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To cite this version:

Trung-Kien Pham, Thi Quynh Trang Hoang, Son Ho-Van, Van Hieu Ngo, Quang Duyen Le, et al.. Kinetic study on cyclopentane hydrates in the presence of sodium chloride. Vietnam Journal of Catalysis and Adsorption, 2024, 13 (3), pp.85 à 89. 10.62239/jca.2024.063 . emse-04720351

HAL Id: emse-04720351
https://hal-emse.ccsd.cnrs.fr/emse-04720351v1

Submitted on 7 Oct 2024

Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://jca.edu.vn

Kinetic study on cyclopentane hydrates in the presence of sodium chloride

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ARTICLE INFO

Received: 22/07/2024
Accepted: 25/07/2024
Published: 30/09/2024

Keywords:
desalination, hydrates, formation, kinetics

ABSTRACT

Water is an important resource for human life. The lack of clean water in the world now becomes more serious. As a result, seawater desalination to produce fresh water is becoming indispensable. In recent years, hydrate-based desalination is a potential solution for the drinking water shortage issue. Recently, Cyclopentane (CP) is used as a hydrate former for desalination process via crystallization at low temperature and atmospheric pressure. The objective of this study is to provide the new kinetic data of CP hydrates in the presence of sodium chloride with a concentration of 3.5 wt.%. The experimental data for CP hydrates in the presence of sodium chloride are obtained in a batch reactor system with a setup temperature range of -2.5 to -0.5 ^{o}C and at atmospheric pressure. The effects of temperature, agitation speed and amount of CP on kinetics of CP hydrate formation are also performed.

1. Introduction

Water is a vital and indispensable resource for sustainable and human development. Natural clean water is increasingly scarce due to population growth, urbanization, and climate change. About 1.2 billion people cannot access clean and safe water [1]. Therefore, the seawater desalination to produce drinking water is becoming more important. There have been several methods of salts removal from seawater, such as: thermal distillation, cold freezing, reverse osmosis (RO), ion exchange, etc [2]. However, these processes consume a lot of energy, increasing greenhouse gas emissions [3-4]. A typical seawater desalination is reverse osmosis (RO). This process requires a high energy consumption and a high cost of equipment and regeneration of membrane materials used [5].

There have been several studies on the process of removing salt from seawater using distillation membrane and nanofiltration membrane technology, but the efficiency of salt removal is not high and there are still limitations of traditional salt removal processes. The current new trend to remove salt from seawater is to use solar energy. Although this process is environmentally friendly, it has limited capacity due to the ability to collect solar energy is not large. This process also depends much on the weather as well as geographical location to obtain solar energy.

Currently, a hydrate crystallization process is being applied to seawater desalination [6-7]. In this process, the pure water molecule creates a framework around the guest molecules (gas or/and liquid) that creates hydrate crystals (solids). This way separates the pure water from dissolved ions (salts) in the salty water.

https://doi.org/10.62239/jca.2024.063

These solid hydrate particles are then collected and dissociated, producing (separating) pure water and (gas or/and liquid) guest molecules which are recycled to desalination process [8]. The advantages of salts removed by hydrate process engineering are (1) low energy cost (and can utilize cold energy from other processes as LNG, [9-10]; (2) applicable to high salty solutions; (3) high capacity and efficiency; (4) environmentally friendly (no secondary processes causing environmental pollution and additives/hydrate promoters are regenerated and recycled); (5) simple technique and (6) using cheap and available materials.

Now, Cyclopentane (CP) is reported as a good (hydrate former) candidate for desalination process due to high salt removal efficiency (up to 80% or higher) [11-15] and CP can be separated from fresh water after removing salt (CP is insoluble in water) [16-20]. Previous and current studies using hydrate crystallization engineering to remove salts have not fully addressed the kinetic conditions. This study will focus on kinetics of hydrate-based desalination (HBD) process using CP as hydrate former to form cyclopentane hydrate (CPH) in the presence of sodium chloride with a salt concentration of 3.5 wt.%. Additionally, this work will seek the way to enhance the effectiveness of salt removal by HBD process. In detail, the effects of temperatures, stirring speeds and CP amount on the CPH formation will be investigated. Besides, hydrate washing and dissociation to produce fresh water will be reported.

2. Experimental

Experimental chemicals and apparatus

Chemicals

Cyclopentane used is provided from Aladdin (96% in purity). Sodium chloride is from Fisher Chemical (99.5% in purity). The water used for the experiment is distilled water (produced by a distiller).

Apparatus

The reactor is a cylindrical vessel manufactured by PARR equipment company with an internal volume of 1.35 L. The temperature inside the reactor is ensured by a jacket cooling system. The chiller is manufactured by Lauda Ecoline with a temperature accuracy of ± 0.1 ^{o}C. The coolant used in the cooler consists of water and ethanol (each 50% by volume). The inside of the reactor has two stirrers, the upper one is used to stir the gas phase, and the lower one is used to stir the liquid phase. Next to the stirring blades are two PT100 temperature sensors (one for sensing the temperature of the gas phase, and the other for sensing the temperature of the liquid phase) and a small pipe for liquid sampling. The pressure in the reactor is measured by a pressure sensor. The frequency range of the stirrer is from 10 Hz to 50 Hz, the stirring speed can be adjusted in this frequency range during the experiment. The temperature and pressure data of the liquid and gas phases will be transferred to the computer. This data source will be recorded through the Labview software installed on the computer (Fig 1).

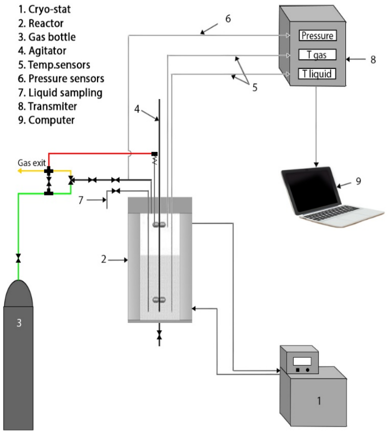

Fig 1: Scheme of experimental equipment system

Experimental procedure

The prepared mixture consists of a solution containing 400 ml of deionized water and a quantity of salt (NaCl, 3.5 wt.%) and is stirred for 10 min. After the mixture was stirred well, 5 ml of solution was withdrawn to measure the salt concentration at the beginning to compare with the salt concentration after hydrate formation. The 122.05 ml of cyclopentane was then added to the reactor (the volume of water and cyclopentane was calculated based on the theoretical molar ratio nH_2O/cyclopentane = 17/1 [21]). The solution is stirred continuously. In the experiment, we tested the hydrate formation process with two different stirring speeds with frequencies 27.9 Hz (400 rpm) and 34.6 Hz (500 rpm). To cool down the solution, the chiller is started at a set-point above the freezing-point of the salt solution to ensure that no ice is present in solution. When the temperature of solution reaches a value close to the set-point, hydrate formation is initiated by introducing approximately 3 g of ice (made previously from deionized water), and an appropriate quantity of salt (0.11 g) added to keep salt concentration of the solution constant. After each 2 hours, when a sufficient amount of CPH has formed, stirring is stopped to separate the salt solution from the cyclopentane and hydrate, 3 ml of salt solution is taken from the reactor (for sampling). This sampling is repeated several times until the end of experiments. Finally, the reactor is opened, hydrate samples are taken, and reactor is washed.

Initial experimental conditions

In this experiment, we tested the hydrate-based salt removal process at different conditions. The initial conditions of each experiment are presented in Table 1. These conditions are based on the thermodynamic results on CPH in the presence of NaCl [22]. The salt concentration is quite the same as it in the seawater.

Table 1: Initial conditions of each experiment

N.o	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5
NaCl (wt.%)	3.5	3.5	3.5	3.5	3.5
H_2O (ml)	400	400	400	400	400
NaCl (g)	14.51	14.51	14.51	14.51	14.51
CP (ml)	121.82 (100%)	121.82 (100%)	60.91 (50%)	60.91 (50%)	121.82 (100%)
Stirring speeds (rpm)	400	500	500	500	500
Set temperature (chiller) (^{0}C)	-0.5	-0.5	-0.5	-2.5	-2.5

Analysis and calculation

The salt concentration in the samples during hydrate formation is measured by the Potentiometric Electrochemical Cell. From the salt concentrations in experiment, we can calculate the water conversion to hydrate. The hydrate solids at the end of experiments are sampled and dissociated into water. This salt concentration is measured to calculate the salt removal efficiency (SRE). Besides, hydrate samples are washed by fresh water to test the salt that may cover (stick) on the surface of hydrate solids. These washed hydrate solids are dissociated and analyzed (the salt concentration) for SRE evaluation. At the end of each experiment (except Exp.5), the mixture is taken out to evaluate the hydrate/liquid ratio (H/L) in volume.

3. Results and discussion

The typical experiment for CPH formation kinetics

The process of hydrate formation and dissociation are significantly two physical change processes. Hydrate formation is exothermic and dissociation is endothermic. Fig 2 shows the temperature diagram of Exp.1.

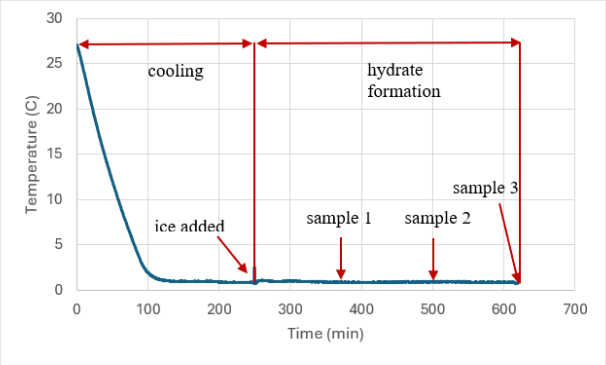

Fig 2: Temperature diagram of cyclopentane hydrate experiment with NaCl 3.5 wt.%, stirring speed at 400 rpm, Tset=-0.5 °C, 100%CP (Exp.1)

The first experiment (Exp.1, Fig 2) is a basic experiment to compare with the other experiments. Initially, the temperature decreased thanks to the cryostat cooling system. After a period of time, when the temperature reaches the desired temperature of 0.7 °C, ice is added into the reactor to stimulate hydrate nucleation. Then, when the ice is added, the temperature jumps up to 2.5 °C (it is because when we open the system to put ice, the liquid temperature sensor will change position in the reactor, leading to an increase in temperature) and then immediately lowers to 0.7 °C. Next, the temperature increases slightly compared to the time before ice was added by 0.8-0.9 °C (this is due to the hydrate formation, causing heat release into the reactor). By the time, the temperature increases and fluctuations from 0.9 to 1.1 °C are observed, the hydrate formation process continues until the end. The temperature was always maintained at 0.8-0.9 °C. From there, it can be seen that after adding ice, the hydrate formation process increased sharply immediately. The hydrate formation process decreased by the time and reached at a stable level. This could be assumed that it is a temporary kinetic equilibrium.

Effects of temperature on CPH formation

Operating temperature greatly affects the conversion of water into hydrate and the salt removal efficiency. At higher temperatures, the rate of hydrate formation decreases due to the lower driving force. Exp.3 and Exp.4 show the CPH hydrate formation process at two different operating temperatures (-0.5 °C and -2.5 °C) and the results of these two experiments are shown in Table 2. From this, the water-to-hydrate conversion decreases with higher operating temperatures. Addtionally, the lower temperature experiment obtained higher salt removal efficiency than the higher temperature one. Besides, hydrate/liquid ratio in Exp.4 with lower temperature is much higher than the one in Exp.3.

Table 2: Effects of temperature on the CPH formation (compare Exp.3 and Exp.4)

	Exp.3 (T_{set}=-0.5 °C, 500 rpm, 50%CP), H/L=1 SRE=5.71%			Exp.4 (T_{set}=-2.5 °C, 500 rpm, 50%CP), H/L=3.5, SRE=7.7%		
Sample	1	2	3	1	2	3
Time to sample (h)	2	4	6	2	4	6
NaCl in time (wt.%)	3.87	3.87	3.85	3.76	3.97	4.08
Water conversion to hydrate (%)	9.56	9.56	9.09	6.91	11.83	14.21

H/L is the Hydrate/Liquid ratio at the end of experiment (-)
SRE is salt removal efficiency (%)

For Exp.3, the NaCl concentration at the 3 sampling points was not different, hydrate may only form immediately after the time of ice application (first sampling). At the time of sampling 2 and 3, we see that there was no additional hydrate formation, the conversion is finished.

Table 3: Effects of temperature on the CPH formation (compare Exp.2 and Exp.5)

	Exp.2 (T_{set}=-0.5 °C, 500 rpm, 100%CP), H/L=4, SRE=7.42%			Exp.5 (T_{set}=-2.5 °C, 500 rpm, 100%CP)		
Sample	1	2	3	1	2	3
Time to sample (h)	2	4	6	2	4	6
NaCl wt.% in time	3.84	3.90	4.04	3.91	4.09	4.35
Water conversion to hydrate (%)	8.85	10.25	13.36	10.48	14.42	19.54

H/L is the Hydrate/Liquid ratio at the end of experiment (-)
SRE is salt removal efficiency (%)

Similarly, compared Exp.2 to Exp.5 (Tset=-0.5 °C and -2.5 °C), we saw that a lower operating temperature, the higher conversion of water into hydrate (see Table 3). The NaCl concentration at each sampling time in Exp.5 was also higher than in Exp.2.

Effects of rotational speed on CPH formation

The results of effects of stirring on the CPH formation kinetics are shown in
Table *4*.

From the results, we can see that Exp.2 with higher stirring speeds led to more hydrates formed or the water conversion to hydrate was higher than that in Exp.1.

We saw that the NaCl concentration at each time point in Exp.2 was larger than in Exp.1, so the kinetics at each time point in Exp.2 was higher. In Exp.2, we also had a much higher hydrate/liquid ratio than in Exp.1, from which we can conclude that hydrates are formed much more at higher stirring speeds. However, the lower rotation speed experiment obtained higher salt removal efficiency than the higher rotation speed one. This may be due to more salt covers on the hydrate solid surface in the higher rotation speed case.

Table 4: Effects of stirring speed on the CPH formation (compare Exp.1 and Exp.2)

	Exp.1 (T_{set}=-0.5 °C, 400 rpm, 100%CP), H/L=1/2, SRE=10.85%			Exp.2 (T_{set}=-0.5 °C, 500 rpm, 100%CP), H/L=4 SRE=7.42%		
Sample	1	2	3	1	2	3
Time to sample (h)	2	4	6	2	4	6
NaCl wt.% in time	3.65	3.73	3.73	3.84	3.90	4.04
Water conversion to hydrate (%)	4.10	6.16	6.16	8.85	10.25	13.36

H/L is the Hydrate/Liquid ratio at the end of experiment (-)
SRE is salt removal efficiency (%)

Effects of CP/H_2O ratio on CPH formation

The kinetics of CPH depends on the amount of CP used. Higher CPH formation rate is determined by increasing the amount of CP used.

Comparing the Exp.2 and Exp.3 (see Table 2 and Table 3), we can see that higher CP amount formed more hydrates and the water conversion to hydrate was also higher. In fact, increasing the amount of CP improves mass transfer, diffusion and thus increases the number of nucleation sites for hydrate formation.

In detail, with Exp.2 (experiment with higher CP/water ratio), we see that the concentration of NaCl solution gradually increases with each sampling point. The conversion of water into hydrate at the two sample time (4h and 6h) was higher in the experiment with more CP amount used. The amount of hydrate formed in Exp.2 was much greater than in Exp.3, the hydrate/liquid ratio is 4 to be compared to 1. The salt removal efficiency was also improved for the experiment with a large amount of CP. This is again confirmed by comparing the Exp.4 and Exp.5 (see details in Table 2 and Table 3).

Hydrate washing and dissociation to produce fresh water

We did the Exp.5 at longer time to obtain more hydrate amount than the other ones. This is to apply a hydrate washing procedure to ensure that the hydrate sample was not surrounded by salt and to achieve a higher salt removal efficiency. The effects of hydrate washing on the salt removal efficiency are as followings: washed with a hydrate/H_2O ratio of 1:1 (in volume), SRE=86%; washed with a hydrate/H_2O ratio of 3:1 (in volume), SRE=67.7%; washed with a hydrate/H_2O ratio of 5:1 (in volume), SRE=44.3%.

From the results, the salt removal efficiency is greatly increased when washing. In sample (1) without washing, we only applied vacuum to dry the sample, so it is likely that the sample was stuck to salt, leading to a NaCl concentration of up to 4.47 wt.%.

In washed hydrate samples, the salt removal efficiency gradually increased when we used more washing water. When using a 5:1 Hydrate/H_2O ratio, we achieved a salt removal efficiency of 44.3%, 3:1 ratio with salt removal efficiency of 67.7% and 1:1 ratio with the salt removal efficiency of 86%.

The experiments without applying the washing process, the highest salt removal efficiency was 10%, approximately.

4. Conclusion

The higher stirring speed, a higher conversion of water to hydrate and a lower salt removal efficiency obtained. At higher operating temperatures, the rate of hydrate formation decreases. As a result, both the water conversion to hydrate and salt removal efficiency decreased with higher operating temperatures. More amount of CP could significantly increase the kinetics of hydrate formation, and thus the salt removal efficiency and amount of water converted into hydrate increased. The amount of salt on the surface of the hydrate is greatly removed when applying washing with salt removal efficiency up to 86%.

Acknowledgments

This research is funded by Kurita Water and Environment Foundation (KWEF) under grant number 21Pvn034-50U.

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