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An experimental study on the formation behavior of single and binary hydrates of TBAB, TBAF and TBPB for cold storage air conditioning applications

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HIGHLIGHTS

- We determine the formation temperature of TBAB, TBAF and TBPB semi-clathrate hydrates.
- We examine the effect of the additives, temperature difference, and memory effect.
- We present sequential images of crystal morphology along the hydrate formation.
- The supercooling and induction time can be modified by SDS and TiO_2 nanoparticles.
- The repeatability can be improved by proper temperature difference driving force.

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ABSTRACT

Thermal storage can be applied to air conditioning systems to shift the demand on electricity grids to decrease the peak load. It is also a feasible backup for solar cooling systems to supply on-site loads during solar outages. Although chilled water has been widely used for thermal storage, phase change materials offer greater energy storage density than chilled water. Semi-clathrate hydrates, having large heat of fusion and phase transition temperatures in the range of 5–10 °C, are proposed for thermal storage in air conditioning applications. This work presents an experimental study on the formation behavior of semi-clathrate hydrates based on tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium fluoride (TBAF) and tetra-n-butylphosphonium bromide (TBPB). The experiments vary the salt mass fraction from 10 wt% to 40 wt%. Single salt hydrates and binary salt mixtures are studied at various proportions. Furthermore, surfactant (sodium dodecyl sulfate, 0.05–0.5 wt%) and nanoparticles (TiO_2, 20–80 nm) are employed to aid hydrate formation. The effect of the temperature difference driving force and memory effect on the hydrate formation are examined through consecutive formation and dissociation cycles. The formation temperature, maximum induction temperature and induction time are measured. It is observed that the supercooling and induction time differ for different salt hydrates. Both these parameters can be modified for air conditioning applications by suitable additives and proper operating conditions. Images of crystal morphology indicate that the columnar crystals of TBAB and TBAF are more compact than the hexagonal crystals of TBPB.

1. Introduction

Air conditioning systems equipped with cold thermal storage offer a means to alleviate the peak load on electricity grids and to utilize power in off-peak periods. Recently, gas hydrates (or clathrate hydrates) have been widely proposed as a suitable phase change material (PCM) in cold thermal storage for the large latent heat storage density. Gas hydrates also offer proper phase transition temperatures that are good for the chiller performance while charging as well as for efficient cooling supply while discharging. However, due to the formation of most natural gas–water hydrates normally requires impractically either low temperatures or high pressures, additives to moderate the formation conditions of natural gas hydrates are of significance. Tetra-n-butylammonium bromide (TBAB) (Ali et al., 2012) has been subjected to the most intensive studies for modifying the phase transition behavior of gas hydrates by forming semi-clathrate hydrates in which TBAB molecules act both as a part of the host (the water cage) and as the guest (the molecules trapped in the water cage). There are still

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small dodecahedral empty water cages left to uptake, store and separate small gas molecules more easily under certain conditions (Zhang et al., 2010; Gholinezhad et al., 2011; Wang et al., 2014). Nguyen et al. Duc et al., (2007) conducted experiments on CO_2–TBAB hydrate formation. In the results, the phase equilibrium pressure declined from 35 bar to 2.73 bar at 279.3 K by using TBAB solution at a concentration of 0.29 mol%. Besides, many findings have lent support to the claim that TBAB is helpful in the formation of other gas hydrates (Su et al., 2013; Meysel et al., 2011). In addition to TBAB, tetra-n-butylammonium fluoride (TBAF) (Strobel et al., 2007; Changyu et al., 2011), tetra-n-butylphosphonium bromide (TBPB) (Ziad et al., 2013), tetra-n-butylammonium chloride (TBAC) and tetra-n-butylammonium nitrate ($TBANO_3$) (Mayoufi et al., 2010), etc. have also been proposed to aid gas hydrate formation.

The formation behavior of ionic semi-clathrate hydrates formed from TBA^+ or TBP^+ inorganic salts, in the absence of gas, is worthy of investigations and optimization to promote gas hydrate formation. For cold storage in air conditioning applications, the phase equilibrium temperature of TBA^+ or TBP^+ salt hydrate is of great importance. To avoid the factors that lead to uncertainty in hydrate formation, such as supercooling and memory effect, hydrate dissociation is mostly used in determining phase equilibrium data. Sato et al. (2013) performed stepwise measurements during the dissociation of TBAB and TBAC hydrate by incrementally increasing the system temperature in steps of 0.1 K and maintaining each step for at least 4 h. The equilibrium temperature was determined as the step immediately before the complete dissociation was visually confirmed. A similar procedure was used by Suginaka et al. (2012) to acquire the phase equilibrium data of TBPB hydrate at mole fractions of 0.1–0.5 wt%. In a vessel immersed in a thermostatic bath, hydrate was formed from TBAB solutions (0.003–0.047 mol%). The equilibrium status was confirmed when a small number of very tiny hydrate crystals remained stable for an extended period of time (5–6 h). Sakamoto et al. (2008) used the "T-cycle method". In this experiment, a content of formed hydrate was heated gradually by a step of 0.1 K until there was a negligible amount of hydrate left. Suffice it to say, above studies and other relevant studies (Ye and Zhang, 2014; Kamran-Pirzaman et al., 2013) all adopted stepwise heating in the hydrate dissociation with very small steps and adequate interval time for each step; also, the phase equilibrium status was identified mainly by observation. However, direct observation is sometimes unreliable. Some researchers also employed differential thermal analysis (DTA) and differential scanning calorimetry (DSC) to dissociate hydrates with small steps of temperature (Lin et al., 2014, 2013; Zhang et al., 2013). Even though stepwise method is considered accurate to determine phase equilibrium, each step would take a long time to achieve the steady state. Some academics used continuous cooling to investigate hydrate formation. In the study of Nakajima et al. (2008), a reaction vessel was filled with a cyclopentane water solution. The solution was cooled to about 2 °C and continuously agitated by a stirrer. The formation was induced by injecting a trace amount of seed crystals that were prepared in advance. The time-dependent formation was identified by the temperature change inside the vessel due to the exothermic nature of hydrate formation. This study offers a quick way to determine the hydrate formation temperature. Whereas, it has to resort to prepared crystals and mechanical agitation to trigger fast nucleation and alleviate supercooling; otherwise, the large cooling rate would result in unreliability in the measurement. Besides, more phase equilibrium data of TBA^+ and TBP^+ hydrates has been provided as a function of the salt mass fraction (Fukumoto et al., 2014; Deschamps and Dalmazzone, 2009; Rodionova et al., 2013, 2008; Mayoufi et al., 2010; Asaoka et al., 2013).

To optimize the formation behavior of PCMs means to minimize supercooling and accelerate the induction period to adapt the application in air conditioning systems. For this purpose, additives, mechanical agitation and magnetic interference are usually employed. For the stability of PCMs, a static cold storage is preferred, thus additives can be adopted. Surfactants are reported to provide nucleus, around which a crystal can form and create a solid, thus, it helps to break through the metastability. After the metastability, hydrate formation is triggered and the growth of crystals proceeds (Wang et al., 2014). Frequently-used surfactants are sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), sodium hexadecyl sulfate (SHS), cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), dodecyltrimethylammonium chloride (DTAC), dodecylbenzenesulfonic acid (DBSA), sodium dodecylbenzenesulfonate (SDBS), linear alkylbenzene sulfonate (LABS), ethoxylated nonyl phenol (ENP), Tween and Span20, etc. The effect of anionic surfactants, SDS, STS and SHS, on CH_4 hydrate formation was studied in an unstirred chamber (Okutani et al., 2008). In each operation, hydrate formation continued for a limited time and then ceased, leaving only a small proportion (15% or less) of the water solution unconverted into hydrate crystals. The variations in the time-averaged rate of hydrate formation were 7.0 h for SDS at 2000 ppm, 6.4 h for STS at 100 ppm, and 8.2 h for SHS at 100 ppm. By Ganji et al. (2007), the effect of SDS, LABS, CTAB and ENP on the formation and dissociation of methane hydrate was studied, with the surfactant tested at concentrations of 300, 500 and 1000 ppm. By Xie et al. (2010, 2005) a small-scaled clathrate hydrate cold storage apparatus, consisting of a refrigeration system, a cooling release system and a storage tank, was designed. The results showed that SDS with the concentration of 0.04 wt% improved the performance of the cold storage, with the stored energy raised to 27.2 MJ and the average hydrate growth velocity increased to 0.5876 kg min^{-1}.

In addition to surfactants, the effect of nanoparticles was reported on accelerating the hydrate formation by enhancing the thermal conductivity of the gas and water system thus speeding up the growth of crystals (Jinping et al., 2006). Chandrasekaran et al. (2014) presented a study on a water based nanofluid PCM, which was prepared by dispersing copper oxide nanoparticles and a nucleating agent in the solution. The nanofluid PCM exhibited a 35% reduction in the solidification time due to enhanced heat transfer properties. Further, 50% mass was solidified during 25% solidification time in both modified PCMs. In the work of Hossain et al. (2015, 2014), a cyclohexane and CuO nanoparticle enhanced PCM was developed. The inclusion of nanoparticles improved the effective thermal conductivity, so that a faster melting rate was observed for the nano-PCM with higher particle fraction. The incorporation of more nanoparticles also reduced the energy required to complete the melting process. Park et al. (2014) studied Fe_3O_4 with various concentrations in a nano-capsuled PCM, based on a paraffin core and polyurea shell. It was reported that the embedment of Fe_3O_4 increased the thermal conductivity of the capsules and reduced supercooling of the paraffin.

Besides additives, some studies were carried out on the memory effect in hydrate formation. Memory effect is a phenomenon that the hydrate recrystallization occurs under milder conditions than the initial nucleation, which is considered favorable to reduce time or save cooling energy during hydrate formation. In the study of Oshima et al. (2010), the recrystallization in a tetragonal TBAB semi-clathrate hydrate was studied by optical microscopy in TBAB solutions. The recrystallization of TBAB hydrate was observed under milder condition than that of the initial crystallization. It was also found that the recrystallization occurred first in the vicinity of the place where the last piece of initial crystal was dissociated. Wu and Zhang (2010) conducted