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Crystallization of tetra-n-butyl ammonium bromide clathrate hydrate slurry and the related heat transfer characteristics

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ABSTRACT

Tetra-n-butyl ammonium bromide (TBAB) clathrate hydrate slurry (CHS) is a promising phase change material slurry for cold storage and transport in air-conditioning system. This slurry can be generated from the supercooled TBAB aqueous solution. In the present study, TBAB CHS was generated under different thermal conditions, i.e. different initial mass concentrations of TBAB aqueous solution and different supercooling degrees. The crystallization of TBAB CHS and the overall heat transfer coefficient under different thermal conditions were clarified. It was concluded that the crystallization characteristics of TBAB hydrate crystals mainly depended upon the thermal condition of the supercooled TBAB aqueous solution. In addition, the dropping of pre-produced TBAB CHS into supercooled TBAB aqueous solution could immediately induce the crystallization of TBAB hydrate crystals, and the initial type of TBAB hydrate crystals was only related to the status of the supercooled TBAB aqueous solution regardless of the type of the dropped TBAB CHS. Furthermore, the overall heat transfer coefficients before crystallization and during crystallization were also measured. It was found that more hydrate crystals would adhere to the vessel wall at larger supercooling degree and higher mass concentration of aqueous solution, which would deteriorate the heat transfer significantly. Moreover, images of TBAB hydrate crystals under different thermal conditions were recorded in order to help clarifying the crystallization characteristics.

1. Introduction

In recent years, the electricity load in peak time increases significantly because of large demand for the refrigeration and air-conditioning particularly in summer time. In order to alleviate this issue, cold energy storage is often employed in the refrigeration and air-conditioning systems to shift the peak-load to the off-peak time [1,2]. Another big issue for conventional air-conditioning is the emission of environment-negative-impact refrigerant. The Montreal Protocol and Kyoto Protocol have prohibited the utilization of the conventional refrigerants such as CFCs, HCFCs and HFCs because of their ozone depletion or global warming potentials [3]. The utilization of secondary-loop refrigeration is regarded as a solution to overcome this problem. In the secondary-loop refrigeration system, environment-friendly secondary refrigerants can be employed to transport cold energy to the individual terminals. Therefore, the utilization of primary refrigerant is reduced, resulting in much less leakage risk [4].

The commonly used media for cold storage and secondary refrigeration system are water or ice for their easy implementation [5]. However, cold storage by water or ice exhibits many disadvantages. The volume of the storage tank for cold storage by water is very large because it is realized by the sensible heat. Moreover, the flow rate of the cold water as secondary refrigerant is very high, resulting in large energy consumption by pumping. The volume of the storage tank can be reduced using ice as cold storage medium because of the latent heat involved. However, the cold storage air-conditioning system using ice requires temperature below 0 °C because of the existence of supercooling. Consequently, the cold charging process is very energy-intensive due to the low evaporation temperature, which hampers its practical application.

Recently, tetra-n-butyl ammonium bromide (TBAB) clathrate hydrate slurry (CHS) has been identified as a potential cold storage medium. Fukushima et al. firstly proposed TBAB CHS as cold storage medium for air-conditioning system [6]. Zhang and Ma [1] concluded that TBAB CHS was quite suitable for the air-conditioning application due to several merits, including the adjustable equilibrium temperature in the range of 5–12 °C, the large cold storage density which is about 2–4 times of that of chilled water and the good fluidity which enables the application as the secondary refrigerant.

However, TBAB hydrate crystals may not be generated at the equilibrium temperature, which is similar to the ice slurry generation. Therefore, understanding the crystallization characteristics of TBAB CHS at different supercooling degrees is essential for

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Nomenclature

A	area (m^2)
c	specific heat capacity ($J\ kg^{-1}\ K^{-1}$)
K	overall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
L	latent heat ($J\ kg^{-1}$)
m	mass (kg)
M	molar mass ($g\ mol^{-1}$)
n	hydration number
T	temperature (°C)
ΔT	supercooling degree (°C)
t	time (s)
w	mass concentration (-)
ω	mass fraction (-)

Subscripts

0	initial
c	coolant
cry	crystal
H	hydrate
i	initial time for calculation

practical application of TBAB CHS. Researchers have conducted many investigations on the crystallization characteristics of TBAB hydrate crystals. Shimada et al. [7] found that two types of TBAB hydrate crystals can be generated in aqueous solution, i.e. types A and B. The two types of TBAB hydrate crystals have different hydration numbers, resulting in different transmittance, different crystal morphology and different equilibrium temperature. As can be seen from the phase diagram in Fig. 1, the equilibrium temperature of type B hydrate was higher than that of type A hydrate at mass concentration of aqueous solution lower than about 22.5 wt%. On the contrary, the equilibrium temperature of type A hydrate was higher than that of type B hydrate [8]. Oyama et al. [9] investigated the fundamental properties of TBAB hydrate crystals generated in TBAB aqueous solution of 35.7 wt% at 9.6 °C. They concluded that the hydration number is 26.0 for type A and 38.0 for type B. And they also reported that type A has columnar shape and type B has an undefined form composed of thin crystals. However, there is not yet systematic analysis about the crystallization characteristics of TBAB CHS under different thermal conditions.

In addition to the crystallization characteristics of TBAB CHS, the heat transfer characteristics were also important for the practical application because it apparently affected the crystallization characteristics and the energy efficiency of TBAB CHS generation process. Many researchers have carried out researches on the heat transfer characteristics of ice slurry. Daisuke et al. [10] studied the heat transfer characteristics of ice slurry in a vessel. They found that ice would start to adhere to the cooling surface earlier at lower coolant temperature, resulting in severe decrease of the overall heat transfer coefficient between ice slurry and the coolant. Hiki et al. [11] studied the heat transfer characteristics of ternary

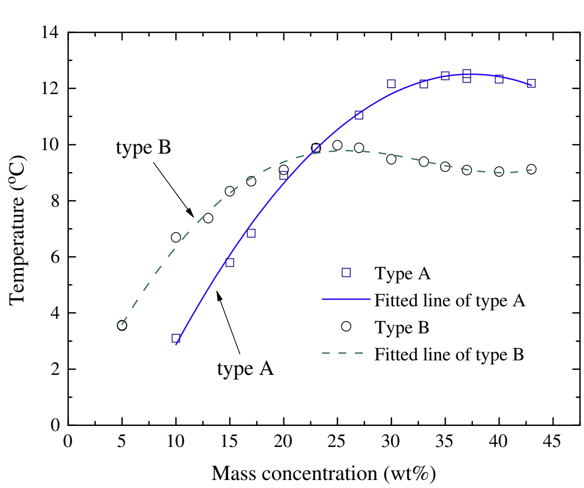

Fig. 1. Phase diagram of TBAB CHS [8].

aqueous solution with ethylene glycol, silane coupling agent and water. They concluded that ice adhesion was suppressed when the initial mass concentration of ethylene glycol or silane coupling agent in aqueous solution was high or the brine temperature was high. However, few researches were carried out on the heat transfer characteristics of TBAB CHS during generation and there was almost no knowledge about the influence of heat transfer characteristics on the crystallization characteristics.

Moreover, the actual crystallization temperature is generally lower than the equilibrium temperature of TBAB hydrate due to the existence of supercooling. Therefore, the aqueous solution would have to be chilled to a very low temperature during the generation process of TBAB CHS, resulting in decrease of energy efficiency. Consequently, several methods were adopted to promote the supercooling release. Kumano et al. [12] reported the effect of electric field on the supercooling release of TBAB aqueous solution and they found that the electric field was effective for nucleation of TBAB hydrate crystal. Song et al. [13] validated the effect of ultrasonic vibration on TBAB CHS generation, and reported that ultrasonic vibration strongly promoted the supercooling release and crystallization of TBAB hydrate crystal. Moreover, there is a concept of adding nucleating agent to artificially induce the crystallization of crystals, and this method has been proved effective. Bédécarrats et al. [14] utilized the method of seed ice crystals to induce the crystallization of ice crystals when the water was at the supercooling state, and the results showed its effectiveness. Sakamoto et al. [15] found that the seed crystals of tetra-n-butyl phosphonium chloride (TBPC) and tetra-n-butyl ammonium acrylate (TBAAc) hydrate, which were prepared separately in advance, could artificially induce nucleation and growth of the hydrate crystal. Therefore, the nucleating agent makes it easier to generate crystal at relatively small supercooling degree. The crystallization characteristics of TBAB hydrate crystal with accession of seed crystals into supercooled TBAB aqueous solution are similar to that of other crystals [16]. However, the knowledge of crystallization characteristics using this generation method is still limited.

In this study, crystallization of TBAB CHS and the overall heat transfer coefficient in a cylindrical vessel were investigated. Experiments of TBAB CHS generation at different thermal conditions were carried out. And the crystallization characteristics at different TBAB mass concentrations of aqueous solution and supercooling degrees were studied and summarized. Moreover, the overall heat transfer coefficients before crystallization and during crystallization were obtained by measuring the temperature variation in the vessel, so as to clarify the influence of hydrate crystal adhesion on the heat transfer. Thereafter, many experiments were carried out to identify the effect of the seed crystals on TBAB CHS generation. Furthermore, the images of the crystals generated under different thermal conditions were obtained in order to help identifying the crystallization characteritics.