EFFECT OF IMPELLER AGITATION ON PREPARATION OF TETRA-N-BUTYL AMMONIUM BROMIDE SEMI-CLATHRATE HYDRATE SLURRIES

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ABSTRACT
The slurries containing tetra-n-butyl ammonium bromide (TBAB) solution and its semi-clathrate hydrate have attracted a lot of interest as latent heat transport media. These hydrate slurries contain some microparticles of crystal, and the size and shape of these hydrate particles could affect the mobility of slurries. Hence, it is essential to investigate the efficient preparation method of hydrate slurries and the effect of hydrate particles on the fluid property of slurries for the application to latent heat transport media. In the present study, the effect of agitation on particle size distribution and aggregation of particles was studied to prepare runny TBAB hydrate slurries that were suitable for fluid transport. First of all, the effect of speed of impeller rotation and impeller type on the particle size and frequency of aggregation was investigated. The results suggested that the particle size distribution and the frequency of particle aggregation may be strongly affected by the intensity of shear rate and its uniformity, which was controllable with impeller type and its rotation speed.

Keywords: hydrate slurry, impeller agitation, quaternary ammonium salt, particle aggregation

NOMENCLATURE
C: concentration [wt%]
D: diameter of vessel [m]
H: height of vessel [m]
h: height of working fluid [m]
Hc: hydrate fraction in slurries [-]
nr: rotation speed of impeller [rpm]
P: required power for agitation [W]
T: temperature [K]
γ: shear rate [s⁻¹]

INTRODUCTION
Recently, a large-scale district cooling system has attracted attention of many researchers because it works on saving energy and global sustainability. In such system, the pumping energy loss of the transportation of heat media is not small. To solve this problem, a high-density heat transportation system by use of slurries with phase change materials (hereafter, PCM) having latent heat has been developed, e.g., ice/water slurries [1]. The utilization of such PCM slurries can reduce flow rate of heat media, since latent heat of some materials is much larger than sensible heat. Fukushima et al. [2] reported the ability of slurries containing tetra-n-butyl ammonium bromide (hereafter, TBAB) semi-clathrate hydrate and its solution as latent heat transport media, which was more favorable than ice/water system because they can be operated at relatively high-temperature (~285 K) and atmospheric pressure. Unlike ordinary gas hydrates, in these semi-clathrate hydrates, the quaternary ammonium cation and anion are incorporated with the hydrogen bonds of water molecules to construct the hydrate cage [3]. In addition, four butyl groups are one-by-one

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encaged with a large cage separately in this semi-clathrate system. There are various reports about the crystal structure and the role of bromine for the TBAB hydrates [3, 4]. The hydration numbers of these structures are 26 and 38, which are described as Type A (tetragonal) and Type B (orthorhombic), respectively [4, 5]. The concentration of aqueous TBAB solutions results in differences of the crystal structure and thermodynamic stability of TBAB hydrate. TBAB semi-clathrate hydrates have become the object of much attention as an attractive medium for not only refrigerant but also H₂ storage [6-8].

There are a few reports about thermodynamic properties such as phase equilibria and dissociation enthalpy of TBAB hydrate [9] and about rheological property of these hydrate slurries [10] for the application to latent heat transport media. These hydrate slurries contain some microparticles of crystal, and the size and shape of these hydrate particles may affect the mobility of slurries. In addition, with the view of heat conductivity, it is necessary to make hydrate particles smaller and spherical and to control their agglomerating property so that hydrate particles dissociate rapidly and uniformly. Therefore, it is essential to investigate the efficient preparation method of hydrate slurries and the effect of hydrate particles on the fluid property of slurries for the application to latent heat transport media.

Generally, impeller agitation has been adopted as the method for efficient crystallization of hydrate particles. However, there are few reports about the control of particle property for clathrate hydrates by means of impeller agitation. In the present study, we aim at searching for the best condition of agitation that minimizes the total power needed for both agitation and pumping of the prepared hydrate slurries and the effect of agitation on particle size distribution and aggregation of particles to prepare runny TBAB hydrate slurries that are suitable for fluid transport. In this paper, the effect of speed of impeller rotation and impeller type on the particle size and frequency of aggregation was investigated. In addition, the key factor to control particle characteristics in TBAB hydrate slurries was briefly discussed.

**EXPERIMENTAL**

**Materials**
Research grade TBAB (mole fraction purity 0.980) was obtained from Wako Pure Chemical Industries, Ltd. All of them were used without further purifications. In addition, deionized water was produced using water-manufacturing equipment made by Nihon Millipore K. K.

![Table 1. The characteristics of three impellers.](#)

<table>
<thead>
<tr>
<th></th>
<th>2-BP</th>
<th>MB</th>
<th>RC</th>
</tr>
</thead>
<tbody>
<tr>
<td>n₀</td>
<td>100</td>
<td>17</td>
<td>33</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>300</td>
<td>50</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>Uniformity of shear rate</td>
<td>low</td>
<td>middle</td>
<td>high</td>
</tr>
</tbody>
</table>

**Apparatus and procedures**
The experimental apparatus in the present study consisted of the following parts: acrylic cylindrical vessel (diameter, D: 120 mm, height, H: 200 mm, handcrafted), three types of agitating impeller (handcrafted), agitating motors (HEIDON, BLh-300), torque meter (Type:YT, Shintou Kagaku, Co., Ltd.), temperature controller (TAITEC, CL-80R), and CCD camera (KEYENCE, VH5910). Figure 1 shows the details of three types of agitating impeller used in the present study: two-bladed paddle (2-BP), Maxblend® (Sumitomo Heavy Industries, Ltd., MB), and rotational cylinder (RC). The 2-BP impeller was attached in height of 60 mm. In addition, the characteristics of three impellers are summarized in Table 1. The average shear rate, \( \gamma_{av} \), can be calculated by use of Metzener & Otto’s equation [11] as follows:

\[
\gamma_{av} = Kn_r
\]

where \( K \) (depending on the type of impeller) and \( n_r \) stand for Metzener & Otto’s constant and the rotation speed of impeller, respectively.

Figure 2 shows the thermodynamic stability of TBAB hydrate (temperature, \( T \) – concentration, \( C \) diagram) at atmospheric pressure. The TBAB hydrate is stable at the temperatures below the line.
that is equivalent to the stability boundary of TBAB hydrate. As shown in Figure 2, the stoichiometric concentration of Type A TBAB hydrate is 40.5 wt% where the TBAB hydrate can exist stably at ~285 K. In the present study, the hydrate fraction in slurries, \( H_f \) was determined by the following equation:

\[
H_f = \frac{C_i - C_{eq}}{C_s - C_{eq}}
\]  

(2)

where \( C_i \), \( C_{eq} \), and \( C_s \) stand for the initial concentration of TBAB in aqueous solution, steady concentration of TBAB in the liquid phase of slurries, and stoichiometric concentration of TBAB hydrate respectively. In general, \( H_f \) decreases monotonically as temperature rises. In the present study, 20 wt% of TBAB in aqueous solution was adopted as a working fluid.

Firstly, the working fluid (20 wt% solution of TBAB) was poured into the vessel up to 120 mm (liquid height, \( h = D \)). Then, the fluid was cooled down up to 280.6 K (sub-cooling degree is ~0.7 K and then \( H_f = ~0.1 \)) and the rotation of impeller was started. After the system reached the cyclostationary state, some seed crystals of Type A TBAB hydrate, which were prepared in advance and annealed at 280.6 K, were injected into the vessel, and then crystallization occurred. In this case, it was confirmed that the particles of TBAB hydrate reached to the steady state after an hour. Hence, appropriate amount of hydrate particles was picked up from the mother fluid and observed by use of CCD camera on the stage that was chilled with Peltier device. Typical picture of hydrate particles were shown in Figure 3. In the present study, 300-500 particles in total were used for analysis of each experimental run. The particle diameter was defined as the major axis of rod-like hydrate particle. In addition, the aggregation particle was defined as the particle that consisted of more than two particles. Incidentally, the density of Type A TBAB hydrate particle was measured by means of falling ball method. The density of hydrate particle was comparable with the theoretical value, which can be calculated from the lattice constant of unit cell for tetragonal TBAB hydrate. Additionally, it is slightly larger than that of aqueous solution. In this case, it is reasonable to decide that the hydrate particles float completely in the vessel.

Figure 2  Temperature – composition diagram for the TBAB + water mixed system containing stability boundary of Type A (tetragonal) hydrate [2, 9].

![Temperature – composition diagram](image)

Figure 3  The particles of TBAB hydrate (a) and typical aggregation particle (b).

RESULTS AND DISCUSSION

The experimental data obtained in the present study are summarized in Table 2. Hereafter, the detailed discussion about the difference of results among three impellers is performed in each section.

Table 2. The summary of experimental results.

<table>
<thead>
<tr>
<th>Impeller</th>
<th>( n_c )/ rpm</th>
<th>Average diameter / mm</th>
<th>Aggregation frequency / %</th>
<th>( P/W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-BP</td>
<td>100</td>
<td>1.32</td>
<td>14.1</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.16</td>
<td>1.5</td>
<td>0.21</td>
</tr>
<tr>
<td>MB</td>
<td>100</td>
<td>1.13</td>
<td>6.3</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.77</td>
<td>0.4</td>
<td>1.08</td>
</tr>
<tr>
<td>RC</td>
<td>100</td>
<td>0.75</td>
<td>20.1</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.75</td>
<td>16.6</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.76</td>
<td>16.2</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Particle size and its distribution

Figure 4 shows the particle diameter of TBAB hydrates and its distribution for three types of impeller. In the case with 2-BP and RC, the particle diameter and its distribution do not change with the increase of shear rate. On the other hand, they change drastically as shear rate increases in the case with MB. This indicates that the growth of hydrate particle is suppressed considerably under the shear conditions above a certain level. In addition, even though the shear rate of RC is lowest among three impellers at the equal speed of impeller rotation, the particle diameter and its distribution is relatively small in RC. Hence, the uniformity of shear rate is one of dominant factors for the control of particle diameter and its distribution. Although the shear rate of MB is inhomogeneous compared with that of RC, the average shear rate of MB at \( n_r = 300 \) rpm is very high. Consequently, the region of low shear rate can be kept away in the vessel and particle diameter becomes small.

![Figure 4](image)

Figure 4 The particle diameter of TBAB hydrate and its distribution for three types of impeller; (a) \( n_r = 100 \) rpm, (b) \( n_r = 300 \) rpm.

Aggregation frequency of hydrate particle

The open keys in Fig. 5 stand for the aggregation frequency of hydrate particles. The aggregation frequency becomes smaller in the order of RC, 2-BP, and MB. In addition, it becomes small as the shear rate increases. That is, the aggregation of hydrate particles is suppressed by the collision between hydrate particles and impeller blade, and the existence of field that has locally-high shear rate.

Required power for the agitation of hydrate slurries

The closed keys in Figure 5 represent the required power to agitate hydrate slurries. As mentioned previously, MB can create the flow field that has a distinct advantage for the control of hydrate particles and restrain of its aggregation. As expected, however, the required power for agitation in MB is extremely large compared with the other impellers.

![Figure 5](image)

Figure 5 The aggregation frequency of hydrate particles (open keys, left axis) and required power to agitate hydrate slurries (closed keys, right axis) for three types of impeller.

Based on these results, to prepare the hydrate particles that have small diameter and sharp distribution of diameter, three factors is essential as follows: 1. uniformity of shear rate, 2. cancellation of the region of low shear rate, and 3. existence of field that has locally-high shear rate. The findings obtained in the present study are useful for the development of new impeller that is suitable for the preparation of runny TBAB hydrate slurries.

**SUMMARY**

To prepare runny TBAB hydrate slurries, the effect of speed of impeller rotation and impeller type on the particle size and frequency of aggregation has been investigated. The findings are summarized in Table 3.

<table>
<thead>
<tr>
<th>Impeller</th>
<th>( n_r ) / rpm</th>
<th>Particle diameter</th>
<th>Aggregation frequency</th>
<th>Required power</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-BP</td>
<td>100</td>
<td>large</td>
<td>high</td>
<td>small</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>large</td>
<td>low</td>
<td>small</td>
</tr>
<tr>
<td>MB</td>
<td>100</td>
<td>large</td>
<td>middle</td>
<td>small</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>small</td>
<td>low</td>
<td>large</td>
</tr>
<tr>
<td>RC</td>
<td>100</td>
<td>small</td>
<td>high</td>
<td>small</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>small</td>
<td>high</td>
<td>small</td>
</tr>
</tbody>
</table>

Table 3. The simple summary of findings.
ACKNOWLEDGMENTS
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REFERENCES