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Behavior of cyclopentane hydrates formation and dissociation in pure water and in the presence of sodium chloride

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Abstract

This paper reports the temperature and conductivity behaviors of the cyclopentane hydrate formation and dissociation with and without sodium chloride. The experiments were all performed in a jacketed vessel connected to a chiller having the operating temperature down to -20 °C. The equilibrium temperatures of cyclopentane hydrate were determined in the presence of sodium chloride solution with concentration from 0% to 26% in mass fraction (the saturated concentration of NaCl at 20 ^{o}C) according to an environmental dissociation method. The results showed that the temperature of mixture inside the vessel increased when cyclopentane hydrates formed due to the exothermic nature property of the crystallization. The slope of the temperature curve decreased when cyclopentane hydrates dissociated intensely resulting from its endothermic characteristic. The conductivity of mixture had illogical tendencies owing to the appearance of air bubbles and hydrate solid phase during crystallization and dissociation. The results also showed that the equilibrium temperatures of cyclopentane hydrate range from 7.7 °C down to -13.2 °C, and are inversely proportional to the salt concentration.

Keywords: Cyclopentane hydrate; Equilibrium temperature; Sodium chloride.

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1. Introduction

Nowadays, clathrate hydrates are very important in many applications in both science and engineering aspects. Clathrate hydrates, or simple hydrates, are ice-like non-stoichiometric crystalline compounds consisting of lattice cage-like structures formed by hydrogen-bonded water molecules that enclose different guest molecules stabilizing the lattice structure. The guest molecules can be small molecules such as CO_2, H_2, CH_4, C_2H_6, N_2 or relatively large molecules such as Cyclopentane, Neohexane, Dimethyl sulfide, Tetrahydrofuran (THF). Hydrates are mostly stable at low temperature and high pressure conditions which are similar to the deep-sea petroleum operation conditions (0 to 10 °C, tens to hundreds of bars). In the crude oil pipeline, light hydrocarbon gases are soluble in the oil phase at high pressures leading to hydrate formation under appropriate conditions causing a partial plugging and even complete blockage of pipeline (E. Dendy Sloan and Jr, 2003). The blockage due to hydrate formation not only leads to an increase of pressure drop in the pipeline but can also lead to an emergency shutdown or even damage devices and environment, because of the formation of a plug, and after due to the risks associated to its dissociation.

Currently, hydrate is potentially beneficial to be utilized for some applications such as natural gas storage (Mimachi et al., 2014; Sun et al., 2003), (2005; Zanota et al., 2005); hydrogen storage (Veluswamy et al., 2014) ; carbon dioxide capture (Duc et al., 2007) ; ground/ocean sequestration (A. Yamasaki et al., 1998; Burnol et al., 2015); and transportation (Aspelund et al., 2006) ; isolation of greenhouse gas (Yu-Taek Seo et al., 2005); gas separation (Babu et al., 2015; E. Dendy Sloan and Jr, 2003); frozen food (Muromachi et al., 2013; Peters et al., 2010); refrigeration and cold thermal energy (Darbouret et al., 2005; Douzet et al., 2013; Masahiro Nakajima et al., 2008). In addition, an interesting potential application for gas hydrate is water treatment, especially desalination (Bradshaw et al., 2008). Based on the possibility of hydrate in forming an ice-like compound of clean water and guest species, the potential of using hydrates for desalination of water has been investigated and currently being developed at both laboratory and industrial scale.

In fact, offshore well operates under the seafloor, so that the effect of the salinity of aqueous phase in water produced with petroleum is an important factor being considered for hydrate formation (Zylyftari et al., 2014). Furthermore, considering natural gas transportation from an offshore to the land-based fields, presence of seawater is an appropriate condition to form natural gas hydrate in the gas pipeline. Seawater is also the environment for carbon dioxide sequestration in the ocean. In addition, hydrate-based desalination of seawater is certainly performed in salty water environment. For many of the mentioned hydrate applications, there is a need to study and understand the hydrate formation in presence of salts, such as NaCl, KCl, $MgCl_2$ and $CaCl_2$, or sea-water, in order to develop hydrate-based technologies. It implies describing the liquid thermodynamic, and especially the chemical potential of water, for example by using an eNRTL model (Kwaterski and Herri, 2014).

It is well known that, clathrate hydrate stability depends on the guest molecule, and its ability to fit the size of cavities built by water molecules. Some of the guests are solubilized gases such as CO_2, H_2, CH_4, C_2H_6, N_2 and they imply to operate a process under high pressure. Cyclopentane is also a hydrate former, and it is a liquid at atmospheric pressure. It is a promising candidate for every industrial process where pressure is a handicap, such as separation processes. In addition, because it is un-miscible with water, it can be recovered easily after dissociation of hydrate.

In this study, we performed experiments on cyclopentane hydrate with the mass fraction of NaCl in aqueous solution from 0 to 26% in order to investigate the behavior of the temperature and conductivity of the mixture during hydrate formation and dissociation. The equilibrium temperatures of cyclopentane hydrate at each salt concentration were also reported.

2. Experimental

2.1. Materials

In this study, the experiments were carried out in the presence of ultrapure water obtained from Milli-Q® Advantage A10 Water Purification System. This system permits to produce water with conductivity $\sigma \leqslant 0{,}055$ $\mu S.cm^{-1}$ and TOC (total organic carbon content) less than 5 ppm. Cyclopentane (>95% pure) are supplied by Across, sodium chloride (99.5% pure) is supplied by Sigma-Aldrich. Relevant physical properties of the materials are provided in Table 1.

As we mentioned before, cyclopentane is immiscible in water, therefore, it is needed to disperse cyclopentane into water by mixing. In addition, due to the relatively high melting point of cyclopentane hydrate at atmospheric pressure, measurements can be made above the freezing point of water and assure that ice has not formed.

Table 1. Materials physical properties

Material	Chemical formula	Mol.weight g. mol^{-1}	Density $g.cm^{-3}$	Viscosity	Solubility in water	Purity	Manufacturer
Cyclopentane	C_5H_{10}	70.1	0.751 (25 °C)	0.44 (20 °C)	156 mg/l (25 °C)	95%	Acros
Sodium chloride	NaCl	58.4	2.16 (25 °C)	-	36.0 g/l (20 °C)	99.5%	Sigma-Aldrich
Water	H_2O	18.0	1.00 (4 °C)	1.00 (20 °C)	-	-	-

2.2. Experimental apparatus description

Figure 1 presents the experimental apparatus which are installed for studying the thermodynamic equilibrium of cyclopentane hydrate.

The reactor is a jacketed batch vessel (1) which is made from glass applied by Verre Equipments (France) with a total volume of approximate one liter. The vessel is equipped with a double jacket controlled by an external temperature bath which is supplied by the cryostat (2). The cryostat RE 307 supplied by Lauda Ecoline has the operating temperature range from -20 °C to 200 °C with temperature accuracy of ±0.2 °C. The heat transfer fluid is ethylene glycol 44 wt%. The mixture inside the vessel is mixed by an impeller (3) and a motor (7). The temperature probe (PT100) with the uncertainty of ±0.1 °C and conductivity probe are immersed in the solution to measure real-time temperature and conductivity values of the solution. The results are monitored by a computer (9) thanks to two transmitters (6), (8) and a Labview software installed in the personal computer.

The salt concentration of solution is measured by both ion chromatography Dionex DX-500 IC system (13) and by drying oven Binder (12) at 60 °C from a liquid sample taken from the bottom of the vessel at the end of the experiment, when all cyclopentane hydrate is completely dissociated. This procedure allows to cross-check the initial and final salt concentration of each experiment.

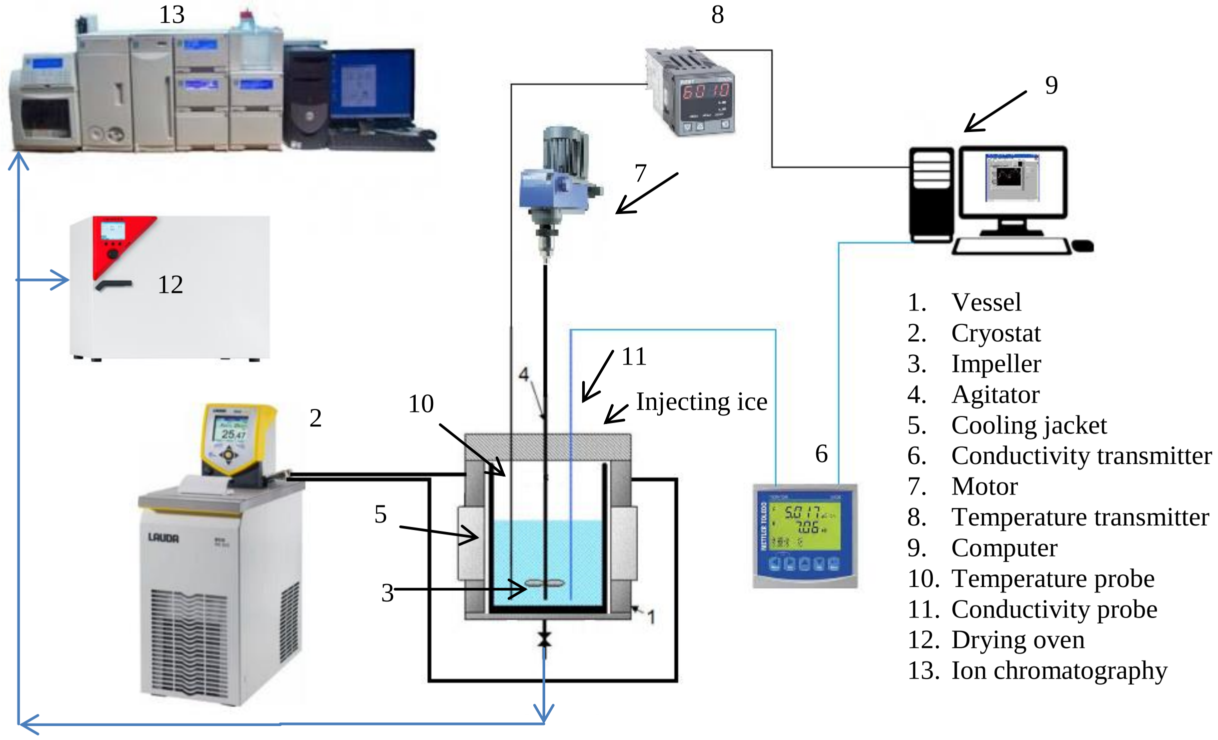


Fig 1. *Simplified schematic diagram of the main experimental apparatus*

2.3. Experimental protocol

Firstly, before each experiment, all the beakers and the vessel were washed and cleaned by absolute ethanol and then by deionized water. About 500 g salt solution was prepared and mixed for 10 min, then 1 ml of solution was taken to measure the salt concentration by ion chromatography in order to compare it to the concentration at the end of experiment when the equilibrium temperature was recorded. The solution was then injected into the glass vessel, followed by cyclopentane with a theoretical stoichiometric composition ($n_{water}/n_{cyclopentane}$=17) (Sloan, 1998).

The solution was continuously agitated by a stirrer at 300-400 rpm. The cryostat was then started at a set-point, above the ice equilibrium temperature around 1-2 °C, depending on the salt concentration. When the temperature of sample reached a value close to the set-point, the hydrate formation was initiated by injecting a trace amount of ice (made previously from deionized water), and salt to keep the salt concentration of the sample constant. The temperature and conductivity of sample were continuously measured and recorded. Visual observations were also performed. After around 1-2 hours, when a sufficient amount of hydrate was formed inside the vessel, the cryostat was stopped. It led to the cyclopentane hydrate dissociation due to the heat from environment. When cyclopentane hydrate could not be observed, the temperature and conductivity curve slopes changed immediately. At this time, 1 ml and 5 ml of salt solution at the bottom of the vessel were taken to measure the salt concentration by ion chromatography and drying oven methods respectively. If the initial and final salt concentrations are identical, the equilibrium temperature is then recorded.

3. Result and discussion

3.1. The behavior of cyclopentane hydrate formation and dissociation

The process of formation and dissociation can be recorded from the temperature and the conductivity changes inside the vessel during experiment, due to the both exothermic and endothermic nature of the these two processes respectively, and also due to the change in liquid salt concentration.

Figure 2 presents temperature and conductivity profiles of the experiment in pure water. The abscissa indicates the time lapse (t) from the beginning of the experiment. It can be seen that, at the beginning, the temperature decreased due to the cooling by cryostat. When ice was injected into the vessel at 64 min, the temperature decreased suddenly because of the low temperature of ice. Simultaneously, some hydrate crystals were observed by naked eyes in the vessel. The temperature then slightly increased gradually resulting from the heat release of crystallization. The temperature was stable over the period from 120 to 225 min because the hydrate formation almost finished inside the vessel. A hydrate block was observed in the vessel in this period.

In the first approach, in order to measure the equilibrium temperature, the cryostat was stopped. During the period from 225 to 275 min, cyclopentane hydrates dissociated partially. The temperature inside the vessel rose gradually whereas the temperature of dissociation normally remains constant when the dissociation occurs with pure water. This un-expected non constant temperature dissociation can be explained only by a non-equilibrium dissociation. The temperature in the vessel increased continuously and a shift of temperature must occur between the crystals inside the vessel and the bulk solution. The temperature still increased slightly due to the endothermic nature of the dissociation process. But after, the hydrate dissociation ended at approximately 333 min, we observed a sudden increase of the slope of the temperature curve. Afterward, no hydrate can be observed inside the vessel, and therefore, the final equilibrium temperature was recorded at 7.7 °C. The temperature then increased gradually up to a value close to the ambient temperature.

In the experiment described above in pure water, theoretically, the conductivity can be only affected by two main factors: temperature and phase characteristic of the mixture inside the vessel. However, due to the presence of bubbles and hydrate slurry phase, the conductivity showed illogical tendencies during the experiment.

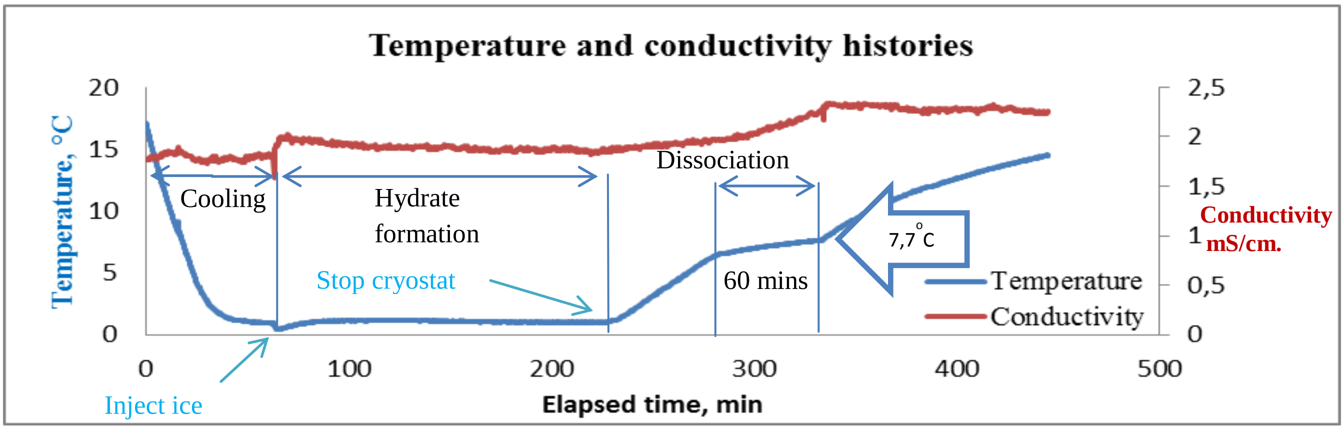
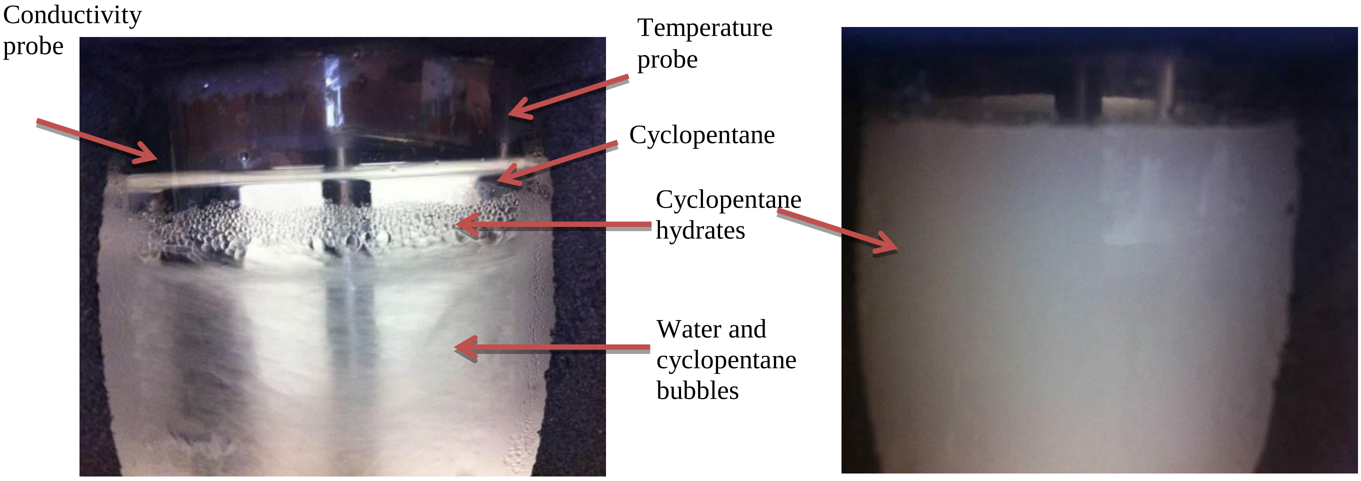


***Fig 2**. Temperature and conductivity histories of CP hydrate experiment with pure water*

It can be observed in Fig 2 that the conductivity was constant around 1.8 mS/cm from the beginning to the time when ice was added into the vessel. The conductivity then suddenly dropped down to 1.6 mS/cm due to again the low temperature of ice, and then it rose very quickly and strangely up to 2 mS/cm.

During cyclopentane hydrate formation, the conductivity decreased slightly due to the appearance of hydrate crystals on the electrode surface of conductivity probe. It caused preventing partially the contact of the aqueous mixture with the probe. The conductivity then increased slowly, probably due to the increase of temperature inside the vessel. When hydrate dissociated intensely from 275 to 333 min, the electrode of conductivity probe was freer. In addition, during this period, a small increase of the temperature of mixture was also observed. This led to a rise in the mixture conductivity value. However, the conductivity then decreased unexpectedly and slightly after hydrate dissociation finished completely. It can be attributed to air bubbles appearance at the end of experiment.



a. Image at 70 min (after 5 min adding ice)

b. Image at 225 min

***Fig 3**. Images of cyclopentane hydrate formation in pure water*

Fig 3 indicates visual observations obtained from hydrate formation in pure water after initiating by adding ice. It can be seen from Fig 3a that cyclopentane hydrate formed and grew at the cyclopentane/water interface and then agglomerated on the wall of vessel. Hydrate formation then occurred continuously inside the vessel. It created a polycrystalline hydrate layer which covered the entire interface. This process almost finished at around 225 min as presented in Fig 3b, a block of cyclopentane hydrate inside the vessel was also observed.

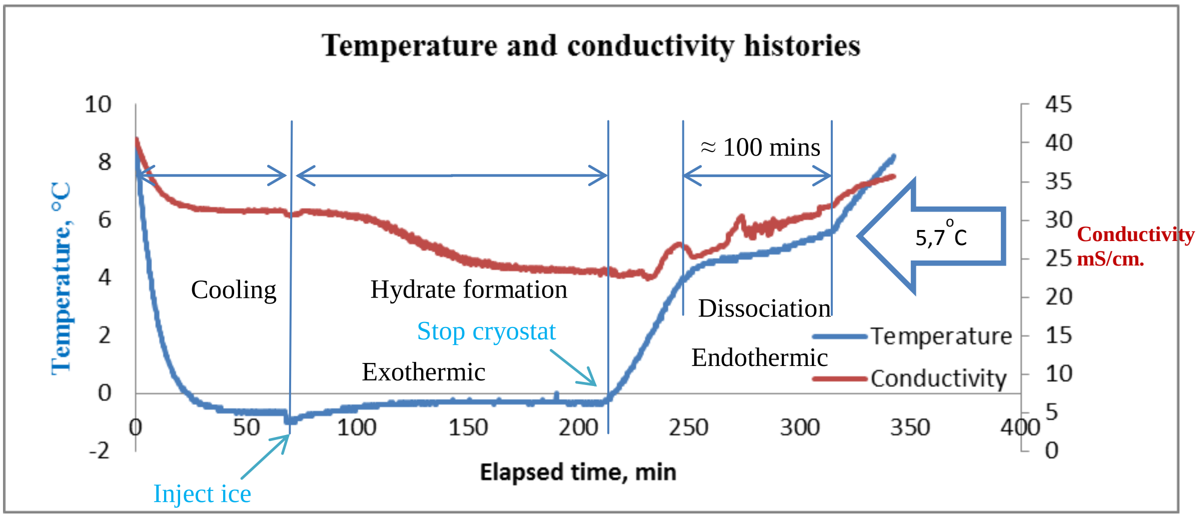


***Fig 4**. Temperature and conductivity histories of CP hydrate experiment with 3.5% NaCl*

Figure 4 illustrates temperature and conductivity profiles of the experiment in the presence of 3.5% NaCl. It can be observed that the trend of temperature in the presence of 3.5% NaCl is the same as in pure water. In contrast, the conductivity exhibited different tendencies due to the presence of sodium chloride in the mixture.

The conductivity dropped from 40 mS/cm to nearly 30 mS/cm during a period from the beginning to 70 min (time of ice adding) due to the initial cooling down. The cyclopentane hydrate formation was observed after injecting ice into the vessel. Although the hydrate formation led to an increase of the NaCl concentration (because this process consumes pure water only and cyclopentane), the conductivity decreased unexpectedly. Indeed, the condense phase was not homogeneous, probably due to the hydrate slurry and also bubbles in the vessel caused by the mixing process.

The conductivity then rose during a period from 250 to 310 min as hydrate dissociated strongly. Theoretically, when hydrate dissociates, pure water from hydrate structures is released leading a decrease in salt concentration and, therefore, in conductivity. In fact, the conductivity increased is this period. It was due to the temperature increase of aqueous mixture, and especially due to the dissociation of hydrate that led the electrode surface to be freer from hydrate slurry in the aqueous mixture.

The slope of conductivity curve increased slightly once no hydrate was observed inside the vessel. Simultaneously, the slope of temperature changed immediately. It indicated the equilibrium temperature of the cylopentane hydrate was 5.7 ^{o}C in the presence of 3.5% NaCl, undoubtedly less than the equilibrium temperature in pure water. The conductivity then increased gradually up to about 36 mS/cm at the end of the experiment as a temperature increase resulting from the environment heating.

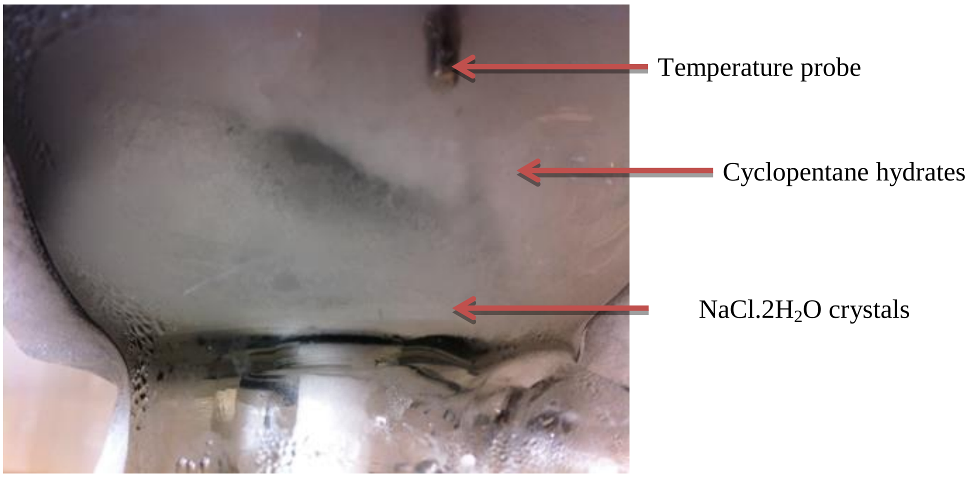


Fig 5. Visual observation of cyclopentane hydrate formation in the presence of 26% NaCl at the bottom of the vessel

The same behaviors of cyclopentane hydrate formation and dissociation in the presence of different salt concentrations were also observed in all the experiments.

Interestingly, at salt concentrations higher than 20% w/w, crystalline rock salt hydrate or hydrohalite ($NaCl.2H_2O$) can be easily observed during the crystallization due to the appearance of halite over-saturated solution inside the vessel leading to the formation of these solid crystals.

Fig 5 presents an image of cyclopentane hydrate formation in the presence of 26% NaCl. A noticeable quantity of $NaCl.2H_2O$ crystals deposited at the bottom of the vessel during the hydrate formation. In fact, this phenomenon has motivated scientists to apply this process for water treatments as desalination and depollution processes. In fact, there was cyclopentane hydrate floating at the surface (composed of pure water and un-miscible cyclopentane after dissociation), and there were salt hydrate crystals ($NaCl.2H_2O$) at the bottom.

3.2. The equilibrium temperature of cyclopentane hydrate

The equilibrium temperatures of cyclopentane hydrate following the environmental dissociation method in pure water and in the presence of sodium chloride with the different concentrations are summarized in Table 2.

As mentioned in the experimental protocol, at each experiment, ion chromatography and drying oven method were applied to cross-check the results. When the initial and final salt concentrations according to these methods are the same, it means that hydrate dissociation has completely finished, the equilibrium temperature is then recorded.

It can be seen from Table 2 that the equilibrium temperature depends strongly on the salt concentration. In fact, it decreases by increasing of salt concentration. The equilibrium temperature of cyclopentane with pure water in this report, 7.7 °C, is identical to literature (E. Dendy Sloan and Carolyn A. Koh, 2008), (Erik Gisle Dirdal et al., 2011), and (Sefidroodi et al., 2013), while (Han et al., 2014) reported the equilibrium temperature of 7.8 °C. It indicates that our equilibrium temperatures of cyclopentane in pure water according to the environmental dissociation method are close to literature data.

Table 2. *The equilibrium temperature of cyclopentane hydrate in the presence of NaCl*

Salt concentration % wt	0	1	2	3.5	5	8	10	12	14	16	18	20	22	23	26
The equilibrium temperature, °C, ±0.1^{o}C	7.7	6.9	6.3	5.7	4.9	3.5	2.0	0.9	-1.0	-2.7	-5.0	-7.2	-9.7	-11.0	-13.2

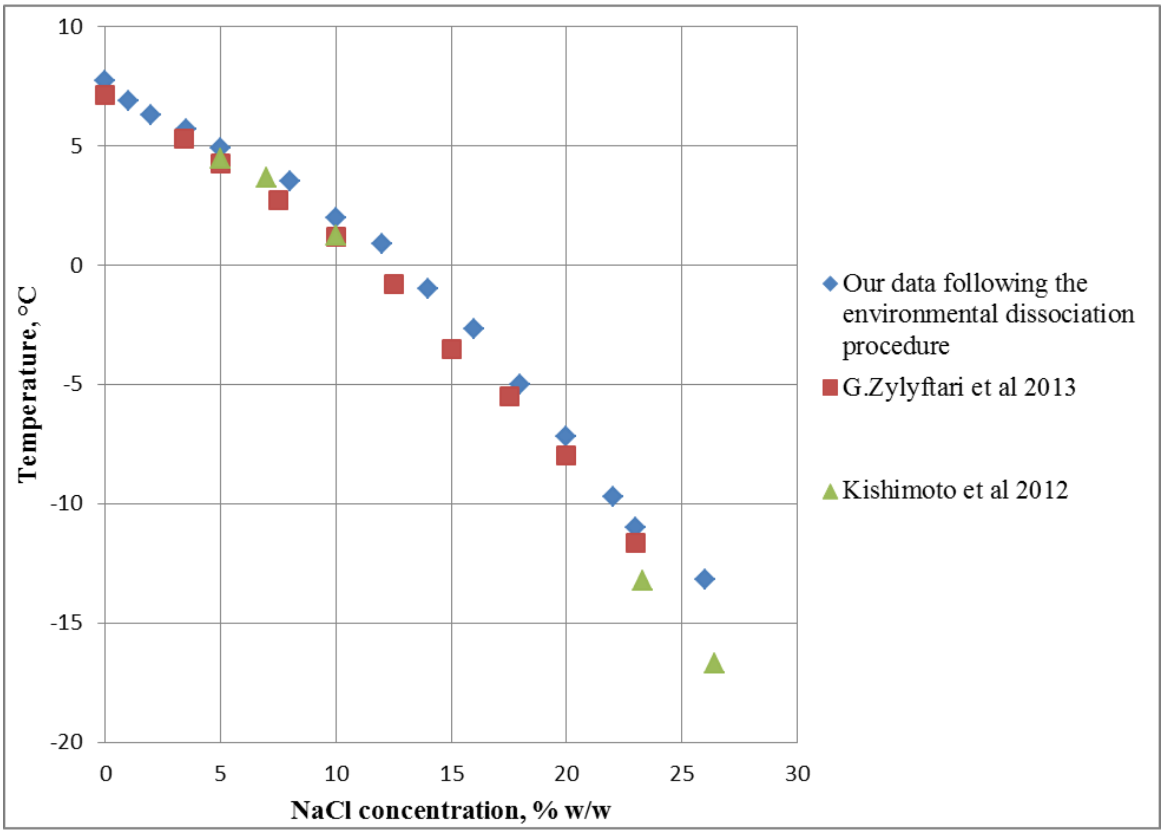


Fig 6. *The equilibrium temperature of cyclopentane hydrate according to the different dissociation methods in the presence of NaCl*

However, the equilibrium temperature in the presence of 3.5% NaCl according to our study (5.7 °C) is less than the result reported by Han et al (6.6 °C). The reason of this gap is probably due to the difference between two procedures applied to determine the equilibrium temperature.

In order to compare our experimental results with the published literature, our data and the data from Zylyftari et al (2013) and Kishimoto et al (2012) are presented in Figure 6.

It can be seen from Figure 6 that our experimental results are relative close to the result in literature. However, our equilibrium temperatures are slightly higher than the equilibrium temperatures reported from both publications at all salt concentrations. In fact, Zylyftari used the micro-Differential Scanning Calorimetry (µ-DSC) to determine the equilibrium temperature of cyclopentane hydrate and the heat of hydrate dissociation. Masatoshi and co-workers applied the slow stepwise dissociation method for determining the equilibrium temperature. Figure 6 indicates also that the data from Zylyftari are close to the data from Masatoshi. This illustrates that these two methods can provide accurate equilibrium data. The environmental dissociation method, in this case, is not a very accurate method to obtain the equilibrium temperature. It is probably due to the high heating rate by environment causing the difficulty to obtain correctly the equilibrium temperature of cyclopentane hydrate at the end of the dissociation process. This means that, we may miss the exact point before it is recorded. However, this method provides a good first approximation, and can be combined with a slow dissociation method.

4. Conclusion

The behavior of cyclopentane hydrate formation and dissociation has been investigated. The experimental results show that the temperature of the sample increased when hydrate formed inside the vessel owing to its natural exothermic characteristic. When hydrate dissociated strongly, the slope of temperature curve decreased, and the temperature was nearly stable during this period due to the heat-releasing of this process. In contrast, the conductivity showed some unexpected trends in pure water and also in the presence of salt. This was due to the appearance of bubbles and hydrate slurry in the bulk and crystals on the system of the electrode. However, at the time when the equilibrium temperature was recorded, the slopes of temperature and also conductivity changed immediately. The change of slopes can provide information on the dissociation process. Our equilibrium data were also compared to data in the published literature. The comparison indicates that our data are relatively close to the others. However, the environmental dissociation method provides values slightly higher compared to the µDSC and slow stepwise dissociation methods. It has motivated us to continuously study the equilibrium temperature of cyclopetane hydrate in order to find the most accurate data.

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References

A. Yamasaki, M. Wakatsuki, and H. Teng (1998). A new ocean disposal scenario for anthropogenic CO_2: CO_2 hydrate formation in a submerged crystallizer and its disposal. Energy.

Aspelund, A., Mølnvik, M.J., and De Koeijer, G. (2006). Ship Transport of CO_2. Chem. Eng. Res. Des. *84*, 847–855.

Babu, P., Linga, P., Kumar, R., and Englezos, P. (2015). A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. Energy *85*, 261–279.

Bradshaw, R.W., Greathouse, J.A., Cygan, R.T., Simmons, B.A., Dedrick, D.E., and Majzoub, E.H. (2008). Desalination Utilizing Clathrate Hydrates (LDRD Final Report).

Burnol, A., Thinon, I., Ruffine, L., and Herri, J.-M. (2015). Influence of impurities (nitrogen and methane) on the CO_2 storage capacity as sediment-hosted gas hydrates – Application in the area of the Celtic Sea and the Bay of Biscay. Int. J. Greenh. Gas Control *35*, 96–109.

Darbouret, M., Cournil, M., and Herri, J.-M. (2005). Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants. Int. J. Refrig. *28*, 663–671.

Douzet, J., Kwaterski, M., Lallemand, A., Chauvy, F., Flick, D., and Herri, J.-M. (2013). Prototyping of a real size air-conditioning system using a tetra-n-butylammonium bromide semiclathrate hydrate slurry as secondary two-phase refrigerant – Experimental investigations and modelling. Int. J. Refrig. *36*, 1616–1631.

Duc, N.H., Chauvy, F., and Herri, J.-M. (2007). CO_2 capture by hydrate crystallization – A potential solution for gas emission of steelmaking industry. Energy Convers. Manag. *48*, 1313–1322.

E. Dendy Sloan, and Carolyn A. Koh (2008). Clathrate Hydrate of Natural Gases.

E. Dendy Sloan, and Jr (2003). Review article Fundamental principles and applications of natural gas hydrates. Nature.

Erik Gisle Dirdal, Chandrakala Arulanantham, Hamidreza Sefidroodi and Malcolm A., and Hamidreza Sefidroodi and Malcolm A.Kelland (2011). CAN CYCLOPENTANE HYDRATE FORMATION BE USED TO RANK THE PERFORMANCE OF KINETIC HYDRATE INHIBITORS? Proc. 7th Int. Conf. Gas Hydrates ICGH 2011.

Fidel-Dufour, A., Gruy, F., and Herri, J.-M. (2005). Rheological characterization and modelling of hydrates slurries during crystallization under laminar flowing. In Fifth International Conference on Gas Hydrates (ICGH 5), Norvège, 13 Au 16 Juin 2005, p.

Han, S., Shin, J.-Y., Rhee, Y.-W., and Kang, S.-P. (2014). Enhanced efficiency of salt removal from brine for cyclopentane hydrates by washing, centrifuging, and sweating. Desalination *354*, 17–22.

Kishimoto, M., Iijima, S., and Ohmura, R. (2012). Crystal Growth of Clathrate Hydrate at the Interface between Seawater and Hydrophobic-Guest Liquid: Effect of Elevated Salt Concentration. Ind. Eng. Chem. Res. *51*, 5224–5229.

Kwaterski, M., and Herri, J.-M. (2014). Modelling of gas clathrate hydrate equilibria using the electrolyte non-random two-liquid (eNRTL) model. Fluid Phase Equilibria *371*, 22–40.

Masahiro Nakajima, Ryo Ohmura, and Yasuhiko H.Mori (2008). Clathrate hydrate formation from cyclopentane-in-water emulsions. Ind Eng Chem Res2008.

Mimachi, H., Takeya, S., Yoneyama, A., Hyodo, K., Takeda, T., Gotoh, Y., and Murayama, T. (2014). Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate. Chem. Eng. Sci. *118*, 208–213.

Muromachi, S., Nagashima, H.D., Herri, J.-M., and Ohmura, R. (2013). Thermodynamic modeling for clathrate hydrates of ozone. J. Chem. Thermodyn. *64*, 193–197.

Peters, T.B., Smith, J.L., and Brisson, J.G. (2010). Production of CO_2 clathrate hydrate frozen desserts by flash freezing. J. Food Eng. *100*, 669–677.

Sefidroodi, H., Abrahamsen, E., and Kelland, M.A. (2013). Investigation into the strength and source of the memory effect for cyclopentane hydrate. Chem. Eng. Sci. *87*, 133–140.

Sun, Z., Wang, R., Ma, R., Guo, K., and Fan, S. (2003). Natural gas storage in hydrates with the presence of promoters. Energy Convers. Manag. *44*, 2733–2742.

Veluswamy, H.P., Kumar, R., and Linga, P. (2014). Hydrogen storage in clathrate hydrates: Current state of the art and future directions. Appl. Energy *122*, 112–132.

Yu-Taek Seo, Igor L. Moudrakovski and John A. Ripmeester, and Jong-won Lee and Huen Lee (2005). Efficient Recovery of CO_2 from Flue Gas by Clathrate Hydrate Formation in Porous Silica Gels. Env. Sci Technol.

Zanota, M.-L., Périer-Camby, L., Chauvy, F., Brullé, Y., and Herri, J.-M. (2005). Improvement of methane storage in activated carbon using methane hydrate. In Fifth International Conference on Gas Hydrates (ICGH 5), p.

Zylyftari, G., Ahuja, A., and Morris, J.F. (2014). Nucleation of cyclopentane hydrate by ice studied by morphology and rheology. Chem. Eng. Sci. *116*, 497–507.

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