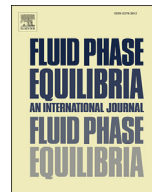




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# Thermodynamic inhibition of CO<sub>2</sub> hydrate in the presence of morpholinium and piperidinium ionic liquids

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## ABSTRACT

The phase equilibrium conditions of CO<sub>2</sub> hydrates were examined in the presence of morpholinium and piperidinium ionic liquids (ILs) with a mass fraction of 0.1. The equilibrium conditions were in the ranges of (274.6–281.2) K and (1.80–3.95) MPa. The addition of ILs shifted the hydrate equilibrium conditions to a higher pressure and lower temperature region compared to the hydrate formed from pure water. Piperidinium and morpholinium ILs showed similar inhibition effects in the higher temperature range  $\geq 278.5$  K, whereas at lower temperature piperidinium ILs had a slightly better inhibition effect than morpholinium ILs. The anionic species also affected the hydrate inhibition effectiveness. Smaller anions, i.e., Br<sup>-</sup>, had a slightly better inhibition effect than the bigger ions of BF<sub>4</sub><sup>-</sup>.

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## 1. Introduction

Gas hydrates are crystalline compounds consisting of guest gas species, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub>, N<sub>2</sub>, etc., situated in host water cage frameworks supported by hydrogen-bonding between water molecules [1]. Naturally occurring gas hydrates have been found in permafrost regions and under the sea floor along the continental margins of seabeds. Since the total amount of hydrocarbon in the form of gas hydrate exceeds that in forms of conventional resources combined, gas hydrates have been considered as a new energy source of natural gas [1–3]. Gas hydrate can store approximately 180 v/v STP CH<sub>4</sub> in one volume of hydrate. Such large gas storage capacity offers a new application of gas hydrate as potential media for energy gas storage and transportation [4–9]. Gas hydrate formation can also be used in greenhouse gas separation by utilizing a

different thermodynamic stability of the gas hydrate for each gas species [10–13]. Gas hydrate has also been proposed as an alternative desalination technique, particularly in high salinity brine, because hydrate formation excludes mineral salts from the hydrate structure [14–17].

In the oil industry, gas hydrates pose a major flow assurance problem during the deep water production and transportation of hydrocarbons [18,19]. Those formed at high pressure and low temperature conditions in submerged pipelines are deposited on the walls [19]. Hydrate plugs could lead to excess pressure buildup and pipeline explosion as a result of blockages of the hydrocarbon stream. Thus, the failure of flow assurance is a serious threat to safe and economical operation of production facilities. The flow assurance issue has recently become more critical as drilling operations have moved to deeper water where there are higher pressure and lower temperature conditions. In addition to CH<sub>4</sub> hydrate, the formation of CO<sub>2</sub> hydrates is also an issue when CO<sub>2</sub> is injected for more oil and gas recovery and for sequestration in the wells [20–22]. As is well known, CO<sub>2</sub> hydrate is more thermodynamically stable than CH<sub>4</sub> hydrate. CO<sub>2</sub> injected into a pipeline more readily reacts with water to form CO<sub>2</sub> hydrate than CH<sub>4</sub> does.

Hydrate formation can be avoided by the removal of gases, water, and hydrate forming pressure and temperature. However, some of the above conditions may be encountered in the operation. One of

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the most practical ways is to use thermodynamic hydrate inhibitors (THIs) such as methanol and ethylene glycol [18,19,23,24]. They are able to shift hydrate formation conditions to a higher pressure and lower temperature region and keep the system out of the hydrate formation conditions. However, a prominent shift of the hydrate equilibrium boundary which enables the pipeline conditions to enter the hydrate inhibition region occurs with the inclusion of a large amount of THIs more than 25 wt% in severe conditions [19]. Alternatively, low dosage hydrate inhibitors (LDHIs) with typical amounts of 0.5–2.0% by volume can be used in a more cost-effective and practical manner [18,19]. There are two types of LDHIs: one is kinetic hydrate inhibitors (KHIs) and the other is anti-agglomerates (AAs). Unlike THIs, LDHIs do not significantly influence the hydrate phase boundary. The definitive hydrate kinetic inhibition mechanism is not yet available. However, it is thought that the KHIs can interfere with growth of hydrate crystals by strong interaction of their active functional group with the hydrate lattice or nuclei [18,19]. The AAs allow the hydrate to be produced in the form of very fine particles and to be dispersed in an oil or water phase. The inhibition mechanism might be explained by the separation ability of AAs for water or hydrate from the hydrocarbon phase [19]. Shorter carbon end of AAs would be attached to water droplet or hydrate phase while long carbon chain end stabilizes the hydrocarbon phase, which hinders the migration of hydrocarbon to water or hydrate phase. As a result, fine hydrate particles could not agglomerate or grow into masses that could become a plug.

Ionic liquids (ILs) are a salt existing as a liquid form below 100 °C and typically consist of bulky nitrogen-containing organic cations and either inorganic anions such as a halide, BF<sub>4</sub>, and PF<sub>6</sub> or organic anions such as nitrate and methanesulfonate [25]. They have a very low vapor pressure and adjustable polarity depending on the nature of anions and cations. It is possible to prepare an enormous number of ILs by combining cations and anions of different families and by introducing functional groups in their chemical structures. With these desirable characteristics, ILs are receiving growing attention as a powerful organic solvent, liquid electrolyte, catalyst, and separation medium [25]. More recently, some ILs were proposed as either THIs [26–28] or KHIs [29,30], and dual functional inhibitors working in both thermodynamic and kinetic ways [31–33]. Their merits are their environmentally friendly nature due to negligible vapor pressure and their ease of recyclability as well as their excellent hydrate inhibition effectiveness caused by strong electrostatic attraction with water molecules.

In this work, we propose a new type of IL-based THI that produces an excellent effect in inhibiting CO<sub>2</sub> hydrate. Here, we prepared four types of ILs, N-ethyl-N-methylmorpholinium bromide ([EMMor][Br]), N-ethyl-N-methylmorpholinium tetrafluoroborate ([EMMor][BF<sub>4</sub>]), N-ethyl-N-methylpiperidinium bromide ([EMPip][Br]), and N-ethyl-N-methylpiperidinium tetrafluoroborate ([EMPip][BF<sub>4</sub>]). We then examined the phase equilibrium boundary of CO<sub>2</sub> hydrates when the ILs were included in the water phase. The results showed that the phase boundaries were shifted to a higher pressure and low temperature region and could be compared with those of the THIs reported in the literature. These obtained phase boundaries can be used as the thermodynamic basis to set pipeline operating pressure when ILs are injected into pipelines for gas hydrate inhibition.

## 2. Experimental Section

### 2.1. Chemicals

Carbon dioxide (CO<sub>2</sub>, purity > 0.99999) was purchased from MillSung Gas Inc. (South Korea). The de-ionized water (water purity ≥ 0.9999) was obtained from a Wellix Plus ultrafiltration

system. The ILs used in this work were synthesized with the procedure described in the [Supplementary Material](#).

### 2.2. Apparatus and experimental procedure

Fig. 1 shows a schematic diagram of the experimental setup. A cylindrical vessel made of stainless steel 316 with an outer diameter of 6.0 cm and height of 5.5 cm (inner volume of 155 cm<sup>3</sup>) was used for hydrate formation and dissociation. A magnetic spin bar was placed into pure water or IL aqueous solutions in the vessel to agitate the fluid and hydrate crystals and provide a fresh interface between the gas and water/hydrate. A thermometer Pt 100Ω (Sungrim Industrial Co.) was inserted into the liquid phase to measure the temperature during the hydrate formation/dissociation processes. The pressure in the vessel was measured with a KELLER PA-21SR pressure transducer. The thermometer and pressure transducer were connected to a Meps datalogger and a personal computer to record the temperature and pressure as functions of time. The standard uncertainties of temperature and pressure were ±0.1 K and ±0.02 MPa, respectively. The temperature of the vessel was controlled using a thermostatic bath made of plexiglass in which coolant was circulated by a Jeitech RW-0525G refrigerator.

Three phase equilibrium conditions of liquid water (L<sub>w</sub>)-hydrate (H)-vapor (V) were measured in an isochoric condition. The aqueous solutions of ILs were prepared at a mass fraction of 0.1. The 55 ml of aqueous solution was charged in the vessel, and gas was supplied from a cylinder through a pressure regulating valve into the vessel. The vessel was purged one time with CO<sub>2</sub> gas to remove the trapped air in the head space and tubes. After the vessel was pressurized to the desired pressure, all valves were closed and the temperature started to decrease at a rate of 2 K/h to form the hydrate. Agitation speed was kept at 200 rpm. Hydrate formation was confirmed by both visual observation through a glass window and pressure depression in the pressure–time profiles. When system pressure reached a steady-state condition, which implies that hydrate was formed to its full extent, the temperature was then slowly raised at steps of 0.2 K/h for the dissociation. The hydrate equilibrium points were determined at the intersection between two slopes; one sharply increased due to hydrate dissociation and the other slowly increased due to volume expansion of the gas phase after completion of dissociation in the pressure–temperature profiles.

## 3. Results and discussion

Prior to the experiments, the three phase equilibrium data of

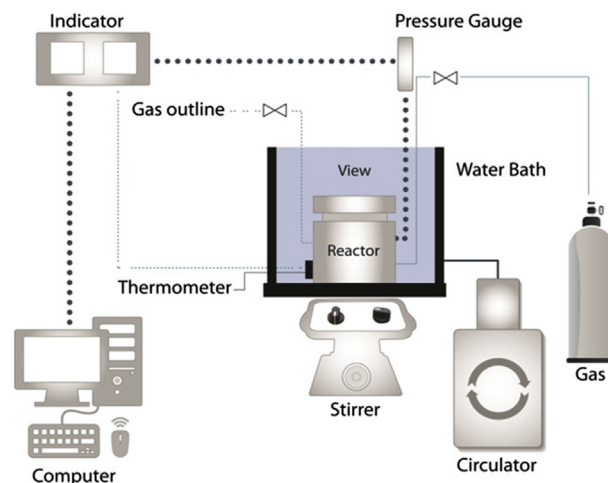


Fig. 1. Schematic of experimental apparatus.

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