Experimental investigation on TBAB clathrate hydrate slurry flows in a horizontal tube: Forced convective heat transfer behaviors

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ABSTRACT
Tetra-n-butyl-ammonium bromide (TBAB) clathrate hydrate slurry (CHS) is one kind of secondary refrigerants, which is promising to be applied into air-conditioning or latent-heat transportation systems as a thermal storage or cold carrying medium for energy saving. It is a solid–liquid two phase mixture which is easy to produce and has high latent heat and good fluidity. In this paper, the heat transfer characteristics of TBAB slurry were investigated in a horizontal stainless steel tube under different solid mass fractions and flow velocities with constant heat flux. One velocity region of weakened heat transfer was found. Moreover, TBAB CHS was treated as a kind of Bingham fluids, and the influences of the solid particles, flow velocity and types of flow on the forced convective heat transfer coefficients of TBAB CHS were investigated. At last, criterial correlations of Nusselt number for laminar and turbulent flows in the form of power function were summarized, and the error with experimental results was within ±20%.

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Etude expérimentale sur l’écoulement des coulis d’hydrate de clathrate au bromure de tétra-n-butyl ammonium à l’intérieur d’un tube horizontal : transfert de chaleur par convection forcée

Mots clés : Coulis de glace ; Clathrate ; Hydrate ; Expérimentation ; Convection forcée ; Transfert de chaleur ; Tube horizontal

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In order to reduce the pumping power consumption of cold medium in central air-conditioning or district cooling systems, some new materials with high thermal capacity are desirable to be applied as the secondary refrigerant to replace the traditional water. Those new refrigerants should usually have high density of cold transportation and compatible working temperature close to that of traditional water. Tetra-n-butyl-ammonium bromide (TBAB) clathrate hydrate slurry (CHS) is one of those materials (Hayashi et al., 2000; Ogoshi et al., 2001; Takao et al., 2002). This new working medium is a mixture comprising of TBAB clathrate hydrate crystals and its aqueous solution. It has good fluidity and high thermal energy carrying density (193.5 kJ kg\(^{-1}\) for type A and 205 kJ kg\(^{-1}\) for type B) because of its phase-change latent heat. The diameters of crystal particles distribute in the range of 10\(^{-4}\)–10\(^{-3}\) m (Darbouret et al., 2005a,b), and the particles hardly conglomerate with each other, so it is easy to be transported through pipe and pump. Furthermore, its phase-change could take place under the conditions of normal atmospheric pressure and temperature of 278–285 K, which just fits the application temperatures of air-conditioning. So many advantages make TBAB CHS more possible to be applied extensively and achieve the effects of energy saving in the industry of air-conditioning.

According to the difference of hydrate crystal structure, TBAB CHS is classified as type A and type B. The fluid behaviors have been studied by several researchers around the world and both types are treated as Bingham fluid based on Darbouret and our own works (Darbouret et al., 2005a,b; Xiao et al., 2006). For the aim of industrial applications, the forced convective heat transfer behaviors are worthy of research. However, only a few works have been done by far. Since 1998, Ogoshi and Takao (2004) of JFE Engineering Corporation (Japan) have done some research works on heat transfer characteristics of TBAB CHS using flat-plate heat exchanger and fan-coil unit, which focused on the engineering applications and seldom on the theoretical analysis (Obata et al., 2003; Ogoshi and Takao, 2004). Xiao et al. (2007) experimentally measured the convective heat transfer coefficients under constant heat flux in a horizontal copper tube with type A hydrate, and obtained a correlation of Nusselt number with Reynolds number, but their data were not valid for the type B CHS. Except those mentioned above, few literatures on the heat transfer of TBAB CHS are found on public publications. However, studies on some other slurries, such as ice slurry, could provide some useful ideas and references (Knodel et al., 2000; Ayel et al., 2003; Lee et al., 2006; Niezgoda-Zelasko, 2006; Niezgoda-Zelasko and Zelasko, 2008).

In this paper, the forced convective heat transfer characteristics of TBAB CHS were investigated in a horizontal stainless steel tube with constant heat flux. Two types of CHS, namely type A \(((\text{C}_4\text{H}_9\text{N})_4\text{NBr}_2\cdot2\text{H}_2\text{O})\) and type B \(((\text{C}_4\text{H}_9\text{N})_4\text{NBr}_3\cdot3\text{H}_2\text{O})\) generated from the solutions with initial aqueous concentration of 30.0 wt% and 17.3 wt% respectively, were studied. The characteristics of heat transfer were revealed by comprehensively analyzing the influence of solid mass fraction \(\chi\) and flow regimes. And some useful correlations for evaluating the heat transfer coefficients under different flow types were proposed.
upstream section of the test tube, there was an adiabatic PVC tube long enough to enable the flow to be fully developed. A transparent plexiglass tube was installed on the upstream section in order to observe flow state of the TBAB CHS. Heat was introduced into the flowing medium homogeneously along the test tube wall by passing a direct electric current through the test tube. This could ensure uniformity of heating along the whole tube length as long as the stainless steel resistance was uniform. The manner of directly heating satisfied the requirement of constant heat flux density condition. In this work, the heat flux density \( q_m \) was kept at 15 kW m\(^{-2} \).

To measure the mean temperature of TBAB CHS at the inlet and outlet of the test tube, the highly sensitive resistance sensors Pt100 were adopted, which with the nominal accuracy of \( \pm 0.15 \) K (a diameter of the sensor mantle about 5 mm, and the minimum active length of 0.02 m). The temperature of test tube wall was measured by means of K type thermocouples which were soldered into the outer wall of the test tube. And so the temperature difference between the tube wall and the core of the flowing medium could be calculated. Eight mantled thermocouples of K type were utilized along the test tube for ancillary measurement of the core temperature of CHS. The temperature sensors were installed as shown in Fig. 2. In order to ensure the measurement precision, sensors were calibrated in whole temperature range using a sensor Pt100 with \( \pm 0.018 \) K nominal accuracy.

One coriolis mass flow meter was used to measure the mass flow flux of TBAB CHS. In the meantime, it can also measure the fluid density which would be used as an auxiliary function for determining the mass fraction of solid phase \( \chi \).

The most important measuring devices were listed in Table 1. All the measured parameters were recorded by a data acquisition system.

### 2.2. Determination of solid mass fraction

In this paper, solid mass fraction of \( \chi \) of CHS was determined indirectly by measuring the equilibrium temperature of CHS. According to phase diagram (Oyama et al., 2005; Wataru et al., 2005), the type and solid mass fraction of hydrate are uniquely determined by a certain initial concentration and a certain temperature of TBAB aqueous solution. The solutions with initial concentrations of 30.0 wt\% and 17.3 wt\% were prepared, which could form the type A and type B clathrate hydrate, respectively. When CHS comes into being, the relation between equilibrium temperature and concentration of residual aqueous solution \( C_T \) is a one-to-one function. This function can be fitted as following equations for type A and type B, respectively:

\[
\begin{align*}
C_T &= 0.28883e^{-7.1239/1.46918} + 0.03451e^{-7.1239/0.00711} + 0.07418, \quad 281.15 \leq T \leq 284.75 \text{ K type A} \\
C_T &= 0.01144T^2 - 0.14610T + 0.55484, \quad 280.65 \leq T \leq 282.75 \text{ K type B}
\end{align*}
\]

(1)

Then, according to mass conservation of solute, mass fraction of solid phase can be calculated by following equation:

\[
\chi = \frac{C_0 - C_T}{C_f - C_T} \quad (C_T \leq C_0 < C_f)
\]

(2)

where, \( C_0 \) is initial concentration of TBAB aqueous solution. \( C_f \) is the congruent concentration, which is equal to the TBAB mass fraction in TBAB hydrate crystal \(((\text{C}_4\text{H}_9)_4\text{NBr} \cdot n\text{H}_2\text{O})\). For type A, \( C_0 = 0.30 \) and \( C_f = 0.408 \), and \( C_T \geq 0.255 \). For type B, \( C_0 = 0.173 \) and \( C_f = 0.32 \), and \( C_T \geq 0.11 \). When the equilibrium
temperature of CHS is measured, the mass fraction of solid can be determined by equation (2). The accuracy of this method was calibrated via calorimeter off-line measurement. In this work, mass fraction of solid \( \chi \) was corresponding to the value at inlet of test pipe.

### 2.3. Theoretical background

Corresponding to a given \( \chi \) and \( V \), the local heat transfer coefficient is calculated from the equation:

\[
a(x) = \frac{q_m}{T_{\text{win}} - T_f}
\]  

where, \( T_f \) is the local bulk temperature of CHS. The local temperature of inside wall \( T_{\text{win}} \) can be deduced from \( T_{\text{wout}} \) and heating power \( P \). The heating power into the test tube was measured by wattmeter, and recorded by the data acquisition system.

Then the mean heat transfer coefficient along the test tube could be obtained by the following equation:

\[
\alpha = \frac{1}{L} \int_0^L a(x) \, dx
\]  

As TBAB CHS yields to the Bingham model, the dimensionless Reynolds number should be defined according to Metzner-Reed definition as (Skelland, 1967)

\[
\text{Re}_M = \frac{DV \rho_s}{\mu_e}
\]

The effective viscosity \( \mu_e \) can be simplified to the following form

\[
\mu_e = \frac{D \tau_0}{6V} + \eta
\]

In equation (6), the plastic viscosity \( \eta \) and yield shear stress \( \tau_0 \) have been determined by the CHS flow experiments in the author’s former works.

Prandtl number is defined as

\[
Pr = \frac{\mu_e c_p}{\lambda}
\]

where, \( \rho, c_p, \lambda \) are the thermal physical properties of CHS, which can be simply calculated from solid mass fraction by the weighted average method.

### 2.4. Measurement ranges of parameters

In the experiments on forced convective heat transfer of CHS, the main parameters both for type A and type B were confined in the ranges as follows:

1. Test tube with diameter \( D = 0.014 \text{ m} \);
2. Constant heat flux density \( q_m = 15 \text{ kW m}^{-2} \);
3. Mean flow velocities \( 0.35 V_{\text{max}} \leq V \leq 6.80 \text{ m s}^{-1} \), with the corresponding Reynolds numbers in the range of \( 300 \text{Re}_M \leq 18,000 \);
4. Mass fraction was \( 0 \leq \chi \leq 18.4\% \) for type A and \( 0 \leq \chi \leq 26.2\% \) for type B.

### 3. Results and discussion

#### 3.1. Effects of flow velocity

Fig. 3 shows the function of \( a(V) \). The heat transfer coefficient of CHS is monotonously increasing with the increase of flow velocity in the whole range of \( \chi \). What is special is that, for example, type A CHS within the limited value (\( \chi < 18.5\% \)), there exists one velocity region (\( 2.0 < V < 3.5 \text{ m s}^{-1} \)) in which heat transfer coefficients are lower than that of TBAB aqueous solution (\( \chi = 0\% \)). The phenomenon is same as that of ice slurry (Niezgoda-Zelasko, 2006), but opposite to the result of Knodel (Knodel et al., 2000).

This velocity region is named as region of weakened heat transfer which similar as region of weakened flow resistance observed in the earlier flow experiments conducted by the authors, and it divides the whole velocity range into three regions. The presence of solid hydrate crystals may give an explanation. In low velocity region (\( V < 1.0 \text{ m s}^{-1} \)), micro-convection by uneven shear stress for dispersed solid particles and large specific heat capacity in the phase change temperature range are the main reasons for heat transfer.
enhancement in laminar region. Except that, CHS of type A with $c > 0$ shows higher convective heat transfer coefficient than CHS with $c = 0$ does because the solid hydrate crystal has higher thermal-conducting abilities than TBAB solution does (the thermal conductivity of type A solid hydrate crystal is 0.42 W m$^{-1}$ K$^{-1}$ and that of the 30 wt% TBAB aqueous solution is 0.34 W m$^{-1}$ K$^{-1}$). The higher thermal conductivity of solid hydrate crystal helps to enhance the convective heat transfer in laminar region. In high velocity region ($V > 4.5$ m s$^{-1}$), the perturbation of solid particles, in full turbulent region, destroys or thins the laminar sublayer of CHS flow, and then enhances the convective heat transfer. Except for the velocity regions mentioned above, flow regime plays a key role in the region of weakened heat transfer. CHS with $c = 0$, which in transition or turbulent flow region, shows higher heat transfer coefficient than CHS with $c > 0$, which still in laminar flow region at the same velocity. Type B CHS behaves very similar as type A (the region of weakened heat transfer within the range of 0.6 < $V$ < 1.2).

Compared with that of type A CHS, the heat transfer coefficient of type B CHS is more sensitive to the variations of solid mass fraction $c$, especially in the fully developed turbulent flow region. In turbulent flows, increasing $c$ could be one effective method to enhance heat transfer for type B CHS.

3.2. Effects of solid mass fraction

Fig. 4 illustrates the heat transfer coefficient as a function of $\chi$. In a gross, it is a monotonic increasing function. However, on each constant flow velocity curve, there exists an inflection segment on which the heat transfer coefficient drops sharply with the increasing of $\chi$. It is doubtlessly that this segment is just the transition region from turbulent to laminar flow based on the common sense of convective heat transfer coefficient differences between turbulent flow and laminar flow. Though the flow velocity keeps constant, the flow state may evolve from turbulent to laminar as the solid mass fraction increasing gradually. That is to say, the presence of solid hydrate crystals tends to keep the CHS flow in laminar state. This phenomenon was named as re-laminarization, which was researched in the former works of the authors on CHS flows.

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Fig. 4 – Nusselt number versus solid mass fraction $\chi$ at different velocities: (a) type A; (b) type B.
One imaginary line can be obtained by linking all the inflection points on different constant flow velocity lines. That is the flow type transition curve represented by solid mass fraction. Above the transition curve, CHS flows in the transition and turbulent states, and under is in the laminar state. Corresponding to critical ReMc, it was in the range of $2000 < \text{Re}_{Mc} < 3500$ for type A and $1800 < \text{Re}_{Mc} < 3500$ for type B.

### 3.3. Correlations of convective heat transfer

Power function has been used to describe the forced convective heat transfer characteristics of CHS flow and has good agreement with the experimental results. It usually has the following form

$$\text{Nu} = A \text{Re}^a \text{Pr}^b \tag{8}$$

In this paper, we did the same work to obtain the relations for type A and type B CHS in laminar and turbulent flow respectively. The values of undetermined parameters, such as $A$, $a$, and $b$, are listed in Table 2. An identification of the criterial relations was proved to satisfy the maximum error within $\pm 20\%$ between the measured and calculated Nu numbers, as shown in Fig. 5(a, b).

### 4. Conclusions

The analysis of results obtained in this work leads to the following conclusions:

1. One velocity region of weakened heat transfer was found. In this region, CHS with $\chi > 0$ has lower heat transfer coefficient than the carrying fluid ($\chi = 0$). Out of this region, however, it is reverse. This finding will be helpful to provide guideline for engineering applications.
2. Re-laminarization phenomenon of CHS was confirmed based on the heat transfer experiments, which was coincident with what observed in flow experiments.
3. It was confirmed that heat transfer coefficients are more significantly affected by solid mass fraction $\chi$ in turbulent region than that in laminar region, especially for type B CHS.
4. Criterial relations, used to evaluate heat transfer coefficients in the laminar and turbulent regions for type A and type B CHS, were proposed. The error with experimental results was within $\pm 20\%$.

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