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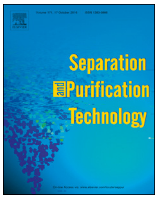

Clathrate hydrate formation in NaCl and $MgCl_2$ brines at low pressure conditions

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ABSTRACT

Hydrate-based desalination (HBD) has been developed to obtain fresh water from seawater in an economic and environmental sustainable manner. As a low-pressure hydrate former for the HBD process, chlorodifluoromethane (R22) hydrates were formed in the pressure range of 1–6 bar under brine environments, aqueous NaCl and $MgCl_2$ solutions. Synchrotron X-ray diffraction and Raman spectroscopy measurements revealed that the R22 hydrates formed with NaCl and $MgCl_2$ show structure I and enclathration of R22 molecules into the large cages. These results also confirmed that the salt ions cannot be encaged in the gas hydrate framework, reflecting the ion exclusion behavior for HBD above the eutectic of water and hydrated salts. The formation kinetics of R22 clathrate hydrate in the presence of salts show that both the initial growth rate and pressure drop of the R22 hydrates heavily depend on the salinity of aqueous solutions. A new theoretical approach adopting the transient time-dependent apparent rate constant of hydrate formation with salts was proposed to predict the formation kinetics of R22 hydrates under brine environments, which was in good agreements with the experimental results. These results provide good information for separating ionic compounds from aqueous solutions by hydrate-based separation processes.

1. Introduction

Over the past several decades, demand for fresh water has continuously increased throughout the world as a result of sustained population growth and improved living standards [1–4]. At the same time, the availability of good quality water is central to sustainable development and further improvements in quality of life. Given the limited availability of fresh water resources, and unreliable water quality for industrial and human needs, desalination technologies involving processes to recover pure water from sea water, have attracted considerable attention [5–10]. Fundamentally, desalination technology removes salts from sea water to provide fresh water, and various approaches have been proposed over the last several decades to accomplish this, with a range of efficiencies, performance and cost.

Gas hydrates are ice-like inclusion compounds comprised of a ‘host’ water-framework and small ‘guest’ molecules such as methane, ethane, carbon dioxide, etc. Hydrate structures are typically categorized based on differences in the size and shape of the hydrate cages. Huge amounts of gaseous molecules can be selectively stored in the hydrate cages [11–23]. For this reason, gas hydrates are currently considered one of the promising functional materials in the energy and environmental fields because of their possible applications for gas storage and

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transportation [24–27], carbon capture and sequestration [28–32], the selective separation of gas species [33–38], and desalination [39–41].

Among the various desalination approaches, hydrate-based desalination (HBD) technology is a promising method for recovering fresh water from sea water. The key mechanism of the HBD technology is a simple temperature- and pressure-dependent phase transition from liquid to solid. HBD technology is considered a novel method for reducing the energy costs of desalination, and increasing the level of freshwater recovery. In addition, HBD technology is also regarded as an environmental-friendly method because hydrates can be directly formed from seawater under low-temperature and high-pressure conditions [39–41]. However, achieving the appropriate high-pressure condition for gas hydrate formation is a major obstacle to improving hydrate formation efficiency, and accordingly, the development of an efficient way to form gas hydrates under more moderate conditions is one of the key objectives of current research.

The refrigerant chlorodifluoromethane (R22) is widely used as an alternative to highly ozone depleting materials, such as dichlorodifluoromethane (R12) and trichlorofluoromethane (R11). Despite it's relatively low ozone depletion potential of 0.055, R22 is still considered to be one of the ozone depleting materials [42,43]. In addition, R22 is regarded as one of the more powerful greenhouse gases due to its global warming potential, which is 1810 times as high as carbon dioxide. For these reasons, controlling R22 using gas hydrates has been studied in several researches [44–49]. R22 is known as a structure I (sI) hydrate former and R22 can only be captured in the large cages of a sI hydrate due to its large molecular size. In addition, the phase equilibrium conditions of R22 hydrates are milder than those of conventional gas hydrates, such as CH_4 or CO_2 hydrates. Controlling R22 using gas hydrates can lead to hydrates with dual hydrate-based functionality, resulting in both R22 capture and an HBD technology [44–49].

To develop a HBD technology using the R22 hydrate, the phase equilibrium conditions of the R22 hydrates in the presence of various salts needs to be determined, as well as the formation kinetics of the R22 hydrate. Chun et al. [44] reported the phase diagram of R22 hydrates in the presence of NaCl, KCl, and $MgCl_2$, and Karamoddin et al. [49] investigated the kinetics of R22 hydrate formation in the presence of sodium dodecyl sulfate (SDS).

In this study, the crystal structures and guest inclusion behaviors of R22 hydrates in the presence of NaCl and $MgCl_2$ were identified using X-ray diffraction (XRD) and Raman spectroscopy. To the best of our knowledge, there have been no prior studies of R22 hydrates using Raman spectroscopy, especially under brine environments; to date, only Raman measurements for gaseous, liquid and solid R22 have been reported [50,51]. We investigated the formation kinetics of R22 hydrates in the presence of NaCl and $MgCl_2$ solutions. This study also provides a new approach for theoretically predicting the formation kinetics of gas hydrates.

2. Material and methods

NaCl and $MgCl_2$, with a minimum purity of 99.5 and 98 mol %, respectively, were supplied from Sigma-Aldrich. R22 gas with a minimum purity of 99.8 mol % was obtained from Korea Standard Gas Co.

To identify the crystal structures and guest inclusion behaviors of R22 hydrates in the presence of NaCl and $MgCl_2$, R22 hydrate samples were prepared by the following processes. High pressure reactors were charged with 100 cm^3 of aqueous salt solutions, and then, the reactors were immersed in a water bath held at 274 K. The reactors were slowly pressurized by R22 gas up to 5 bar, and after the cell was stabilized, hydrate formation was triggered by vigorously agitating the R22 gas and the aqueous solutions. R22 gas was repeatedly injected into the reactors to maintain the system pressure for hydrate conversion. After the formation reaction was completed, R22 hydrate samples were recovered and ground to a fine powder with of 100 μm sieve. A customized Raman spectroscopy instrument with a multichannel air-cooled charge-couple device (CCD) detector (Princeton Instruments, PIXIS 100B) was used to investigate the guest inclusion behaviors of R22 molecules in the R22 hydrates with and without salts. A Nd-YAG laser emitting 532 nm with a power of 150 mW was used as the light source. Raman spectra of the solid hydrate samples and solid R22 were measured at atmospheric pressure and 83 K using a microscope stage (Linkam, THMS 600), while Raman spectra of gaseous and liquid R22 samples were measured at 298 K under pressurized conditions using a high pressure cell with a sapphire window. To identify the crystal structures of the R22 hydrate samples, high-resolution synchrotron XRD measurements were performed in the range of 5–125° with a step size of 0.005° and a wavelength of 1.5183 Å at beamline 9B of the Pohang Accelerator Laboratory (PAL). All XRD samples were measured at 90 K to minimize hydrate dissociation.

The formation kinetics of the R22 hydrate in aqueous salt solutions was investigated using high pressure cells with two sight glasses and an actual internal volume of 277 cm^3. The temperature and pressure of the cell were measured by a digital thermometer and a pressure transducer with a resolution of 0.1 K and 0.1 bar, respectively. Two high pressure cells were prepared in the formation kinetics experiments; one (cell 1) was charged with 100 cm^3 of aqueous salt solutions, and the other (cell 2) was charged with R22 gas up to the desired pressure condition. Then, the cells were immersed into the water bath at 278 K for stabilization. The two cells are connected by a pressure line, and then R22 from cell 2 gas was injected into cell 1 up to 5.2 bar. After the temperature and pressure condition of cell 1 was stabilized, the hydrate formation was triggered by vigorously agitating the contents in the vapor and liquid phases of the cell.

All kinetic experiments were carried out at the stirring rate of 400 rpm using a magnetic drive attached to the top of the cell. The temperature and pressure were monitored and sampled every 5 s by a data acquisition system. The amount of R22 gas consumed during hydrate formation was determined from the pressure-volume-temperature (*PVT*) relationship of the R22 [52]. After the 1st run of the kinetic experiment was completed, the pressure in cell 1 was reduced to atmospheric pressure for hydrate dissociation. After 1 h of the hydrate dissociation process, a 2nd run of the formation kinetics experiment was repeated using the same procedure.

During the 1st runs of the kinetic experiment, we observed a significant hydrate induction time, which is a stochastic phenomenon. However, we noted that there was no induction time for hydrate formation during the 2nd run of the experiment, due to the memory effect. To avoid the effect of induction time on hydrate formation, we modified our experimental procedure by the following process.

In the modified experimental procedure, the high pressure cell was charged with 100 cm^3 of aqueous salt solutions, and immersed in the water bath at 288 K. The cell was pressurized by R22 gas up to 7.8 bar, which is not a hydrate-forming condition. After the temperature and pressure condition in the cell was stabilized, the temperature of the water bath was reduced to 278 K at a continuous cooling rate of 0.2 K/min. Then, the system pressure was adjusted to 5.2 bar, and hydrate formation was triggered by agitation at a stirring rate of 400 rpm. The temperature and pressure were monitored and sampled every 5 s by a data acquisition system. In both the 1st and 2nd runs of the kinetic experiments, when the modified experimental procedure was applied, we did not observe any induction time for hydrate formation.

3. Results and discussion

3.1. XRD and Raman spectroscopic investigation

High-resolution synchrotron XRD was used to identify the crystal structure of the R22 hydrates with and without salts. Fig. 1 shows the XRD patterns of the R22 hydrates formed in pure water (black line), 5 wt% NaCl (red line), and 5 wt% $MgCl_2$ (blue line) aqueous solutions,