

The Cooling Characteristics of Clathrate Compound according to Concentration of TMA

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Abstract

The ice storage system uses water for low temperature latent heat storage. However, a refrigerator capacity is increased and COP is decreased due to supercooling of water in the course of phase change from solid to liquid. This study investigates the cooling characteristics of the TMA-water clathrate compound including TMA (Tri-methyl-amine, $(\text{CH}_3)_3\text{N}$) of 20~25 wt% as a low temperature latent heat storage material. The results showed that the phase change temperature and the specific heat is increased and the supercooling degree is decreased as the weight concentration of TMA increased. Especially, the clathrate compound containing TMA 25 wt% has the average phase change temperature of 5.8 °C, the supercooling degree of 8.0 °C and the specific heat of 3.499 kJ/kgK in the cooling process. This can lead to reduction of operation time of refrigerator in low temperature latent heat storage system and efficiency improvement of refrigerator COP and overall system. Therefore, energy saving and improvement of utilization efficiency are expected.

Key words: Low temperature latent heat storage, TMA-water clathrate compound, Phase change temperature, Supercooling degree, Specific heat

Nomenclature

T_p : Phase change temperature [°C]
 T_s : Supercooling temperature [°C]
 ΔT : Supercooling degree [°C]
 t : Time [sec]
 t_L : Time of liquid phase retention [sec]
 At : Cooling times [sec]
 c_p : Specific heat [kJ/kgK]
 W : Water equivalent [kg]
 m : Mass [kg]

Subscript

p : Phase change
s : Supercooling
w : Pure water
m : Latent heat storage material
B : Pyrex Bottle
b : Brine

1. Introduction

The low temperature latent heat storage system is supplied more and more so that power load in the daytime due to refrigeration demand in summer time is moved into nighttime and load equalization of whole power is achieved. The ice storage system uses water as low temperature latent heat storage material. However, a refrigerator capacity is increased and COP is decreased because refrigerator is operated at low temperature due to supercooling of water in the course of phase change from solid to liquid. This leads to high operation cost of system and low energy utilization efficiency. For this reason, study on restraint or removal of water supercooling and use of material other than water as low temperature latent heat storage material has been conducted.⁽¹⁾

The materials that can store low temperature solidification latent heat are organic/inorganic chemicals, eutectic salt system and clathrate compound. The clathrate compound is the material that host in hydrogen bond forms cage and guest is included into it and

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Table 1. Characteristics of TMA.⁽³⁾

Clathrate	Ideal properties			Critical decomposition	Critical properties		
	Boiling point [°C]	Freezing point [°C]	hydrate number	temperature [°C]	temperature [°C]	Pressure [kPa]	Specific volume [m ³ /kg]
TMA (CH ₃) ₃ N	2.9	-117.2	11	5.3	160.2	4090.0	0.00429

combined. The crystallization of hydrate is formed at higher temperature than that of ice from pure water. Physical properties according to temperature are stable and congruent melting phenomenon occurs without phase separation and it has relatively high latent heat. But the clathrate compound still has supercooling problem occurred in the course of phase change. Therefore, various studies on additives to restrain this or heat storage methods have been conducted.

This study investigates the cooling characteristics of the TMA-water clathrate compound including TMA (Tri-methyl-amine, (CH₃)₃N) of 20~25 wt% as a low temperature latent heat storage material.

TMA, the third amine series, is colorless gas and soluble to water, ether and alcohol. TMA gaseous molecule is included by water molecule in hydrogen bond at temperature of phase change and forms clathrate compound of cluster type.⁽²⁾ The properties of TMA are shown in Table 1.

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2. Experimental devices and method

In this study, experimental device is prepared as Fig. 1 to measure cooling characteristics of TMA-water clathrate compound. The low temperature reservoir is made sufficiently bigger than Pyrex bottle set to get reliability. The low temperature thermostat and reservoir are connected by circulating pump to maintain constant cooling source temperature constantly during experiment. The reservoir is insulated by using 100mm thickness insulating material to minimize influence from outside and thermocouple is installed to measure temperature. Pyrex bottle set is sealed with epoxy and silicon because K-type thermocouple is installed.

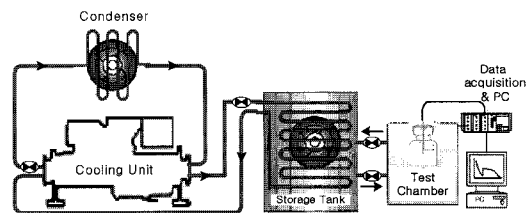


Fig. 1. Schematic diagram of cooling characteristics test.

TMA of 20~25 wt%-water clathrate compounds is filled up to 60g Pyrex bottle set. They are maintained at 20°C in high temperature reservoir. After that, it is refrigerated at low temperature reservoir that cooling source temperature controls at -5°C. The cooling characteristics are analyzed on phase change temperature, supercooling degree and specific heat of TMA-water clathrate compounds.

3. Experimental result and discussion

3.1 Phase change temperature

In this study, the clathrate compounds with 20~25 wt% of TMA are refrigerated in reservoir and maintained at phase change temperature. By repeating the cooling experiment, a mean value for its cooling characteristics was obtained. Fig. 2 is the phase change temperature according to weight concentration of TMA.

The temperature change of TMA-water clathrate compounds showed a sudden change from its initial cooling temperature to its lowest supercooling temperature. The TMA-water clathrate compounds had reached to supercooling temperature and showed a temperature change nearly closed to a vertical line, and after this, reached its phase change temperature. They were solidified as the gas molecules of TMA and the water molecules of hydrogen bond were fused together to form a clathrate compound in a cluster form at phase change temperature. The phase change temperatures were 5.4~5.8°C on average according

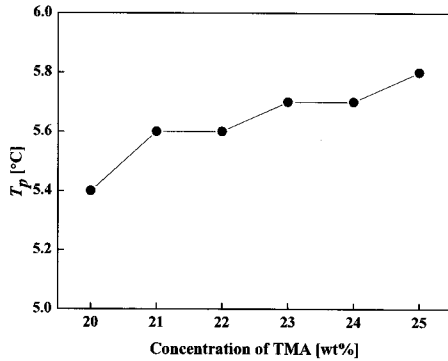


Fig. 2. The phase change temperature as weight concentration of TMA at cooling source temperature of -5°C .

to the weight concentration of TMA. Their phase change temperatures were higher than pure water, and were found to be higher as the weight concentration of TMA became larger. Especially, a clathrate compound with TMA of 25 wt% showed an average of 5.8°C of phase change temperature, which was the highest of all. The phase of TMA-water clathrate compounds were not separated during a phase transition process. It could be considered that such phase separation phenomenon did not happen according to its temperature change because TMA had formed a stable solution by dissolving well enough in water.

3.2 Supercooling degree

The supercooling is the phenomenon that low temperature thermal storage material is not crystallized and existed as liquid for some time below phase change temperature. Because phase change into solid is delayed heat transfer from low temperature thermal storage material is lowered. Because it is not crystallized at original phase change temperature and crystallized after supercooling, operation time of refrigerator is increased. The supercooling depends on volume and purity of solution, cooling velocity, container surface condition, and agitation state of solution.⁽⁴⁻⁵⁾ In this study, same container (Pyrex bottle) was used and weight was maintained the same and cooling source temperature was fixed for constant cooling velocity.

The supercooling degree (ΔT) is the difference between phase change temperature (T_p) and minimum supercooling temperature (T_s), and is calculated by equation (1).

$$\Delta T = T_p - T_s \quad (1)$$

Fig. 3 is the supercooling degree according to weight concentration of TMA. The clathrate compound as TMA per weight concentration and a pure water was cooled to its cooling temperature of -5°C . Pure water was cooled to its cooling temperature without a supercooling. But TMA-water clathrate compounds showed a phase change from a supercooled state after maintaining its liquid state to a certain extent. The average supercooling degree decreased as the weight concentration of TMA increased. Especially, in the case of a clathrate compound with 25 wt% of TMA, the average supercooling degree was the lowest at 8.0°C .

The time of liquid phase retention was shortened as the weight ratio of TMA was higher. As in the case of 25 wt% of TMA, the liquid state maintained for average 651sec and it could be considered to have a better suppressing effect on supercooling than other TMA concentration. Furthermore, the time of liquid phase retention of the clathrate compounds with 23~25 wt% of TMA was 651~2341 sec on average. And the time of liquid phase retention while being cooled at a constant cooling source temperature was shortened as the weight ratio of TMA became higher. This showed that it would be advantageous to add a TMA concentration of higher than 23 wt% for application as a low temperature latent heat storing material.

Fig. 4 is a distribution map which showed both the supercooling temperature and the time of liquid phase retention following the repeated experiment. It could be confirmed that the supercooling temperature was decreased and the time of liquid phase retention was shortened as the weight concentration of TMA became higher. The cooling process as liquid state could be considered to affect the supercooling.

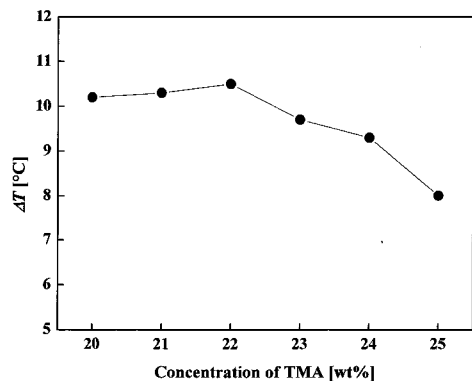


Fig. 3. The supercooling degree as weight concentration of TMA at cooling source temperature of -5°C .

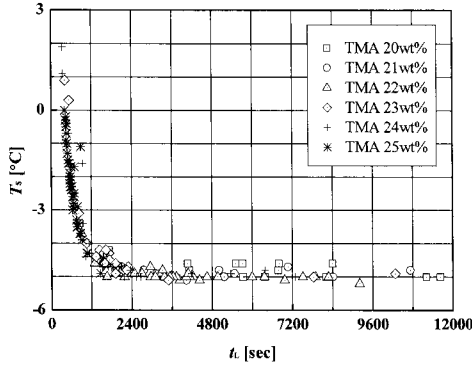


Fig. 4. The distributions of supercooling temperature (T_s) and the time of liquid phase retention (t_l) as weight concentration of TMA at cooling source temperature of -5°C .

The weight concentration of TMA could be concluded to affect the formation of the clathrate compound of the water molecules and TMA gas molecules. Especially, in the case of a clathrate compound with TMA concentration of over 23 wt%, a suppressing effect on supercooling is significant and the activity for forming a clathrate compound is considered to increase. It is considered that the speed of TMA molecules becoming a clathrate compound and forming a cluster is increased by activating the hydrogen bonding of the water molecules because the enthalpy is increased as the weight concentration of TMA becomes higher.

3.3 Specific heat

In this study, time is measured during temperature change from 15°C to 10°C based on cooling curve. It is cooled with pure water at -5°C . The specific heat (c_{pm}) is calculated by using following equation (2).

$$c_{pm} = \frac{m_w c_{pw} \Delta t_w + W_B (\Delta t_m - \Delta t_w)}{m_m \Delta t_w} \quad (2)$$

Where, m_w and m_m are masses of pure water and TMA-water clathrate compound filled in Pyrex bottle, respectively. W_{Bw} and W_{Bm} are water equivalent of Pyrex bottle. c_{pw} is average specific heat of water. Δt_w and Δt_m are time change while a low temperature latent heat storage materials are cooled from 15°C to 10°C . Fig. 5 is the specific heat according to the weight concentration of TMA.

The average specific heats were 3.499~4.051 kJ/kgK depending on 20~25 wt% of TMA. This is 0.135~0.687 kJ/kgK lower than specific heat of water

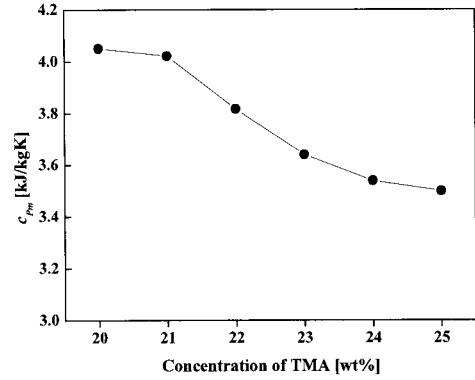


Fig. 5. The specific heat as weight concentration of TMA at cooling source temperature of -5°C .

(4.186 kJ/kgK) according to the weight concentration of TMA. The specific heat increased as the weight concentration of TMA became higher. In this manner, the formation of a clathrate compound by the hydrogen bonding of the water molecules and the gas molecules of TMA is considered to accelerate because the enthalpy and the specific heat of TMA-water clathrate compound is increased during cooling process at liquid phase as the weight ratio of TMA increases.

4. Conclusions

In this study, the cooling characteristics of the TMA-water clathrate compound including TMA (Trimethyl-amine, $(\text{CH}_3)_3\text{N}$) of 20~25 wt% as a low temperature latent heat storage material at cooling source temperature of -5°C are investigated.

- (1) The phase change temperature was $5.4\sim 5.8^\circ\text{C}$ on average according to the weight concentration of TMA. Especially, TMA 25 wt%-water clathrate compound showed an average of 5.8°C which was the highest of all.
- (2) The supercooling degree was decreased as the weight concentration of TMA was higher. In the case of a clathrate compound with 25 wt% of TMA of the average supercooling degree was the lowest at 8.0°C .
- (3) The average specific heats were 3.499~4.051 kJ/kgK depending on 20~25 wt% of TMA. It is increased as the weight concentration of TMA increased.

In this manner, the phase change temperature is higher than water and the supercooling is suppressed for TMA 25 wt%- water clathrate compound. This

can lead to reduction of operation time of refrigerator in low temperature latent heat storage system and efficiency improvement of refrigerator COP. Therefore, energy saving and improvement of utilization efficiency are expected.

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