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Phase Equilibria and Kinetic Behavior of CO_2 Hydrate in Electrolyte and Porous Media Solutions: Application to Ocean Sequestration of CO_2

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Abstract−Understanding the phase behavior and formation kinetics of CO_2 hydrate is essential for developing the sequestration process of CO_2 into the deep ocean and its feasibility. Three-phase equilibria of solid hydrate, liquid water, and vapor were determined for aqueous mixtures containing CO_2 and NaCl/clay to examine the effect of both ocean electrolytes and sediments on hydrate stability. Due to the capillary effect by clay pores and inhibition effect by NaCl the corresponding hydrate formation pressure appeared to be a little higher than that required for simple and pure hydrate at specified temperature. In addition, the hydrate formation kinetics of carbon dioxide in pure water and aqueous NaCl solutions with or without clay mineral were also measured at various conditions. The formation kinetic behavior was found to be strongly influenced by pressure, temperature and electrolyte concentration. A simplified kinetic model having two adjustable parameters was proposed and the estimated results agreed well with the experimental data.

Key words: Carbon Dioxide, Hydrate, Kinetics, Equilibrium, Sequestration

INTRODUCTION

Clathrate hydrates (or gas hydrates) are a kind of inclusion compounds which are formed by physically stable interactions between water and relatively small guest molecules entrapped in the cavities of a three dimensional lattice-like structure built by water molecules under low temperature and high pressure conditions. Those nonstoichiometric crystalline compounds are divided into three distinct structures, I, II and H, which differ in cavity size and shape. Structure I and II hydrates consist of two types of cavities, while structure H hydrate consists of three types of cavities. The structure H hydrate especially needs both large and small guest molecules to stabilize the structure. Carbon dioxide is known to form the structure I hydrate.

The thermodynamic properties of clathrate hydrates and phase equilibria of various hydrate-forming systems have been investigated extensively and compiled historically in the various sources [Englezos, 1993; Makogon, 1997; Sloan, 1998]. However, much effort has been focused on the formation and decomposition kinetics of gas hydrates by many researchers in very recent years. Englezos et al. [1987] measured the formation kinetics of gas hydrates made from methane, ethane, and mixtures of methane and ethane in the aqueous solution. They also proposed a mechanistic model of the formation kinetics with only one adjustable parameter representing the rate constant for the hydrate particle growth. Dholabhai et al. [1993] obtained the formation kinetics of methane hydrate in various aqueous electrolyte solutions. The mechanism for gas hydrate nucleation from ice and the kinetics of hydrate formation were proposed by Sloan and Fleyfel [1991]. Natarajan et al. [1994] discussed gas hydrate nucleation by observing the induction phenomena. Bishnoi and Natarajan [1996] reviewed the formation and decomposition of gas hydrates. Chun and Lee [1996] investigated experimentally the kinetics of carbon dioxide hydrate formation. Malegaonkar et al. [1997] reported the experimental data on the formation kinetics of methane and carbon dioxide hydrates and modified slightly the kinetic model proposed by Englezos et al. [1987]. Shindo and coworkers [1993] studied the kinetics and mechanism of CO_2 hydrate formation at the interface between adjacent semi-infinite reservoirs of liquid CO_2 and water. Teng et al. [1995] derived a kinetic model of hydrate formation on the surface of a CO_2 droplet in high-pressure and low-temperature water.

Recently, the ocean disposal of carbon dioxide recovered from power plants in the form of CO_2 hydrate has been the focus of many investigators as a means to mitigate global warming [Seo et al., 2000, Sung et al., 2000]. The gas hydrate deposits in the deep oceans and in the permafrost regions have been significant as vast sources of natural gas, and it will be planned to produce the natural gas from those deposits commercially [Makogon, 1997]. Therefore, comprehensive information on the formation and decomposition kinetics of gas hydrates as well as the thermodynamics and structural properties becomes essential in solving the related problems generated from the technological point of view. In these connections the purpose of this work was mainly to investigate the phase equilibria and the formation kinetics of the carbon dioxide hydrate in pure water and aqueous NaCl solutions.

EXPERIMENTAL SECTION

1. Apparatus and Materials

The experimental apparatus schematically shown in Fig. 1 was primarily designed to measure the flow rate of a hydrate-forming gas consumed during hydrate formation that might be the most important in the kinetic study. The hydrate-forming reactor with an

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‡ This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

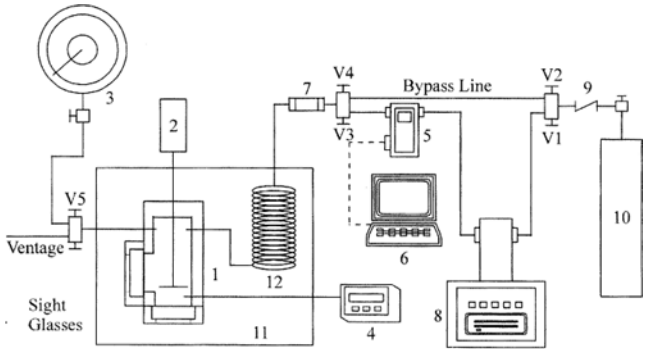

Fig. 1. Schematic diagram of the experimental apparatus of hydrate formation kinetics.

1. Reactor
2. Mechanical magnetic stirrer
3. Pressure gauge
4. Thermometer
5. High-pressure digital flowmeter
6. Data acquisition system
7. Check valve
8. Micro flow syringe pump
9. Line filter
10. Gas cylinder
11. Constant temperature water bath
12. Precooler

internal volume of about 140 cm^3 was made of a type 316-stainless-steel. It had two sight glasses equipped at the bottom and one side of the reactor that allowed a visual observation of hydrate formation inside the reactor. These sight glasses were perfectly sealed by rubber o-rings and the chamber was initially tested to the pressure of approximately 8.0 MPa. Instead of the commonly used magnetic spin bar, the magnetically-driven mechanical stirrer was used. By using this magnetic drive with strong agitation power, the three-phase mixture having hydrate solid crystals was uniformly mixed during kinetic experiment. The kinetic reactor was kept in the water-ethanol mixture bath and its temperature was controlled by an externally circulating refrigerator/heater (JEIO TECH, RBC-20). The actual temperature in the reactor was measured by a K-type thermocouple with a digital temperature readout (Cole-Parmer, 8535-26) having a resolution of ±0.1 K. A Heise gauge (CMM 44307) ranged 0 to 20.0 MPa was used to measure the reactor pressure with the maximum error of ±0.02 MPa. The reactor was initially pressured with gaseous carbon dioxide supplied from a gas cylinder and then was maintained at a constant pressure condition by using a micro-flow syringe pump (ISCO, Model 260D) operated by two different modes of constant flow rate and constant pressure. The mass flowmeter (BROOKS, Model 5850E) allowed taking an accurate measurement of the flow rate of gases, which enabled us to obtain the amount of a hydrate-forming gas consumed during the hydrate formation. It was able to measure the flow rate ranging from 0 to 1,000 ml/min in the standard condition of 273.15 K and 101.3 kPa with a resolution of ±1% of full scale. A PC-LabCard PCL-711B data acquisition system and a PC486 computer were used to get the flow rate signals from the mass flowmeter. The resolution of the PCL-711B system was 0.015% of reading. The inline filter (NUPRO) was used to remove contaminants as small as one-half micron contained in the carbon dioxide gas. Carbon dioxide with a minimum purity of 99.99 mol% was supplied by World Gas Inc. The water was double distilled and deionized. Sodium chloride was purchased from ALDRICH having a minimum purity of 99.0 mol%. The experimental measurements of the three-phase equilibrium was performed by using the same apparatus used for formation kinetics, except that an equilibrium cell made of 316-stainless-steel and its internal volume was about 50 cm^3 was used instead of a kinetic cell. To observe the inside of the cell, two sapphire sight glasses were equipped at the front and back of the cell. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell in the bath. All other specifications used in equilibrium apparatus were same with those of the kinetic apparatus.

2. Procedure

The formation kinetic experiments of the carbon dioxide hydrate were conducted under isothermal and isobaric conditions. Considering the unique phase behavior of a hydrate-forming system, the kinetic experiments were performed at pressures of 2.5, 3.0 and 3.4 MPa and temperatures of 273.15, 274.15 and 275.15 K. In particular, the pressure must be less than 3.5 MPa because the carbon dioxide is liquefied above this pressure. The reactor was initially vacuumed and then charged with 30 ml of the aqueous solution. The reactor was again purged with the carbon dioxide gas to remove the retained air gas dissolved in the solution and to clean the empty space of the reactor. When the system was cooled to the desired experimental temperature, the reactor was then pressurized below about 0.05 MPa than the $\text{H-L}_w\text{-V}$ three-phase equilibrium pressure. The solution was agitated by the mechanical stirrer for nearly one hour so that the aqueous solution was saturated with carbon dioxide gas. No further pressure change indicated the saturation of a solution and, then, the stirrer was stopped. The carbon dioxide gas was supplied to the reactor up to the pressure just below the experimental point by using the bypass line (Fig. 1). After that, the bypass line was closed and the valves, V1 and V3, were opened to supply carbon dioxide gas to the syringe pump and subsequently to the reactor. At least four hours was needed to obtain the fully stabilized state. The syringe pump was then set to a constant pressure mode and its self-operating pumping was started to maintain the system pressure constant. At the same time, the data acquisition system scanned the flow-rate signals detected by the mass flowmeter. The carbon dioxide gas consumed during supersaturation and hydrate-formation processes was instantaneously supplemented to the reactor by a syringe pump. The gas was precooled before entering the reactor. The flow rate signals from the mass flowmeter were obtained once at intervals of 0.5 s by the on-line data acquisition system. The experiment proceeded through the induction, nucleation and growth periods, successively and each period was confirmed carefully by visual observation. When the mass flowmeter decreased to the zero point after a sufficient time passed, the formation kinetic experiment was finished by stopping the stirring of the reactor. The total reaction time continued to about 150 min from the nucleation point.

In the three phase equilibrium experiments, the equilibrium cell was well cleaned initially, and then an amount of approximately 20 cm^3 of the cell contents containing sodium montmorillonite and/or NaCl was charged into the equilibrium cell. The formation of hydrate crystal could be confirmed by visual observation and pressure-temperature locus. However, for clay-containing solutions, a visual detection of carbon dioxide hydrates formed in clay pores is unattainable and therefore a hydrate phase equilibrium point was exactly determined by checking the pressure-temperature trace of hydrate formation/dissociation according to time.

KINETIC MODEL

The formation reaction of carbon dioxide hydrates is simplified to

$$CO_2\ (\text{gas})+5.75H_2O\ (\text{liquid})\rightarrow CO_2\cdot 5.75H_2O\ (\text{solid}) \tag{1}$$

where it is assumed that carbon dioxide forms structure I hydrate and all cavities are occupied by carbon dioxide molecules. Since hydrates are generally the nonstoichiometric crystalline compounds, all cavities in the unit cell of hydrate structure need not be occupied by the guest molecules.

The kinetic model proposed by Englezos et al. [1987] is based on the assumption that the transport of gas from the vapor phase to the bulk water phase is the rate-determining step for the overall process. Since they used large amounts of liquid water compared with the amount of hydrates produced, the fact that the transformation of the water into the hydrates can exhaust the water and destruct the gas-water interface between the gas and liquid phases is neglected. The gas-water interface was largely destructed very quickly in our experimental systems before entering the growth period, and thus the formation reaction could occur in the surface of the hydrate particles directly. As the amount of the water becomes smaller and smaller through the consumption of the water in the formation reaction of gas hydrates, the gas consumption rate also becomes smaller, which is different from the results of Englezos et al. [1987] having a tendency of constant gas consumption rate.

Therefore, a simplified kinetic model which considers mainly the reaction in the bulk of liquid water phase and the surface of the hydrate particles is proposed to simulate the experimental data obtained in this work. The total gas consumption rate can be described based on the Eq. (1) as follows:

$$\frac{dC_{CO_2}}{dt}=K(f_{exp}-f_{eq})C_{H_2O,l} \tag{2}$$

where C_{CO_2} is the concentration of the carbon dioxide gas consumed during the hydrate formation, t is the time in minute, K is the overall reaction rate constant, f_{exp} is the fugacity of the carbon dioxide in the vapor phase at the experimental temperature and pressure conditions, f_{eq} is the fugacity of the carbon dioxide in the hydrate-liquid water-vapor three-phase equilibrium at the experimental temperature condition, and $C_{H_2O,l}$ is the concentration of the unreacted water remained in the liquid phase. The fugacities of each experimental condition are calculated by using the Soave-Redlich-Kwong equation of state [Soave, 1972] incorporated with a modified Huron-Vidal mixing rule [Huron and Vidal, 1979]. Considering the electrolyte systems containing the NaCl, the Pitzer activity model is introduced in the above fugacity calculation scheme [Pitzer, 1973]. If we assume that a constant system volume is used for all concentration calculations, Eq. (2) can be converted as follows:

$$\frac{dn_{CO_2}}{dt}=K(f_{exp}-f_{eq})n_{H_2O,l} \tag{3}$$

where n_{CO_2} is the mole of the carbon dioxide gas consumed during the hydrate formation and $n_{H_2O,l}$ is the mole of the unreacted water remained in the liquid phase. In Eq. (3), the contribution of the carbon dioxide to the hydrate formation is represented by the difference between the fugacities at the experimental and the equilibrium conditions and the mole of water is used as the limiting reactant of the formation reaction of the carbon dioxide hydrate. Total amount of water molecules, $n_{H_2O,0}$, is the sum of the number of moles of the unreacted water remained in the liquid phase, $n_{H_2O,l}$, and that of the water participated in the hydrate formation, $n_{H_2O,H}$.

$$n_{H_2O,0}=n_{H_2O,l}+n_{H_2O,H} \tag{4}$$

Assuming that all cavities are occupied by the carbon dioxide molecules and the amount of the carbon dioxide entrapped in the matrix of the hydrates is equal to that of consumed gaseous carbon dioxide,

$$n_{H_2O,H}=5.75n_{CO_2,H}=5.75n_{CO_2} \tag{5}$$

where $n_{CO_2,H}$ is the mole of the carbon dioxide entrapped in the cavities of the hydrate phase. Therefore, inserting Eq. (5) into Eq. (4), we can get the following expression.

$$n_{H_2O,l}=n_{H_2O,0}-5.75n_{CO_2} \tag{6}$$

Finally, inserting Eq. (6) into Eq. (3), the consumption rate of the carbon dioxide during the hydrate formation, i.e. the growth rate of the carbon dioxide hydrates, is written by the following equation:

$$\frac{dn_{CO_2}}{dt}=K(f_{exp}-f_{eq})(n_{H_2O,0}-5.75n_{CO_2}) \tag{7}$$

where the initial condition is that n_{CO_2} is $n_{CO_2,0}$ at time t=0. Solving the differential Eq. (7), the amounts of the carbon dioxide consumed during the hydrate formation can be obtained as a function of time as follows:

$$\frac{n_{CO_2}}{n_{H_2O,0}}=\frac{\alpha}{5.75}[1-\exp(-5.75K(f_{exp}-f_{eq})t)] \tag{8}$$

where α is an adjustable parameter. Since the carbon dioxide molecules dissolved in the liquid phase during the induction period can participate in the hydrate formation and all cavities of the hydrates cannot be occupied by carbon dioxide molecules as previously discussed, the amount of the carbon dioxide gas supplied during the growth period might be lower than that ideally occupied in all cavities. To compensate for these defects, we introduce an adjustable parameter, α, in Eq. (8), which considers the highest percentage value of the net amount of the consumed carbon dioxide gas supplied from the syringe pump during hydrate formation divided by the total amount of the carbon dioxide ideally occupied in all cavities.

RESULTS AND DISCUSSION

1. Three Phase Equilibria of Carbon Dioxide Hydrate

Three-phase equilibria of hydrate, liquid water and vapor (H-L_w-V) for CO_2-H_2O-NaCl (or clay) system are measured. The salt effect on the formation of carbon dioxide hydrate was confirmed, and H-L_w-V phase boundaries are given in Fig. 2. As expected, the addition of NaCl inhibited hydrate formation. The H-L_w-V equilibrium curve of the 3 wt% NaCl and 10 wt% clay solution almost overlapped with that of the 3 wt% NaCl-only solution, but was slightly shifted to the left. The capillary action in the pore induced the cor-

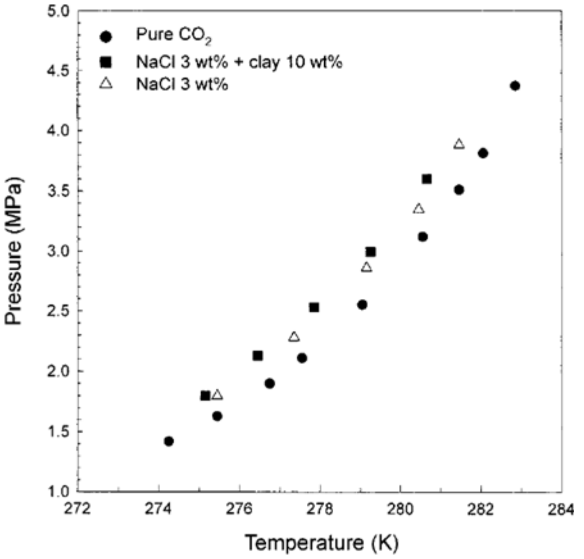

Fig. 2. Hydrate phase equilibrium condition of the carbon dioxide, water, sodium chloride and clay mineral mixture.

responding hydrate equilibrium pressure to rise to a higher pressure than that in the bulk water at a specified temperature. By this effect, system containing both NaCl and clay was inhibited a little more than that containing NaCl salt only. The overall phase behavior can draw a simple but important conclusion that carbon dioxide must be sequestrated to the deeper ocean site than the estimated one chosen from hydrate equilibrium condition of pure water.

2. Formation Kinetics of Carbon Dioxide Hydrate

The formation kinetic experimental results of carbon dioxide hydrates in the pure water solution are presented in Fig. 3 together with the hydrate formation rates predicted by the kinetic model developed in this work. All the experimental curves in Fig. 3 represent the hydrate formation rates only after the turbidity point has occurred at zero point. The temperature effect on the formation kinetics is shown at 2.5, 3.0 and 3.4 MPa. As the temperature increases, the hydrate formation rate decreases as expected, but the general trend is similar for all temperature and pressure conditions. The calculated results represented by the dashed lines agree well with the experimental data. The estimated values of two parameters, K and α, at each isotherm are tabulated in Table 1. The values of both K and α decrease with increasing temperature, but are almost insensitive to pressure change.

The effect of the electrolyte, NaCl, on the formation kinetics of the carbon dioxide hydrates is only taken into account through the calculation of the three-phase (hydrate-liquid-vapor) equilibrium fugacities in the kinetic model. Therefore, only one adjustable parameter, α, is determined by regressing the experimental data. In the systems containing NaCl, the formation kinetic behavior of the carbon dioxide hydrates has a similar tendency to the results of the pure water systems with respect to temperature and pressure change. As the concentration of NaCl and the temperature increase and the pressure decreases, the estimated results deviate from the experimental data. These deviations are considered due to the inaccurate calculation of the three-phase equilibrium fugacities in the high concentration of electrolytes and the limiting capability of the simplified kinetic model. The estimated α values are given in Table 2. The values of α depend a little on the NaCl concentration in the aqueous solution.

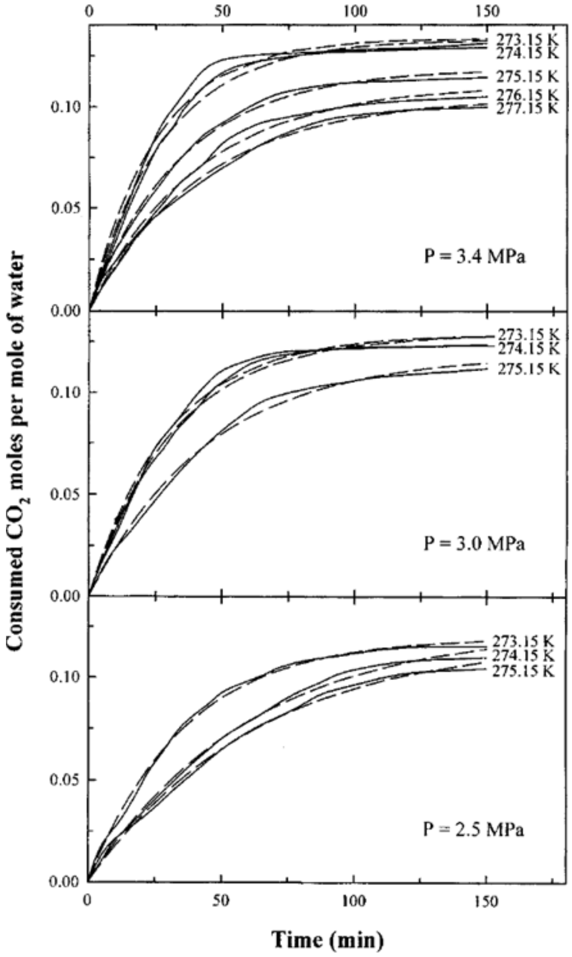

Fig. 3. Formation kinetic curves of carbon dioxide hydrate at pressures of 2.5, 3.0 and 3.4 MPa and at temperatures of 273.15, 274.15 and 275.15 K (straight lines-experimental data; dashed lines-estimated results).

Table 1. Estimated values of two parameters, K and α, of the formation kinetics of carbon dioxide hydrates in the pure water at three isotherms

Temperature (K)	K×10^4 (1/s·MPa)	α (%)
273.15	0.7336	73.24
274.15	0.6907	73.99
275.15	0.6313	68.39
276.15	0.6269	63.87
277.15	0.7158	60.20

The experimental results obtained from the formation kinetics of the carbon dioxide hydrates in the pure water and several aqueous NaCl solutions are plotted in Fig. 4 in order to examine the effect of electrolyte concentration on hydrate formation rate at the conditions of 273.15 K and 3.4 MPa. Similar behavior was also observed at other temperature and pressure conditions. Even if only a small amount of NaCl exists in the water, the hydrate formation rate largely decreases when compared with that in the pure water.

Table 2. Estimated values of parameter, α, of the formation kinetics of carbon dioxide hydrates in the aqueous NaCl solutions at three isotherms

Concentration of NaCl in water	Temperature (K)	α (%)
1 wt%	273.15	61.13
	274.15	57.10
	275.15	55.48
3 wt%	273.15	43.54
	274.15	41.58
	275.15	43.00
5 wt%	273.15	40.42
	274.15	36.38
	275.15	37.93

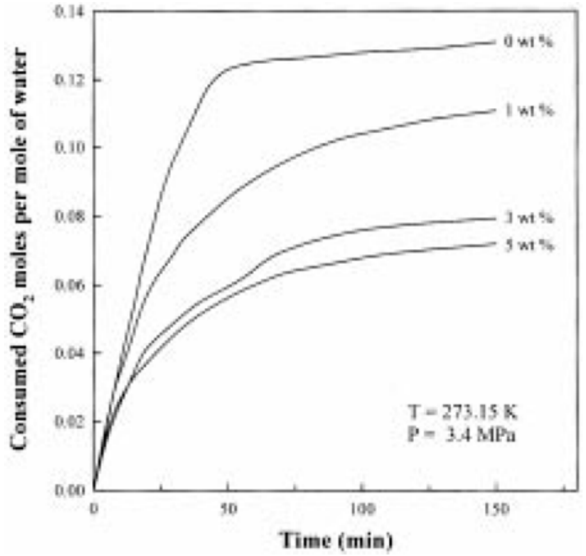

Fig. 4. Formation kinetic curves of carbon dioxide hydrate at 273.15 K and 3.4 MPa in the 0, 1, 3 and 5 wt% aqueous NaCl solutions.

For comparison, four different solutions of pure water, 3 wt% clay, 3 wt% NaCl, and 3 wt% clay/3wt% NaCl were attempted to examine the influencing degree of electrolyte and porous medium and are shown in Fig. 5. All solutions showed the similar pattern that the formation rate of carbon dioxide hydrate decreased with time and kept nearly constant after 1 hr. The 40 min hydration time is considered to be enough for most of the carbon dioxide molecules to be converted to crystalline hydrates. For pure water solution, the final consumed moles of carbon dioxide were 0.1299 per mole of water, but 0.1048 for the 3 wt% clay solution. Interestingly, the initial formation rate of the 3 wt% clay solution was found to be a little higher than that of pure water. This rate difference between two solutions can be understood from the fact that clay can act as a nucleation initiator and thus enhance the formation rate at the initial stage of hydration. For the 3 wt% NaCl solution, the final consumed amount of carbon dioxide was 0.0896 moles per mole of water; furthermore, its initial formation rate was found to be quite slower than that for the solution without salt. For the 3 wt% clay/3 wt% NaCl solution, the final carbon dioxide consumption appeared to be a little smaller than that of the 3 wt% NaCl solution without clay, but its initial formation rate increased because of accelerated nucleation by the presence of clay. However, although the general feature of NaCl and clay effects on hydrate formation can be drawn from the present experimental results, more detailed kinetic measurements must be done to cope with actual marine-sediment conditions.

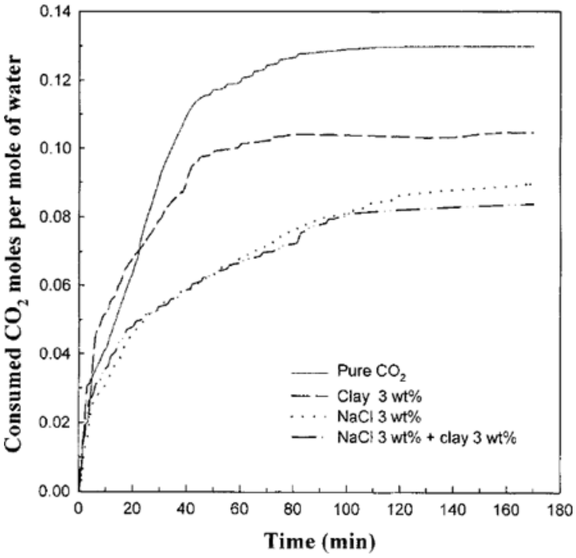

Fig. 5. Formation kinetics of the carbon dioxide, water, sodium chloride and clay mineral mixture at 274.15 K and 3.0 MPa.

CONCLUSION

Two kinds of experiments were conducted to understand the physicochemical characteristics of CO_2 hydrate in the deep ocean floor. First, three phase equilibria were determined for solution containing CO_2, water and NaCl (or clay). The addition of NaCl inhibited hydrate formation as expected. In particular, a special attention must be given to the fact that the hydrate equilibrium line of the 3 wt% NaCl/10 wt% clay system was a little shifted to the left than that of the 3 wt% NaCl solution, which suggested a combined interaction effect between clay and NaCl. The overall results of hydrate phase equilibria indicate that hydrate formation by injecting the liquefied CO_2 into ocean sediments requires a higher pressure than that needed in pure water phase.

Secondly, to secure one of the most important pieces of process information, formation kinetic experiments of CO_2 hydrate were attempted. A simple and unique experimental system was developed in this work to measure the formation kinetics of CO_2 hydrate in the pure water and aqueous NaCl solutions with/without clay. A simplified kinetic model having two adjustable parameters was proposed and the estimated results agree well with the experimental data. The electrolyte concentration, pressure and temperature were found to have a strong effect on hydrate formation rate. Through prescribed experiments, clay was found to play a considerable role in increasing the initial formation rate by inducing nucleation as an acting inhibitor. However, the addition of electrolytes inhibited hydrate formation and furthermore reduced its forming rate. This work gives new information regarding the basic phase behavior and the kinetic formation of CO_2 hydrate. These results can be used to determine the optimal condition for the sequestration of CO_2 into the deep ocean.

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NOMENCLATURE

C_{CO_2} : concentration of carbon dioxide gas consumed [mol/cm^3]
$C_{H_2O,l}$: concentration of the unreacted water [mol/cm^3]
f_{eq} : fugacity of carbon dioxide in three-phase equilibrium [MPa]
f_{exp} : fugacity of carbon dioxide in vapor phase [MPa]
K : overall reaction rate constant [sec$^{-1}\cdot$MPa^{-1}]
n_{CO_2} : nole of carbon dioxide gas consumed [mol]
$n_{CO_2,H}$: mole of carbon dioxide entrapped in hydrate phase [mol]
$n_{H_2O,0}$: sum of the unreacted water [mol]
$n_{H_2O,H}$: mole of the unreacted water in hydrate phase [mol]
$n_{H_2O,l}$: mole of the unreacted water in liquid phase [mol]
t : time [sec]
α : adjustable parameter

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