Comparison on Promotion Effect of Various Types of Surfactants on HCFC-141b Hydrate Induction Time

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Abstract. Cold storage in air conditioning based on refrigerant hydrate is a new-type energy saving technology to reduce initial investment and running cost of air conditioning equipments and improve system stability. Refrigerant hydrate is generated under critical temperature and pressure condition, while surfactant is an effective medium to promote its phase equilibrium. In this paper, in order to research such promotion effect, different type of surfactants with unique mechanism, SDS, Tween80 and Span80, n-BA were selected to compare the respective impact on HCFC141b hydrate induction time based on temperature curve. Experimental results showed that no obvious change had been discovered when no surfactant was added into pure water system, which coincided with phase equilibrium diagram of HCFC141b. All the four kinds of surfactants had realized promotion effect to various degrees. For each hydration system, a large gap existed between the longest and the shortest induction time in 6 groups of parallel experiments, meaning relatively poor system stability. Under the combined effect of Tween80 (2wt%), Span80 (0.1wt%) and n-BA (0.1wt%), average and the shortest induction time was 20.9min and 17.5min respectively, corresponding to the best promotion effect.

1. Introduction

In order to solve the problem of desynchronized energy supply in time and in space, improve energy utilization efficiency and achieve energy saving and environmental protection, thermal energy storage has received more and more attention, which can be divided into thermal heat storage, latent heat storage and chemical reaction energy storage[1]. Cold storage in air conditioning system is a significant manner to realize peak load shifting and decrease total energy consumption, while the cold storage media include water (sensible heat storage), ice and eutectic (both latent heat storage)[2,3]. Refrigerant hydrate is a kind of clathrate crystalline compound, phase change temperature of which is exactly within the temperature range of chilled water, is a preferable medium for cold storage in air conditioning system[4,5].

Formation of refrigerant hydrate can be divided into three steps from the perspective of thermodynamics, dissolution (cooling), induction (nucleation) and crystal growth. Induction time is defined as when the first hydrate crystal occurs. However, refrigerant and water repels each other which leads to hydration reaction only at the interface and long nucleation time[6]. How to increase the interface and improve dissolvability is the key for its practical application. Meanwhile, hydrate nucleation is characterized by randomness and metastability[7]. Therefore, thermodynamics research is of great importance for controlling its formation at specific time and in particular space.
Many studies have demonstrated the oleophilic and hydrophilic property of surfactant which can reduce induction time of hydrate, and the mechanism is divided into four categories, i.e., change of surface tension, generation of micelle, change of morphology and adsorption of surfactant molecule to hydrate surface\cite{8}. SDS belongs to anionic surfactant, Tween80 and Span80 are nonionic surfactants, while n-BA is a cosurfactant\cite{9,10}. Furthermore, each kind of surfactant, its composite ratio, mass concentration and operating condition have unique promotion effect on hydrate formation.

In this paper, HCFC-141b hydrate formation experiment system was designed, four kinds of surfactants mentioned above with various mass concentrations were added into HCFC-141b and pure water compound, hydrate induction time were researched, so as to further discover the promotion effect of surfactants on rapid formation of HCFC-141b hydrate.

2. Experimental Research

2.1. Experiment Scheme

Purity and manufacture of HCFC-141b and surfactants were shown in Tab.1. Five kinds of hydration systems prepared by HCFC-141b, deionized water and surfactants were shown in Tab.2. According to chemical reaction, chemical formula of HCFC-141b hydrate is HCFC-141b·17H₂O, optimal mass ratio of HCFC-141b and water in the experiment was equal to 1:2.617.

| Table 1. Experimental Materials |
|-------------------------------|
| Material Name | Purity | Manufacture |
|----------------|--------|-------------|
| HCFC-141b | Higher than 99.5% | Zhejiang Zhonglong Refrigerant Co., Ltd. |
| SDS | Analytically pure | Tianjin Zhiyuan Chemicals Co., Ltd. |
| Tween80 | Analytically pure | Wuxi Jinke Chemicals Co., Ltd. |
| Span80 | Chemically pure | Sinopharm Chemical Reagent Co., Ltd. |
| n-BA | Analytically pure | Wuxi Jinke Chemicals Co., Ltd. |

| Table 2. Experimental Hydration Systems |
|----------------|-----------------------------|
| No. | Experimental Hydration System and Mass Concentration |
| 1 | R141b + H₂O |
| 2 | R141b + H₂O + SDS (0.1wt%) |
| 3 | R141b + H₂O + Tween80 (2wt%) |
| 4 | R141b + H₂O + Tween80 (2wt%) + Span80 (0.1wt%) |
| 5 | R141b + H₂O + Tween80 (2wt%) + Span80 (0.1wt%) + n-BA (0.1wt%) |

2.2. Experimental Devices and Process

Figure 1. Experimental diagram of hydrate formation system
HCFC-141b hydrate formation experiment system was divided into five parts, weighting system, hydration reactor, stirring system, low-temperature thermostatic control unit, automatic data measurement and collection system, as shown in Fig.1. Electronic scale was utilized to weigh 150g HCFC-141b and surfactant compound which was then filled into glass tube. Digital high-speed dispersion homogenizer was used to stir for 5min at rotating speed of 1200r/min, the purpose was to promote HCFC-141b to dissolve and saturate in water. Then, glass tube, the hydration reactor, was sealed by silica gel plug to isolate air and avoid leakage, and was placed into low-temperature thermostatic control unit which was set at 0.2℃. Finally, sheathed thermoresistor Pt100 was inserted into glass tube and connected to automatic data collection system. Six groups of parallel experiments were conducted for the last four hydration systems to research the variation of induction time.

3. Results and Discussion
During hydrate formation, system temperature rose sharply and a temperature peak occurred for a short time due to heat release in hydration reaction. Then, the temperature recovered to initial value inside the thermostat bath. Hydrate formation and induction time can be determined according to system temperature variation.

Temperature curve for hydration system No.1 was illustrated in Fig.2, which showed no obvious temperature change under static condition for more than 16h. It means the difficulty to generate HCFC-141b hydrate under initial temperature and atmospheric pressure in pure water system as well as the crucial thermodynamic condition for HCFC-141b hydrate formation, which coincided with its phase equilibrium diagram.

![Figure 2. Temperature variation of hydration system No.1](image)

Hydrate induction time in 6 groups of parallel experiments for system No.2 was shown in Fig.3, while temperature variation in the fifth experiment with the minimum induction time of 8.50h was illustrated in Fig.4. It can be seen that average induction time was shortened obviously compared with hydration system No.1, which means significant promotion effect of SDS. The gap between the longest and the shortest induction time was 3.50h, showing low stability of hydration system.

![Figure 3. Induction time of hydration system No.2 in 6 groups of parallel experiments](image)
**Figure 4.** Temperature variation in the fifth experiment (minimum induction time is 8.50h)

Fig.5 and Fig.6 illustrated induction time in 6 groups of parallel experiments (average value of 147.7min) and temperature variation in the sixth experiment (minimum value of 132.4min) respectively for system No.3. It can be seen that hydrate formation rate was improved further, the reason was solubilization effect of Tween80 which accelerated supersaturation of refrigerant molecules in water, facilitated mass transfer among hydrate crystals and provided driving force for hydration reaction. Furthermore, system stability was improved with relatively poor repeatability.

**Figure 5.** Induction time of hydration system No.3 in 6 groups of parallel experiments

**Figure 6.** Temperature variation in the sixth experiment (minimum induction time is 132.4min)

For hydration system No.4, induction time in 6 groups of parallel experiments (average value of 64.5min) and temperature variation in the fifth experiment (minimum value of 54.0min) was illustrated in Fig. 7 and Fig.8 respectively. It showed further promotion effect of Span80 which reduced available energy per unit mass on surface energy, decreased mass transfer resistance and enlarged effective contact area. System stability was similar to that of hydration system No.3.
Figure 7. Induction time of hydration system No.4 in 6 groups of parallel experiments

Figure 8. Temperature variation in the fifth experiment (minimum induction time is 54.0 min)

Figure 9. Induction time of hydration system No.5 in 6 groups of parallel experiments

Figure 10. Temperature variation in the first experiment (minimum induction time is 17.5 min)
In the hydration system No.5, three kinds of surfactants were compounded, induction time in 6 groups of parallel experiments (average value of 20.9 min) and temperature variation in the first experiment (minimum value of 17.5 min) was shown in Fig.9 and Fig.10. It can be seen that such system had the best promotion effect due to the combined impact of surfactant and cosurfactant. Also, system stability was still poor based on large gap between the longest and the shortest induction time.

4. Conclusion
This paper has researched and compared the promotion effect of anionic surfactant (SDS), nonionic surfactants (Tween80 and Span80) and cosurfactant (n-BA) on HCFC-141b hydrate formation. Five kinds of hydration system were prepared with unique mass concentration of surfactant. For each hydration system, 6 groups of experiments were conducted under the same thermodynamic condition to research system stability. Hydrate induction time was determined according to temperature variation.

From experimental results, it can be concluded that no obvious temperature change occurred when no surfactant was added, which coincided with phase equilibrium diagram of HCFC-141b hydrate. Four kinds of surfactants can reduce interface tension in hydration system, accelerate HCFC141b to dissolve in water and shorten hydrate induction time to various degrees. In the last four hydration systems, average induction time was 9.85h, 147.7min, 64.5min and 20.9min respectively, minimum induction time was 8.50h, 132.4min, 54.0min and 17.5min respectively. However, hydration system stability was poor relatively which needs further research.

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