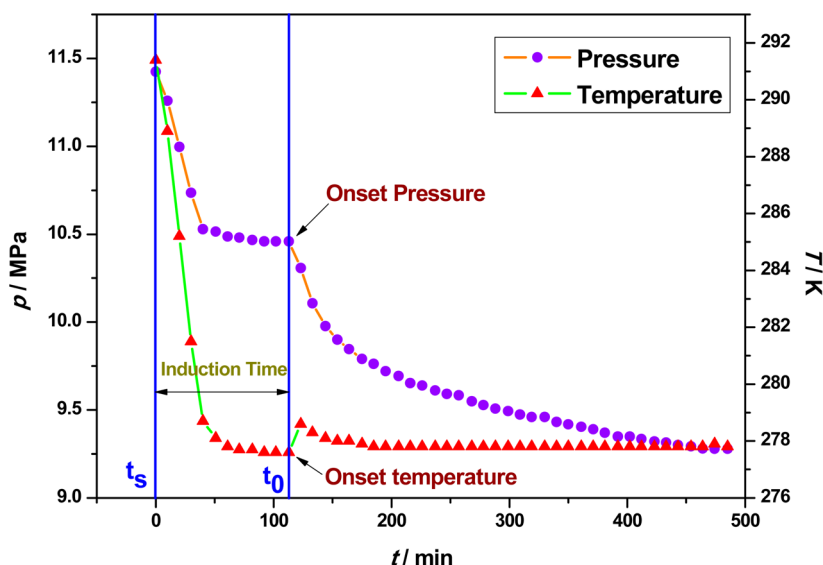
Figure 6. Temperature−pressure response during hydrate formation in 2 % (w/v) NaCl in water under 11.66° subcooling.

nucleation time. The temperature- pressure response during the measurement of the induction time is shown in Figure 6.

The induction time measured is the difference in the hydrate onset time (t_o) and the start time (t_s) of the experiment where hydrate is completely dissociated, i.e., the dissociation point of the hydrate. The hydrate onset time is taken as t_o, where the pressure suddenly falls, followed by an increase in the temperature. This temperature rise is due to the release of the latent heat of crystallization when aqueous solution and gas molecules rearrange themselves into the hydrate state.

The induction time and gas consumption during the formation of hydrate in the presence of NaCl, CaCl$_2$, and synthetic seawater are presented in Table 6.

Table 6. Induction Time and Gas Consumption during Hydrate Formation in Aqueous Electrolyte Solution and Synthetic Seawater

salt	exp. no.	conc./TDS % (w/v)	induction time t/min	gas consumed at the end of exp. n/mol
pure water	9		93	$11.88 \cdot 10^{-2}$
NaCl	10	2	123	$10.95 \cdot 10^{-2}$
	11	3	185	$9.88 \cdot 10^{-2}$
CaCl$_2$	12	2	92	$9.36 \cdot 10^{-2}$
	13	3	81	$8.0 \cdot 10^{-2}$
synthetic seawater	14	3.27	71	$9.7 \cdot 10^{-2}$
	15	3.40	51	$8.2 \cdot 10^{-2}$
	16	3.66	51	$7.9 \cdot 10^{-2}$

The amount of gas consumed during hydrate formation can be calculated from the real gas equation

$$\Delta n = n_i - n_f = \frac{V}{R} \left(\frac{p_i}{z_i T_i} - \frac{p_f}{z_f T_f} \right) \qquad (2)$$

where n is the amount of gas consumed during hydrate formation, V is volume of gas, p_i, T_i and p_f, T_f are the pressure and temperature at initial and final condition respectively, R is the universal gas constant, z_i and z_f are compressibility factors measured at the corresponding pressure and temperature by Brill−Begs correlation for the compressibility factor.[48]

A comparative plot of gas consumption in NaCl, CaCl$_2$, and synthetic seawater is shown in Figure 7, Figure 8, and Figure 9,

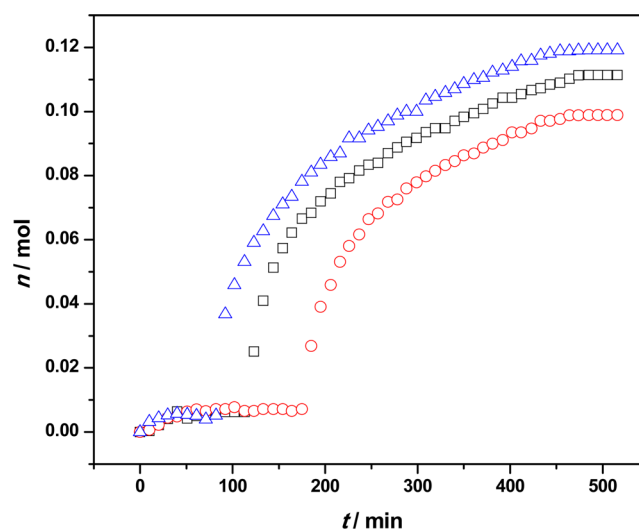**Figure 7.** Gas consumption during hydrate formation in NaCl aqueous solution: □, 2 % (w/v) NaCl; ○, 3 % (w/v) NaCl; △, pure water.

respectively. Gas consumed with pure water is maximum. It can be seen from the figures that gas consumption decreases with increase in concentration of salt in solution. Figure 10 shows the comparative plot between gas uptake until nucleation and final gas uptake.

Normalized Rate of Hydrate Formation. The normalized rate of semiclathrate hydrate formation (NR$_{30}$) was calculated as follows.[53]

$$NR_{30} = \frac{\Delta n_{30}}{V_w t} \text{(mole of gas/min /m}^3) \qquad (3)$$

where Δn_{30} is the number of moles of gas consumed at 30 min of hydrate growth, V_w is the volume of water taken for the experiment in m^3, and t is the hydrate growth time of 30 min.

Figure 11 shows a comparative plot of normalized rate of hydrate formation in 3 % (w/v) NaCl and 3 % (w/v) CaCl$_2$ salt
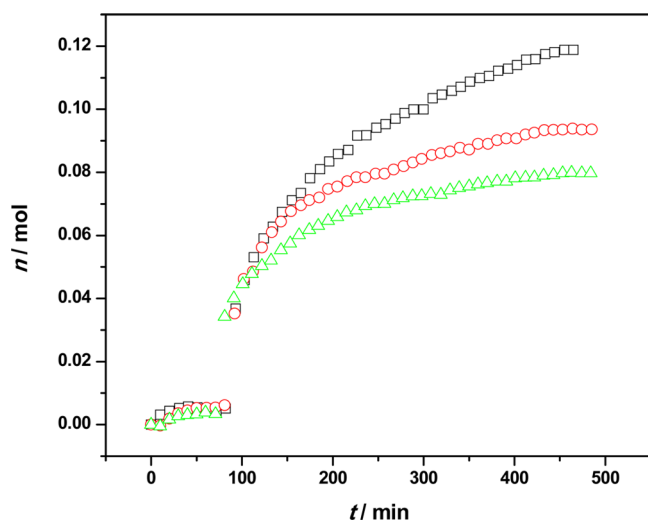
Figure 8. Gas consumption during hydrate formation in $CaCl_2$ aqueous solution: □, pure water; ○, 2 % (w/v) $CaCl_2$; △, 3 % (w/v) $CaCl_2$.

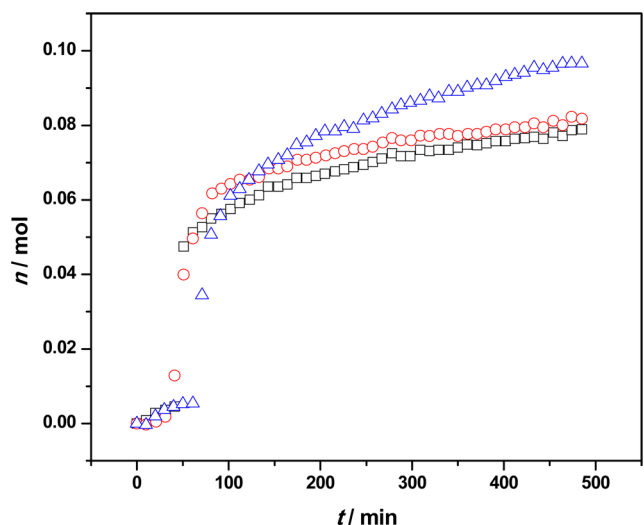**Figure 9.** Gas consumption during hydrate formation in synthetic seawater: □, 3.66 % (w/v) SSW; ○, 3.40 % (w/v) SSW; △, 3.27 % (w/v) SSW.

Figure 10. Comparative plot between gas uptake until induction point and final gas uptake.

Figure 11. Comparison of rate of hydrate formation in pure water, NaCl solution, $CaCl_2$ solution, and synthetic seawater: ■, pure water; ●, 3 % (w/v) NaCl; ▲, 3 % (w/v) $CaCl_2$; ▼, 3.40 % (w/v) TDS. Time zero in the graph corresponds to the nucleation point for the experiment.

solution and in synthetic seawater with salinity 3.40 % (w/v), respectively. The rate of hydrate formation is rapid during initial period after nucleation; then it decreases rapidly. The addition of salt decreases the average rate of hydrate formation. One can see from Figure 11 that the average rate of hydrate formation in water is greater than salt solution and synthetic seawater.

■ CONCLUSION

Experiments were performed to study the phase stability and kinetics of hydrate formation and dissociation condition in the presence of NaCl and $CaCl_2$ at different concentrations and synthetic seawater with varying salinity with $CH_4 + CO_2 + N_2$ mixture. Both NaCl and $CaCl_2$ have significantly inhibited the formation of hydrate. The addition of these salts to pure water system shifts the phase equilibrium curve to lower temperature region at a given pressure. With increase in the concentration, the inhibition effect of the salts increases. The effect with NaCl is higher than $CaCl_2$. The phase equilibrium curves are shifted

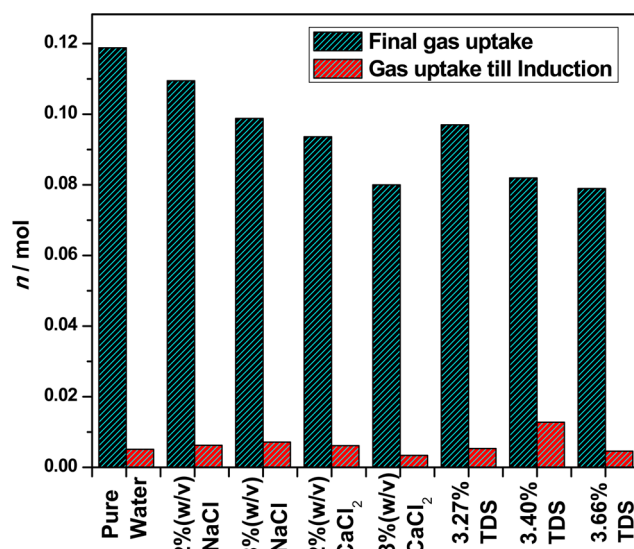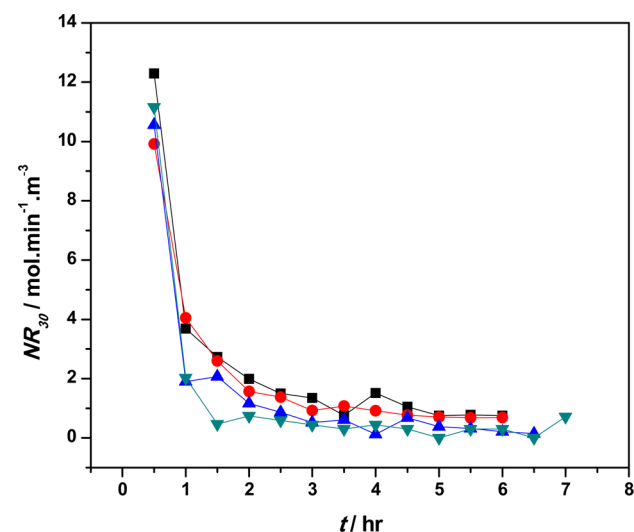to a relatively high-pressure and low-temperature zone with an increase in salinity of synthetic seawater. The dissociation enthalpies of $CH_4 + CO_2 + N_2$ hydrate in aqueous electrolyte solutions of NaCl and $CaCl_2$ and synthetic seawater were calculated using the Clausius−Clapeyron equation. Gas consumed in the formation of hydrate has been calculated using the real gas equation, and it shows that consumption of gas decreases with the increase in concentration of salt in solution. The induction time of hydrate formation and rate of formation of hydrate is also determined. The rate of hydrate formation decreases when salt is added to the pure water.

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