Effect of mass concentration of composite phase change material CA-DE on HCFC-141b hydrate induction time and system stability

Juan Li*, Zhigao Sun, Chenggang Liu, Minggui Zhu
School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou, Jiangsu, China

*Corresponding author e-mail: lijuan@mail.usts.edu.cn

Abstract. HCFC-141b hydrate is a new type of environment-friendly cold storage medium which may be adopted to balance energy supply and demand, achieve peak load shifting and energy saving, wherein the hydrate induction time and system stability are key factors to promote and realize its application in industrial practice. Based on step cooling curve measurement, two kinds of aliphatic hydrocarbon organics, n-capric acid (CA) and lauryl alcohol (DE), were selected to form composite phase change material and to promote the generation of HCFC-141b hydrate. Five kinds of CA-DE mass concentration were chosen to compare the induction time and hydration system stability. In order to accelerate temperature reduction rate, the metal Cu with high heat conductivity performance was adopted to conduct out the heat generated during phase change. Instability index was introduced to appraise system stability. Experimental results show that phase change temperature and sub-cooling degree of CA-DE is 11.1℃ and 3.0℃ respectively, which means it is a preferable medium for HCFC-141b hydrate formation. For the experimental hydration systems, segmented emulsification is achieved by special titration manner to avoid rapid layering under static condition. Induction time can achieve up to 23.3min with the densest HCFC-141b hydrate and the lowest instability index, wherein CA-DE mass concentration is 3%.

1. Introduction
Cold storage technique for air conditioning is a crucial means to reduce the difference between peak and valley of power grid, realize peak load shifting and decrease total energy consumption in the society, its principle is to store the cold energy by a kind of substance (cold storage medium) which is generated by refrigerating unit at off-peak time and release it at peak time of power grid. As a new-type cold storage medium, refrigerant hydrate has special advantage over water, ice and eutectic salt[1,2]. Phase change temperature of refrigerant hydrate resides within the chilled water temperature range (5~12℃) and it is characterized by high phase change latent heat (270~464kJ/kg) which is favorable for conventional water chilling unit. Environment-friendly refrigerants, as the hydration media for cold storage, such as R141b, R134a and R1234yf, are most intensively investigated at present[3-5]. However, low solubility in water, long nucleation time, low growth rate and poor stability, etc. are critical factors influencing its application in industrial practice.
Techniques to promote refrigerant hydrate formation include mechanical stirring, spraying and bubbling, addition of surfactant, magnetic field, ultrasonic wave and porous medium, etc. Phase change material is an advanced technique to improve energy utilization efficiency emerging in recent years, which has similar characteristics as cold storage hydrate including high phase change latent heat and almost stable temperature during phase change. Therefore, composite phase change material, sub-cooling degree of which is a little lower than that of hydration medium, may be used as additive in hydration system. During temperature reduction, such material firstly changes from liquid to solid and crystal particles are generated, which can promote refrigerant to disperse into water uniformly, increase contact area between refrigerant and water molecule, as well as provide more nucleating points. On the other hand, a large amount of heat is released during phase change, which is unfavorable for temperature stability of hydration system and hydrate formation. Therefore, such heat should be conducted out as rapidly as possible. Metal with high thermal conductivity and surface free energy as well as stable chemical property may be used to accelerate temperature reduction rate of hydration system.

In this paper, aliphatic hydrocarbon compound CA-DE with low eutectic temperature was selected to prepare composite phase change material based on step-cooling curve measurement result, and Cu wire was added into HCFC-141b hydration systems with different mass concentration of CA-DE. HCFC-141b hydrate induction time and system stability were researched, so as to lay necessary theoretical basis and application foundation for practical promotion of cold storage technique by refrigerant hydrate.

2. Experimental Devices and Process

2.1. Phase Change Property Measurement Experiment

During liquid-to-solid phase change, a large amount of latent heat is released, system temperature varies with time and break points appear on step-cooling curve which may be taken as the evidence to analyze phase change property. Low eutectic temperature of CA-DE is 11.85°C and mass ratio of such two media is 58.47:41.53. CA and DE used in the experiment is chemically pure and analytically pure respectively, and their freezing point is 26°C and 22.5~25°C respectively.

Experiment devices are shown in Fig.1. Composite phase change material was prepared base on melt-blending polymerization. Electronic scale (Sartorius Mechatronics, Model BSA224S, measurement range of 220g and accuracy of ±0.1mg) was utilized to weigh 20g CA-DE according to mass ratio which was then placed into glass tube (length of 180mm and inner diameter of 18mm); digital high-speed dispersion homogenizer (Shanghai XinXie Industrial, Model XFJ300-S) was used.
to stir for 5 min at rotating speed of 3000 r/min; sheathed thermoresistor Pt100 (Beijing Sailing, accuracy of ±0.1°C) was inserted into glass tube, the other end of which was connected to data collection system (Agilent 34970A, record interval of 10 s); finally, glass tube end was sealed by silica gel plug and placed into low-temperature thermostat bath (Ningbo Tianheng Instrument, Model THD-2015, temperature fluctuation range of ±0.05°C), the temperature of which was set at 5°C.

2.2. HCFC-141b Hydrate Formation Promotion Experiment

Experiment devices and process were similar as Fig. 1, while stirring manner was different and Cu wire (4N, high purity, oxygen free) was inserted into glass tube. Low-temperature thermostat bath was set at 0.2°C. During the preparation of hydration system, it appeared that system dispersion effect was worsened, agglomeration and sedimentation occurred rapidly with the increase of CA-DE concentration, and it had random characteristics to a great degree. Then, rotating speed of homogenizer was adjusted. However, rapid layering under static condition can still not be avoided. Therefore, segmented emulsification measure was taken, rotating speed was controlled at 3000 r/min for 3 min and then increased to 12000 r/min. At the same time, HCFC-141b was added drop by drop according to mass ratio and stirring is maintained for 10 min to prepare emulsion which was then injected into glass tube. Hydrate induction time under separate effect of CA-DE as well as under the combined effect of Cu wire and CA-DE with different mass concentration was measured, so as to search for the optimal condition.

3. Results and Discussion

3.1. Phase Change Property of CA-DE

Sub-cooling curve of composite phase change material CA-DE was shown in Fig. 2, which can be divided into four stages. The first stage started from point 1 to 2, during which sensible heat transfer occurred between CA-DE and air inside low-temperature thermostat bath through glass tube. The second stage was from point 2 to 3. At the point 2, sub-cooled status of CA-DE was broken and a large amount of latent heat was released, temperature rose simultaneously and recovered to point 3 in a short time. The third stage referred to point 3~4, during which CA-DE changed from liquid to solid with both latent heat transfer and sensible heat transfer. Point 4 to point 5 was defined as stage four, phase change terminated at point 4 and only sensible heat transfer existed. Initial status and sub-cooled status of CA-DE inside glass tube corresponded to point 1 and 2 respectively, which accordingly means sub-cooling degree and phase change temperature was 3.0°C and 11.1°C respectively.

![Figure 2. Sub-cooling curve of CA-DE](image)

3.2. HCFC-141b hydrate formation under separate effect of CA-DE

Comparison on temperature curves during HCFC-141b formation in pure water system and in CA-DE system is shown in Fig. 3. It can be seen that no obvious temperature change occurred for more than 230 min under static condition in pure water system, which coincides with phase balance curve of HCFC-141b and means although stirring is applied, it is still very difficult to generate hydrate under
initial temperature and normal pressure condition. With addition of CA-DE, induction time was shortened to 100.2 min which proved the promotion effect. The reason is that carboxyl and hydroxyl of CA-DE are both hydrophilic, alkyl chain is lipophilic, which may combine with water under mechanical stirring to achieve emulsification, so that refrigerant may be able to disperse in water uniformly and contact area between CA-DE and water is increased. Furthermore, phase change of CA-DE occurred firstly during temperature reduction to generate solids-laden system including minor crystal, which provided more nucleation points.

![Figure 3. Comparison on temperature curves during HCFC-141b formation in pure water system and in CA-DE system](image)

3.3. HCFC-141b hydrate formation under combined effect of CA-DE and Cu wire
Temperature curve during HCFC-141b hydrate formation under combined effect of CA-DE and Cu wire are shown in Fig.4. It can be seen by comparison with Fig.3 that HCFC-141b hydrate induction time with addition of Cu wire was further shortened to 24.5 min, which means Cu wire can also promote nucleation and formation of HCFC-141b hydrate, temperature peak was higher and cold storage rate was larger, that is because Cu wire changed the structure of CA-DE base fluid which strengthened energy transfer inside the mixture.

![Figure 4. Comparison on temperature curves during HCFC-141b formation under separate effect of CA-DE and under combined effect of CA-DE and Cu wire](image)

3.4. Effect of mass concentration of CA-DE on HCFC-141b hydrate induction time
It is reported that collision between solid particles are very liable to collide, agglomerate and deposit with increase of dispersant amount, which inhibits micromotion and leads to negative effect on heat conduction[13]. Therefore, mass concentration of CA-DE was changed and temperature change was measured, so as to search for optimal value, as shown in Fig.5. Fig.6 is the hydrate photo taken under...
six kinds of CA-DE mass concentration. It can be discovered that mass concentration of 0.1% corresponded to minimum amount of hydrate, the lowest cold storage rate and the clearest hydrate solution. In case of mass concentration lower than 3%, induction time was shortened with increase of mass concentration and the hydrate was more and more uniform and denser gradually; while in case of mass concentration higher than 3%, induction time was longer with increase of mass concentration, hydrate amount was less and it became nonuniform gradually. Therefore, optimal mass concentration of CA-DE was 3% corresponding to the highest temperature peak and cold storage rate.

![Figure 5. Effect of CA-DE mass concentration on hydration induction time](image)

**Figure 5.** Effect of CA-DE mass concentration on hydration induction time

Furthermore, in order to research the effect of CA-DE mass concentration on stability of hydration system, each group of experiment under six kinds of mass concentration was conducted for 4 times in parallel and the results are shown in Tab.1. It can be seen that mass concentration of 3% corresponded to the shortest average induction time. However, under the same experiment condition, hydrate formation in each system was characterized by randomness. In order to appraise the stability of hydration system, instability index was introduced which was equal to the difference between the maximum and minimum induction time in 4 times of parallel experiments for each system divided by average induction time. High instability index means low system randomness, and vice versa. It is shown by calculation results that mass concentration of 3% also corresponded to the highest stability and the trend was the same as the change of induction time under various mass concentration.

**Table 1.** Effect of CA-DE mass concentration on hydration system stability

| CA-DE Mass Concentration/wt% | Induction Time/min | Average Induction Time/min | Instability Index of Hydration System/% |
|-----------------------------|--------------------|---------------------------|----------------------------------------|
| 0.1                         | 121.5, 128.5, 132.2, 178.3 | 140.1                     | 40.54                                  |
| 1                           | 111.5, 128.0, 136.4, 148.0 | 131.0                     | 27.86                                  |
| 2                           | 46.8, 48.5, 47.6, 53.3    | 49.1                      | 13.16                                  |
| 3                           | 23.3, 24.5, 25.5, 26.1    | 24.6                      | 11.38                                  |
| 4                           | 67.2, 85.6, 87.7, 91.6    | 83.0                      | 29.40                                  |
| 5                           | 93.3, 111.3, 117.5, 137.4 | 114.9                     | 38.38                                  |
4. Conclusion
This paper has presented the favorable effect of composite phase change material CA-DE on formation of HCFC-141b hydrate under static condition. Firstly, CA-DE solution was prepared by melt-blending polymerization, phase change property of which was measured based on sub-cooling curve measurement. Then, HCFC-141b hydrate formation both under separate effect of CA-DE as well as under combined effect of CA-DE and Cu wire were researched based on temperature change during experiment. Six kinds of CA-DE mass concentration (0.1%, 1%, 2%, 3%, 4% and 5%) were involved in hydration system. Induction time was further shortened under combined effect of CA-DE and Cu wire. Furthermore, optimal mass concentration of CA-DE was 3% with the shortest induction time of 23.3 min, the most uniform and densest hydrate, the largest cold storage rate and the highest system stability.

From the experimental results, it can be concluded that sub-cooling process of CA-DE may be divided into four stages in accordance with phase change and heat transfer mode, phase change temperature and sub-cooling degree was 11.1 ℃ and 3.0 ℃ respectively, which means CA-DE may be taken as an additive to promote formation of HCFC-141b hydrate. Hydrate induction time was shortened to 100.2 min under separate effect of CA-DE due to its phase change firstly during temperature reduction which provided more nucleation points. Induction time was further shortened under the combined effect with Cu wire. Furthermore, optimal mass concentration of CA-DE was 3% with the shortest induction time of 23.3 min, the most uniform and densest hydrate, the largest cold storage rate and the highest system stability.

Acknowledgments
This work was financially supported by National Natural Science Foundation for Youths of Jiangsu Province (No. BK20170382) and Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (No. Y607kf1001).

References
[1] C. C. Yan, W. X. Shi, X. T. Li, et al., Optimal design and application of a compound cold storage system combing seasonal ice storage and chilled water storage, Appl. Energ. 171 (2016) 1-11.
[2] A. Efimova, S. Pinnau, M. Mischke, et al., Development of salt hydrate eutectics as latent heat storage for air conditioning and cooling, Thermochim. Acta. 575 (2014) 276-278.
[3] H. Hashemi, S. Babaee, A. H. Mohammadi, et al., Experimental study and modeling of the kinetics of refrigerant hydrate formation, J. Chem. Thermodyn. 82 (2015) 47-52.
[4] S. Zafar, I. Dincer, M. Gadalla, Experimental evaluation of thermal properties of R134a clathrates based PCMs for cooling applications, Int. J. Refrig. 72 (2016) 12-26.
[5] W. X. Zhang, Y. H. Wang, X. M. Lang, et al., Performance analysis of hydrate-based refrigeration system, Energ. Convers. Manage. 146 (2017) 43-51.
[6] M. K. Moraveji, A. Ghaffarkhah, A. Sadeghi, Effect of three representative surfactants on methane hydrate formation rate and induction time, Egyptian J. Pet. Technol. 26 (2017) 331-339.
[7] H. J. Hong, C. H. Ko, M. H. Song, et al., Effect of ultrasonic waves on dissociation kinetics of tetrafluoroethane (CH2FCF3) hydrate, J. Ind. Eng. Chem. 41 (2016) 183-189.
[8] P. F. Wang, S. L. Wang, Y. C. Song, et al., Methane hydrate formation and decomposition properties during gas migration in porous medium, Energ. Procedia, 105 (2017) 4668-4673.
[9] M. G. Zhu, Z. G. Sun, M. M. Yang, et al., Experimental study on promoting HCFC-141b hydrate formation with organic phase change material, Chem. Ind. Eng. Prog. 36 (2017) 1265-1269.
[10] L. Yang, Static enhancement technology of methane hydrate formation, Guangzhou: South China University of Technology, 2013.
[11] Y. Huang, X. L. Zhang, Heat transfer property of lauryl alcohol-capric acid-nanoparticle composite phase change materials, J. Chem. Ind. Eng. 67 (2016) 2271-2276.
[12] X. J. Xu, N. Liu, Y. Q. Wang, et al., Review of latest development on stability of nanofluids, Fluid Mech. 40 (2012) 46-49.
[13] X. Huang, Y. X. Lin, G. Alva, et al. Thermal properties and thermal conductivity enhancement of composite phase change materials using myristyl alcohol/metal foam for solar thermal storage, Sol. Energ. Mat. Sol. C, 170 (2017) 68-76.