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Study of tetra-*n*-butylammonium bromide and tetrahydrofuran hydrate formation kinetics as a cold storage material for air conditioning system

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ABSTRACT

In order to utilize hydrate slurry for cold storage in air-conditioning system, the experimental studies on the phase behavior and formation kinetics of tetra-*n*-butylammonium bromide (TBAB) semiclathrate hydrate, tetrahydrofuran (THF) hydrate and TBAB–THF mixture hydrate have been carried out. By changing the concentrations of TBAB (5–55 wt.%), the variations of phase change temperature, equilibrium temperature, sub-cooling driving force, nucleation rate and electrical conductivity measurements have been compared. The results have revealed that the TBAB solution with 40–45 wt.% may be a promising cold storage material for air conditioning system because of higher temperature phase change of about 11.2 °C and maximum amount of hydrate formed of about 99.8%. In the case of TBAB and THF mixture, which prepared at 0–5.37 mass ratios, the phase change temperature and kinetic parameters depend on the amounts of THF and TBAB into the solution. At the mass ratios higher than 1.0, the above mentioned parameters increase, so that the increase in the TBAB concentration helps to increase the phase change temperature and kinetic parameters.

1. Introduction

Nowadays, the demand of electric power and energy consumption for air-conditioning systems has been increased in general private and public sectors [1]. In a typical central air-conditioner system, the secondary refrigerant circulating system is responsible to satisfy the cold-load [2–5]. The traditional secondary refrigerant, namely water, has a poor capacity of cold energy carrying, a larger flow rate and consequently a larger pump power due to single phase thermal medium [6]. The hydrate cold storage system has been recently developed as the suitable new type energy saving system for its higher refrigerant efficiency and larger cold storage density compared to traditional storage system [7–9].

Gas hydrates are non-stoichiometric crystalline compounds, which are stabilized by guest species (like methane, ethane, carbondioxide) in the cavity of cages formed by water molecules [10]. The refrigerant and ionic clathrate hydrates are related to the structures of gas hydrates [9,11–13]. In the ionic clathrate hydrates, the water molecules together with anions/cations form a water-ion polyhedral framework by means of hydrogen bonding [11]. They are usually formed above 273.15 K and under atmospheric pressure [12,14]. Because their formation heat is comparable to the fusion heat of ice, they can be considered as suitable alternative energy storage materials in air-conditioning systems [15–17].

As a new kind of phase change slurry material, tetra-*n*-butylammonium bromide (TBAB) hydrate slurry has been studied by many researches in recent years [9,11,18]. TBAB in water forms a semiclathrate hydrate which presents similar properties to true clathrate hydrates [11]. Semiclathrate hydrates are applied in many fields such as carbon dioxide sequestration, gas transportation and storage [19–21]. Joshi et al. have determined the phase equilibrium temperature and pressure conditions of semiclathrate hydrate system of carbon dioxide in TBAB with small amount of surfactant. The increase in the concentration of TBAB in their system has helped to decrease the time required for semiclathrate hydrate re-nucleation [22]. Bouchafaa and Dalmazzone have found that the addition of TBAB in the solution increases the dissociation temperature of mixed hydrates containing CO_2 and stabilizes it [23].

In addition, the phase change temperature of TBAB hydrate is from 0 to 12 °C and the latent heat is relatively large, so it is considered promising in an air-conditioning system [18]. Ogoshi and Takao have studied clathrate hydrate slurry (CHS) for use in next generation energy saving air-conditioning systems. They have found that it has a cooling storage capacity 2–3 times as large as that of the conventional chilled water and significantly reduces cooling medium transportation costs [24]. Ma et al. have investigated a cold storage air-conditioning system using TBAB clathrate hydrate slurry as cold storage medium. Their studies have been shown that the system corresponding performance (COP) generally decreased by increasing the TBAB mass fraction during the generation, so that 8–27% cost saving has been achieved [25].

Relating to those studies, the thermophysical properties of TBAB hydrate slurry such as latent heat are required. Oyama et al. have

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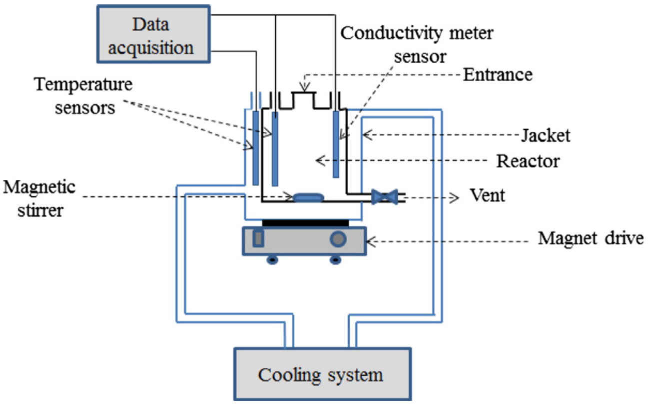

Fig. 1. Experimental apparatus for hydrate formation.

measured the thermophysical properties of TBAB hydrate including latent heat by using differential scanning calorimetry (DSC) [26]. While Asaoka et al. have formed a large size pure TBAB hydrate crystal and measured its latent heat from the variation of specific enthalpy of TBAB hydrate [18]. With regard to mixture, Li et al. have studied thermal properties of TBAB–THF (tetrahydrofuran) hydrate mixture. Their results have showed that TBAB–THF hydrate has the superiority for more suitable phase change temperature and increased fusion heat, so that the hydrate mixture have been represented to be more suitable for cold storage [9,27].

In this work, the refrigerants TBAB hydrate, THF hydrate and their mixtures have been selected for cold storage materials. Recently, many researches have studied the TBAB hydrate formation from the viewpoints of structure, phase equilibrium, thermophysical properties, and heats of fusion [11,14,28], but a few studies has been carried out for the kinetics of TBAB hydrate formation or even mixture hydrate. In this paper, the phase change temperature and hydrate formation kinetics of TBAB hydrate, THF hydrate and TBAB–THF hydrate mixture have been investigated.

2. Materials and methods

2.1. Materials

The materials used in the experiments have been deionized and distilled water, tetra-*n*-butylammonium bromide of 99.9% (volume basis) certified purity (Merck Co.) and tetrahydrofuran liquid with a normal purity of 99.5% (Merck Co.).

2.2. Experimental apparatus

The apparatus that is used in the hydrate formation experiments has been essentially the same as that used in the previous studies [29,30]. The heart of the experimental setup is an atmospheric pressure reactor of 500 cm^3 shown in Fig.1. It is made up of pyrex glass with height of 12 cm and diameter of 6 cm. The reactor has a jacket within which ethylene glycol and water solution is circulated from the cooling bath at a desired temperature of about 243.15 K. Inside of the reactor; a magnetic stirrer (Heidolpg–Hei-mixs) has been applied for the sake of mixing and homogeneity of the solution which has a maximum rotation speed of 800 rpm. Two temperature sensors are installed in the apparatus to measure the temperatures of solution within (1) the reactor and (2) the jacket, which was recorded by a data acquisition system. A conductivity meter (AQUALYTIC/AL20CON) has been also applied to measure the electrical conductivity of the solution. List of sensors used is given in Table 1.

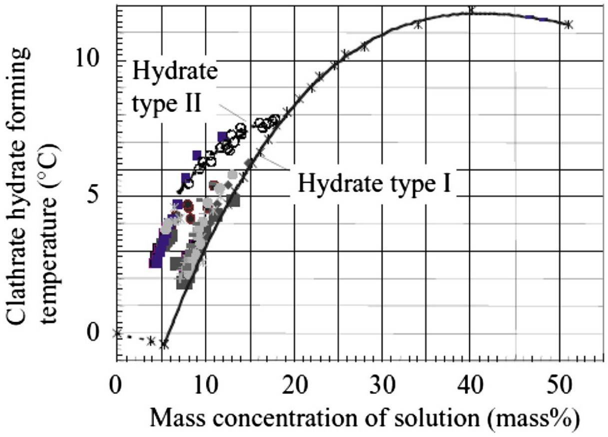

Fig. 2. Phase diagram of TBAB hydrate [20]. There are two types of hydrate with different hydration numbers.

2.3. Experimental procedure

The TBAB hydrate is a kind of solid–liquid suspension with white color, which can be easily generated at atmospheric condition (P ≈ 1 atm and low temperatures). TBAB hydrate particles of 10–100 μm in size produce a fluid hydrate slurry [18,24,25]. Various concentrations of TBAB solution have been used for the supply solution according to the hydration reaction equation:

$$R + nH_2O \rightarrow R.nH_2O + \Delta H \ ; \ R = \mathrm{TBAB}, THF \tag{1}$$

where n is the number of water molecules and ΔH is the heat of formation. The solid–liquid equilibrium temperature depends on the hydrate type and the concentration of the solution, as shown in Fig. 2. In addition, THF forms structure II hydrate in molar composition of $THF\cdot 17H_2O$ under the same conditions as TBAB [12,29]. In these cases, TBAB hydrates have been prepared by various concentrations of TBAB (5–55 wt.%) and THF hydrate also in a water–THF with a 17:1 mol ratio ($n = 17$). Concerning TBAB–THF hydrate mixture, the proportion of water and THF is held at 17:1 mol ratio, while the concentration of TBAB is changed. The initial solution prepared for hydrate formation, which is 100 ml, is placed on a shaker–heater system to get homogeny solution with initial temperature of 16 °C. When the temperature of jacket is fixed at about 268.15 K, the solution is injected into the reactor and the stirrer is activated, so that it is allowed to cool the solution. Whilst hydrate forms, the temperature suddenly increases because of heat generation (ΔH). All experiments have been operated by constant the stirrer speed of 700 rpm and the jacket temperature of 268.15 K. Time, temperature and electrical conductivity of solution during process are recorded.

Table 1
List of sensors used in this work.

Sensor	Type	Accuracy	Range
Thermocouple	Pt-100	±0.1 °C	−100 to +400 °C
Electrical conductivity	AL20 Conductivity Sensor 4-Pole Technology	±0.1 μS/cm	0–2000 μS/cm 0–200 mS/cm