The Effect of DC Voltage on Solidification of Tetrabutyl-Ammonium Bromide (TBAB) Aqueous Solution

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Abstract. This study aimed to investigate the nucleation process of 23 wt% tetrabutylammonium bromide (TBAB) aqueous solution due to DC voltage. TBAB hydrate is an example of a thermal energy storage system with a phase change temperature of around 0–12 °C. The commonly sold copper electrodes are inserted into the sample to supply the voltage continuously. The diameter of the electrodes was 1 mm, and the gap was approximately 0.5 mm. The applied voltage varied as the experimental parameter is in the range of 0 to 30 V. Two repetitive freezing-thawing experiments are performed to ensure data repeatability. The experimental results showed that the TBAB hydrate would not form until a minimum value of 20 V of DC voltage was applied. The increase of the voltage used led to higher solidification temperature and reduction of the supercooling degree.

1. Introduction
There are many ways to store the energy, that is mechanically, electrically and thermally [1]. An appropriate energy storage method can transform a type of energy to another form, to be ready used at another time. It can be a solution to reduce the mismatch between energy supply and demand and dramatically affects the energy conservation level [2,3]. This paper focuses on studying thermal energy storage (TES) using phase change materials (PCM). TES deals with thermal energy storage by transforming the material through heating or melting the material and serving the thermal energy when the process is reversed [3]. PCM is a material that can store and release heat in the form of sensible and latent heats. The sensible heat storage is marked by the temperature change of the storage medium, while the latent heat storage at a relatively constant temperature related to the phase change of the material. The phase change usually involves solid-liquid phases that transform to each other at melting or freezing temperature [1,3,4].

Generally, the suitable temperature range for TES material to undergo phase changing for cooling is between 5–10 °C. Tetrabutylammonium bromide (TBAB) is a potential PCM for an air conditioning system with phase change temperature for TBAB hydrate is in the range of 0–12 °C [5]. Furthermore, TBAB hydrate forms a slurry, and the efficiency of thermal energy storage systems can be enhanced
using TBAB hydrate slurry as a PCM. TBAB is a white powder at normal temperature and pressure and considered non-toxic and soluble in water. During the hydrate formation from a TBAB aqueous solution, supercooling occurs. In general, supercooling causing a decrease in the coefficient of performance (COP) of the refrigeration [5,6].

Several researchers have conducted many attempts to control the supercooling actively by adding the electric field to the material, the so-called electrofreezing or electronucleation. Kumano et al. [7] investigated the effect of electric field and electrode materials on TBAB nucleation. They found that the probability of nucleation is high under the electric field application, and the copper (Cu) electrode is the most effective in inducing the electrofreezing process. Oyama et al. [8] reported two types of TBAB hydrates formed from TBAB aqueous solution: type A and type B. Hydrate type A was created from the higher concentration of TBAB solution, while type B from the lower concentration. The difference between the two types of hydrates is the hydration number, melting point, and crystal morphology. Furthermore, Kumano et al. [6] study the nucleating activity of TBAB 20 wt% due to electrode products by applying 20 V DC voltage for 3 minutes at a fixed supercooling degree of 4 K and found that the electrode products generated by the application of DC voltage affected the nucleation of TBAB hydrate. Kumano also found that electric current did not affect the nucleation significantly.

In this paper, we report the results for an attempt to investigate the effect of DC voltage toward the supercooling degree during the solidification process of TBAB 23 wt.% from its aqueous solution. We varied the DC voltage from 0 V to 30 V. We analysed its effect to the supercooling degree as Orlowska et al. [9] found that applying high DC voltage (2–12 kV) to water caused the increase of nucleation temperature and reduction of supercooling degree. We also attempt to observe the change in electric current during the solidification. Based on the phase diagram reported by Oyama et al. [8] the melting point of TBAB 23 wt.% is approximately 9.5 °C, which is in the range temperature of our cold-water bath.

2. Experiment

Figure 1 shows a schematic diagram of the experimental setup used in this experiment. The experimental apparatus consists of a DC power supply with a maximum voltage of 30 V, digital multimeter, data logger, PC, copper (Cu) electrodes with a diameter of 1 mm, 10 kΩ resistor, and cold-water bath with a minimum temperature of 2 °C.
TBAB 23 wt.% prepared by dissolving 6 mg of TBAB powder into 20 ml of distilled water. The sample then placed into 50 ml beaker glass. Two copper electrodes with the gap were approximately 0.5 mm immersed into the sample and placed in the glass center. The Cu electrodes used in this experiment were commonly sold in the market that already coated with an insulator. One electrode is connected to an external resistor with relatively high resistance to minimize the current passing through the resistor to get a more precise voltage reading on the multimeter installed parallel to the circuit to record the voltage changes during the process. The voltage data used to study the evolution of the electric current during the nucleation process based on equation \( I = \frac{V}{R} \), with \( R \) is the resistance of the external resistor (10 k\( \Omega \)). Two temperature sensors placed into the sample, each located at the beaker glass wall and in the center of the glass near the electrodes to record the changes in temperature every 5 seconds.

The experimental process started by immersing the beaker glass containing the sample into warm water until the sample reached a thermal equilibrium at 35 °C. The sample then suddenly exposed to a cold-water bath with a temperature of 2-6 °C. DC voltage is applied when the temperature of the sample reached 25 °C. The temperature of the sample is maintained to be in the range 2-5 °C during the solidification process. The experimental parameter values of applied voltage are 15 V, 20 V, 25 V, and 30 V, and sample with 0 V as a comparison. Each parameter is repeated two times to ensure data repeatability.

3. Results and Discussion

Figure 2 shows the temperature profile obtained during the nucleation process. It appears that the sample did not nucleate when 0 V dan 15 V DC voltage applied, signified by there was no rising in temperature, which indicates the heat release when TBAB hydrate formed. Nucleation occurred when a minimum 20 V DC voltage was applied.
Experimentally, we observed a change in the color of the sample and the electrodes' tips. The sample turned bluish and turbid, while the ends of the electrodes experiencing erosion, with the level of erosion, are more for the cathode than the anode.

Figure 3 presents a way to determine the solidification temperature and supercooling degree. The melting temperature for TBAB 23 wt.% was approximately 9.5 °C [8]. Solidification temperature defined as the actual temperature when the hydrate started to form and induced the rising in temperature. The difference between the melting temperature and the solidification temperature of the hydrate defined as the supercooling degree [7].

Apart from the notation proposed by Kumano et al. [7], we determined another temperature characteristic at the peak in Figure 3 as the freezing temperature and defines supercooling degree as the
difference between freezing temperature and solidification temperature. Table 1 presents the value of the solidification temperature ($T_{\text{solid}}$), the supercooling degree according to Kumano ($\Delta T_{s-1}$), the freezing temperature ($T_f$), and the supercooling degree according to our definition ($\Delta T_{s-2}$). The supercooling degree tends to decrease when the applied voltage is higher (Figure 4).

**Table 1** The average values for $T_{\text{solid}}$, $\Delta T_{s-1}$, $T_f$, and $\Delta T_{s-2}$, and standard deviation values for $\Delta T_{s-1}$ and $\Delta T_{s-2}$ from 2 sets of experiment.

| Voltage (V) | $T_{\text{solid}}$ (°C) | $\Delta T_{s-1}$ (°C) | St. dv | $T_f$ (°C) | $\Delta T_{s-2}$ (°C) | St. dv |
|------------|--------------------------|------------------------|--------|------------|------------------------|--------|
| 0          | -                        | -                      | -      | -          | -                      | -      |
| 15         | -                        | -                      | -      | -          | -                      | -      |
| 20         | 3.46                     | 6.04                   | 0.24   | 8.65       | 5.19                   | 0.01   |
| 25         | 3.76                     | 5.74                   | 0.13   | 8.9        | 5.14                   | 0.33   |
| 30         | 4.98                     | 4.52                   | 0.21   | 9.26       | 4.28                   | 0.62   |

**Figure 4.** Relationship between supercooling degree and applied DC voltage.

Besides the temperature parameter, the time characteristic consists of solidification time ($t_{\text{solid}}$), the freezing time ($t_f$), and the period of supercooling ($\Delta t_s$). In this case, $\Delta t_s$ defined as the time difference when the sample undergoes solidification until it reaches the freezing temperature. The period of supercooling tends to be longer when the applied voltage is increased (Figure 5).

**Figure 5.** Relationship between the supercooling period and applied DC voltage.
Figure 6 presents the temperature profile and electric current profile obtained during the solidification process. The relation between the current and the formation of TBAB hydrate apparently cannot be determined with certainty. Kumano [5] reported that for the same electrode material and applied DC voltage, the impurity of the solution and the contamination of the electrodes into the sample might cause different measurement of the current.

4. Conclusion

We investigated the effect of the DC voltage on the nucleation process of 23 wt% tetrabutyl ammonium-bromide (TBAB) aqueous solution experimentally by varying the DC voltage from 0 V to 15 V, 20 V, 25 V, and 30 V. The experiment performed by applying the voltage through a 1 mm diameter of copper electrodes inserted into the sample. The gap between the electrodes is about 0.5 mm. We found that DC voltage plays an essential role in the nucleation of the 23 wt% TBAB. The sample did not nucleate until the application of a minimum voltage value of 20 V. The increase of the applied voltage led to the higher the solidification temperature to reduce the supercooling degree. The electric current decreases when the sample solidifies, signifying the sample resistance decrease in the solid phase.

Acknowledgements

This paper is a result of Kerja Mandiri (FI-6097) study in the Magister Physics of Physics Department, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung.

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