

The Effect of Surfactant in the Absorptive and Generative Processes

Jung-In Yoon*, Oh-Kyung Kwon**, Choon-Geun Moon** and Takao Kashiwagi***

(Received March 11, 1998)

This study investigates the effect of additives such as normal octyl alcohol into lithium bromide-water (LiBr/H₂O) solutions in the absorption and generation processes of absorption refrigerating machines. The experimental results confirmed the positive effect of additive use in the absorber. Little is known, however, on the effect of additives on generator performance. In this study, the authors carried out experiments to investigate the possible positive or negative effects of additive, which enhances the absorption process, on the generator behavior. The results showed heat transfer at the generator improved as pressure increased and concentration decreased; the boiling heat transfer coefficient was shown to be more strongly influenced by concentration than by pressure. The boiling curves showed that the heat transfer of solution in the generator was not significantly affected by the addition of surfactant. The result of this study showed that the surfactant in absorption heater/chiller made enhanced absorption effect in the absorber but it didn't give any influence in the generator. Therefore the additive was devoted to helping high performance in the absorption system.

Key Words: Absorption Enhancement, Surfactant, Absorber, Generator

Nomenclature

A	: Heat transfer area, m ²
AR	: Aspect ratio
d	: Outside diameter of test tube, m
FO	: Fourier number
h	: Boiling heat transfer coefficient, W/(m ² K)
q''	: Heat flux, kW/m ²
r_1	: Inside radius of test tube, m
r_2	: Outside radius of test tube, m
T_{sat}	: Saturation temperature, K
T_r	: Average temperature of thermocouples, K
T_w	: Surface temperature of test tube, K
ΔT_{sat}	: Wall superheat, K
λ	: Thermal conductivity of copper, kW/(mK)

1. Introduction

The major components of absorption machines consist of heat and mass exchangers. Their design and operation have a direct effect on the cost and efficiency of the system. In Korea and Japan, most absorption machines use H₂O/LiBr as a typical refrigerant / absorbent pair. In USA and Europe, the machines utilizing H₂O/LiBr are applied very little, but system utilizing NH₃/H₂O are used for industrial waste heat recycling in some sectors. It is well known for this combination that the viscosity of the LiBr aqueous solution increases considerably with LiBr concentration. This results in the decrease of mass diffusivity in the practical high concentration range of LiBr (Lee et al., 1990; Kashiwagi, 1985). From this point of view, absorption enhancement are achieved in most commercial machines by adding a small amount of surfactants as additives, which reduce the surface tension of the absorbent solution and also generate Marangoni convection near the solution surface during the refrigerant vapor

* Department of Refrigeration and Air-conditioning Engineering, Pukyong National University

** Graduate School, Pukyong National University

*** Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology

absorption process.

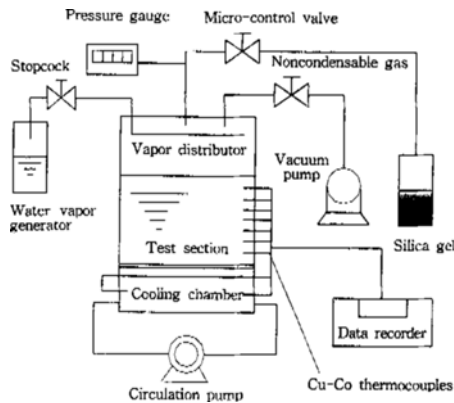
A vapor absorption enhancement mechanism for inducing interfacial turbulence has been reported by Kashiwagi(1988), who conducted experimental analyses to clarify the basic mechanism involved in the inducement of interfacial turbulence. Although non-absorbable gases could hinder absorption considerably, its actual effect on vapor absorption have not been reported yet. Therefore it is necessary to understand and quantify the influence of such a gas on the phenomenon of water vapor absorption enhancement in LiBr aqueous solutions with interfacial turbulence generated by normal octyl alcohol addition.

The effect of additives on heat transfer in the absorption process, often attributed to Marangoni convection, has been reported in the literature (Kashiwagi, 1985). An enhancement of boiling heat transfer coefficients can be obtained by a proper choice of additives. When the capacity of an absorption heat pump is limited by its generator capacity and the generator is of the pool boiling type, it is possible to increase the machine capacity by means of surfactant(Takada, 1988). Small amounts of a certain surfactant in aqueous solution have been known significantly to enhance the rate of nucleate boiling heat transfer of water(Yang et al., 1983). Nevertheless, the effect of a surfactant additive on the boiling characteristics of LiBr/H₂O solution has not been studied systematically(Calus et al., 1974; Jontz et al., 1960; Yoon et al., 1994).

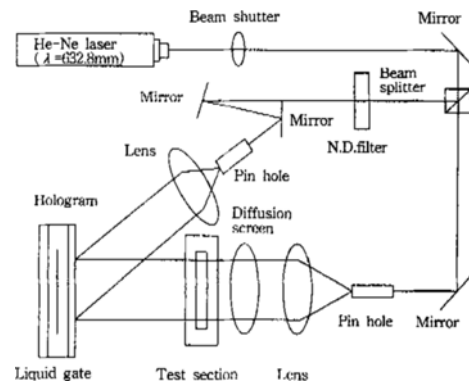
Even though many experimental works were performed(Hijikata et al., 1992; Kim et al., 1995), the results and physical interpretation of the phenomena are not fully consistent and partly contradictory. The understanding of the surfactant effect in a absorber and a generator does not seem to be well established yet. The authors have thus carried out the experiments to understand the absorption and the generation behavior when a non-absorbable gas(dry air) and surfactant(normal octyl alcohol) were present in the absorber and the generator.

2. Experimental Apparatus and Procedure

The absorption experimental apparatus is schematically illustrated in Fig. 1(a). Aqueous solutions of LiBr are used as absorbents, with surfactant added in concentration of 0.6 mass%. The bottom of the test section has a cooling chamber to ensure efficient removal of the absorption heat from the absorbent to the cooling water; a bronze plate is installed between the absorbent and cooling chamber. Distilled water was used as a refrigerant, and kept in a water vapor generator connected to the absorbent chamber. The water temperature is kept constant during the absorption experiment, at the initial LiBr aqueous solution temperature, by using an electric mantle heater with constant temperature control. The observation of unsteady-state phase changes inside the



(a) Diagram of absorption experiment



(b) Optical set-up of holographic interferometer

Fig. 1 Diagram of absorption experiment and optical set-up of holographic.

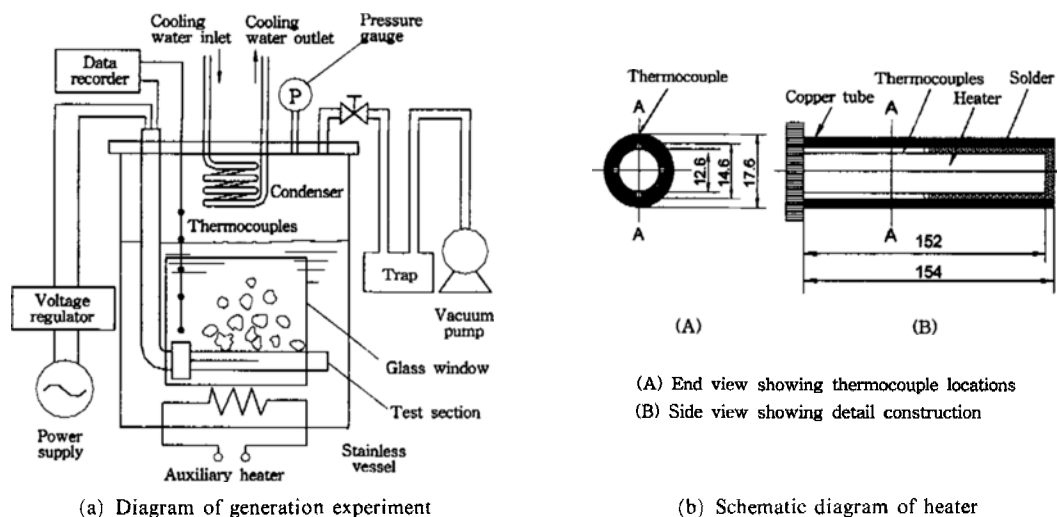


Fig. 2 Diagram of generation experiment and test section.

solution, as interference fringes, are made possible by a real time holographic interferometer. A 30 mW He-Ne gas laser (wave length = 632.8 nm) is used as a laser light source, in the setup shown in Fig. 1(b).

The experiments are done by changing the AR, Aspect Ratio, as well as the LiBr/H₂O and surfactant concentrations. The following procedure describes the methodology of experiments. Initially, the non-absorbable gas effect is eliminated by reducing the pressure in the test vessel and boiler to below that of the saturated vapor pressure of the refrigerant water at room temperature, by using a vacuum pump. After filling the vessel with steam, the LiBr aqueous solution is introduced up to the specified height. A hologram is taken after the vacuum pump was turned off. Steam absorption begins on the stationary solution surface. Temperature measurement by thermocouples and filming of the interferograms are started at the same time. During the test runs with a non-absorbable gas, dry air is supplied into the vessel by a copper tube. The amount of non-absorbable gas introduced is controlled by a semiconductor pressure gauge and adjusted by a micro-control valve. Using the ideal gas law, the amount of air that entered the vessel is controlled by changing pressure.

The generation experimental apparatus is shown in Fig. 2(a). The system includes mainly a

test chamber with a vacuum insulation as in Fig. 2(a). The test heater is completely immersed in the solution pool and is made of a stainless steel chamber with a height of 200 mm, width 55 mm, length 230 mm, and wall thickness 3 mm. The heating surface is polished by No. 2000 sandpaper to obtain a smooth surface. The test electric heater is installed inside the base tube, using a sliding transformer to change the heat flux. The condenser is set above the liquid pool to ensure that the condensed liquid returns directly to the liquid pool, maintaining the concentration and quantity of the pool liquid constant to an initial setting. Ten thermocouples are installed at different levels in the liquid pool, to measure the liquid and vapor temperature. To ensure that the pool liquid is maintained at the saturation temperature, there are auxiliary heaters installed near the bottom of the liquid pool. Schematic diagram of the test unit is shown in Fig. 2(b).

K type thermocouples are inserted into the inner wall of the heater and placed in the middle of the heating region. The measurement uncertainty of the thermocouples is $\pm 0.3^{\circ}\text{C}$ and four readings are averaged to obtain the inner wall temperature. The outer tube surface temperature can be computed from the inner tube surface temperature and the heat flux values (Yang et al., 1983; Hou et al., 1993; Ohnishi et al., 1974).

$$T_w = T_r - \frac{\ln\left(\frac{r_1}{r_2}\right)}{2 \cdot \lambda} \cdot d \cdot q'' \quad (1)$$

where, T_r , λ , d and q'' are measured average temperature, thermal conductivity of copper, outer diameter of the test tube and heat flux, respectively.

The temperature difference, ΔT_{sat} , is the difference between the surface temperature of the copper tube and the saturation temperature of the pool liquid, i. e.,

$$\Delta T_{sat} = T_w - T_{sat} \quad (2)$$

where T_w , and T_{sat} are the heater surface temperature and saturation temperature, respectively. The steady state is obtained by monitoring the reading fluctuations of two inserted thermocouples in the test heater and the temperature of the outlet cooling water. The heat flux q'' and the heat transfer coefficient h are obtained by the following equations:

$$q'' = \frac{V \cdot I}{A} \quad (3)$$

$$h = \frac{q''}{T_w - T_{sat}} = \frac{q''}{\Delta T_{sat}} \quad (4)$$

where V , I and A are voltage input, AC current and heat transfer area, respectively. The absolute pressure is measured by a digital pressure gauge. The concentration of the lithium bromide in the water solution is obtained by mixing the distilled water with commercially available lithium bromide. A hydrometer is used to measure the concentration of the test liquid.

Prior to data collection, the test unit is preheated and preboiled for at least an hour at a low heat flux in order to remove the trapped air. The steady state data is taken after approximately three to five minutes following a change in heat flux. The chamber is insulated but considerable heat losses are noticeable. Boiling on the surface of the heater can be illuminated, observed, and photo-graphed through view windows on the front and rear side of this apparatus. After the last experiment of each set, another run using pure water is also made to check whether there is any significant change in the condition of the heating surface during the experiments. The additive used

in this work is normal octyl alcohol ($C_8H_{17}OH$). The amount of surfactant is 0.002, 0.007, 0.02, and 0.1 mass%.

3. Experimental Results and Discussion

3.1 Absorptive processes

The $H_2O/LiBr$ pair which was widely used in Korea and Japan was selected for refrigerant and absorbent, and normal octyl alcohol was used as a surfactant additive. The basic configuration of absorption into a stationary solution of $LiBr$ of 50 % by mass was considered in these experiments. The influence of non-absorbable gases on the heat and mass enhancement process in the absorbers was studied by analysis of the temperature distributions. Fig. 3 shows the temperature distribution for a 50 mass% concentrations with $AR=0.7$ and surfactant addition. The aspect ratio, AR , is defined as the ratio of absorbent solution depth to solution vessel length. As representative examples, the temperature distributions inside the $LiBr$ aqueous solution were obtained by using thermocouples. The marks on figures (a) and (b) indicate the times (100, 200 and 300 seconds) elapsed from the beginning of vapor absorption. From the figure (a), it can be clearly seen that in the presence of non-absorbable gas the occurrence of droplets on the absorbent surface, caused by 0.6 mass% normal octyl alcohol addition, does not result in broader temperature profiles. Non-absorbable gases seem to create a resistant layer which disturbs absorption at the vapor-liquid interface. As a result of this phenomenon, temperature distributions did not change rapidly as compared with the case where a non-absorbable gas was absent (Fig. (b)). Also, generation of violent interfacial turbulence could not be observed.

Fig. 4 shows the absorption enhancement ratio calculated for each aspect ratio by comparison with the basic condition of a $LiBr$ solution without a surfactant addition. The vapor absorption enhancement ratio is defined as the vapor absorption rates divided by those without surfactant. The maximum absorption ratio is found

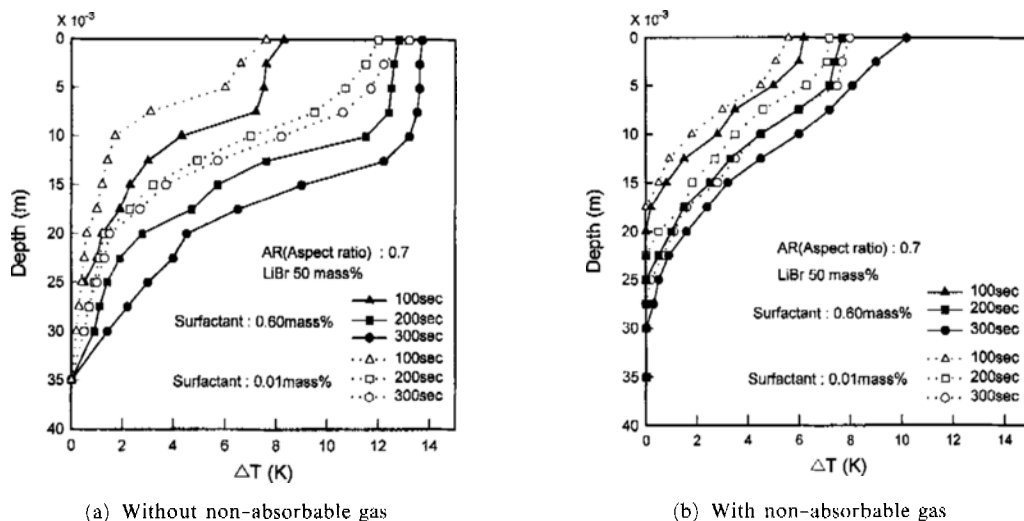


Fig. 3 Temperature distribution for 50 mass% LiBr solution, AR=0.7.

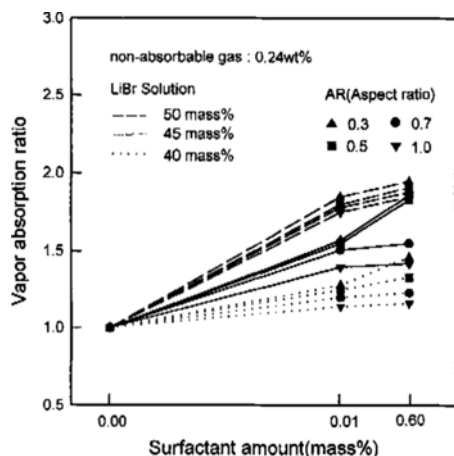


Fig. 4 Vapor absorption ratio for various AR and LiBr concentration. (with non-absorbable gas, 0.24 volumetric%).

when 0.6 mass% surfactant is added to a 50 mass% LiBr solution of AR=0.3 in the experimental range. There is a clear tendency of vapor absorption to increase with higher solution concentration and lower AR values. In the presence of a non-absorbable gas, vapor absorption enhancement ratios lay between 1.2 and 2.0 for most of the LiBr aqueous solution concentrations and aspect ratios considered. Water vapor absorption ratios are thus less than half of those obtained under the same experimental conditions when the non-absorbable gases are not present and where the absorption enhancement ratios between 4 and

5 have been reported. (Kashiwagi, 1985)

Fig. 5 and 6 show the photos of turbulence, without and with non-absorbable gases (Kashiwagi and Yoon, 1995). A conventional holographic real-time interferometric technique was used to visualize the absorption process by the interference fringes. Black parts in the photos are aqua drops of normal octyl alcohol. Cells on the aqua drops circumference are Marangoni cells and their shapes are nearly circular. As the Fourier number increased, the size of the cell got big, however the number of cell decreased and finally vanished. As shown in Fig. 5, in the case without non-absorbable gas, the endurance power of the cell was identified until Fo number reached 53.3. In the case with non-absorbable gas, the cell was found to vanish earlier as shown Fig. 5, Marangoni convection occurred more actively and the absorption ability was sustained for a longer time than in Fig. 6.

3.2 Generative process

The boiling heat transfer performance in 30 mass% and 50 mass% LiBr aqueous solution and in distilled water has been determined. To find the effect of pressure and concentration on the boiling phenomena, the boiling curves and the boiling heat transfer coefficient were arranged with pressure as the dependent parameter as shown in Figs. 7 and 8. These curves showed the

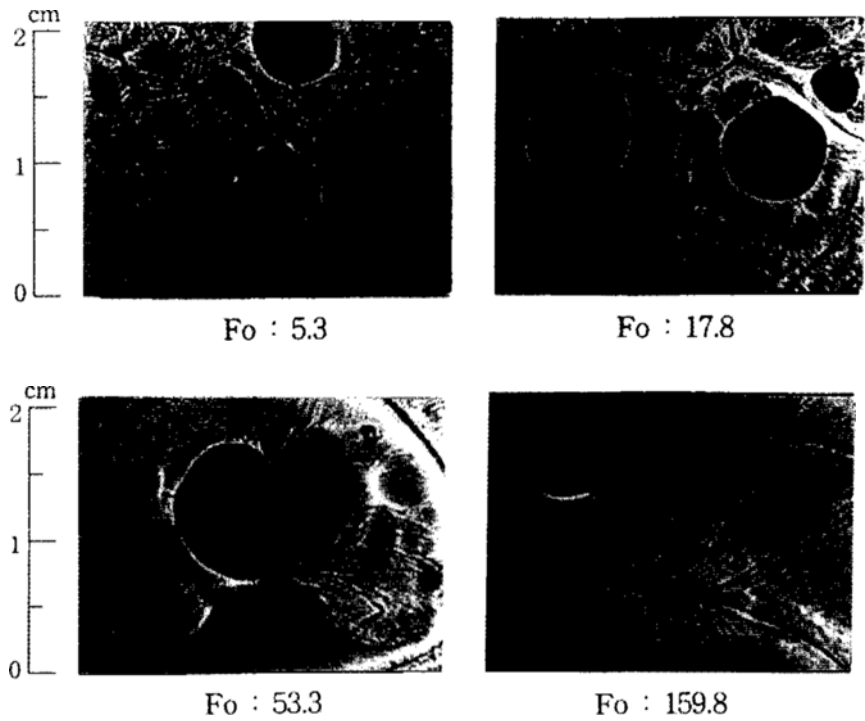


Fig. 5 Visualization of interfacial turbulence, 0.6mass% surfactant addition (without non-absorbable gas).

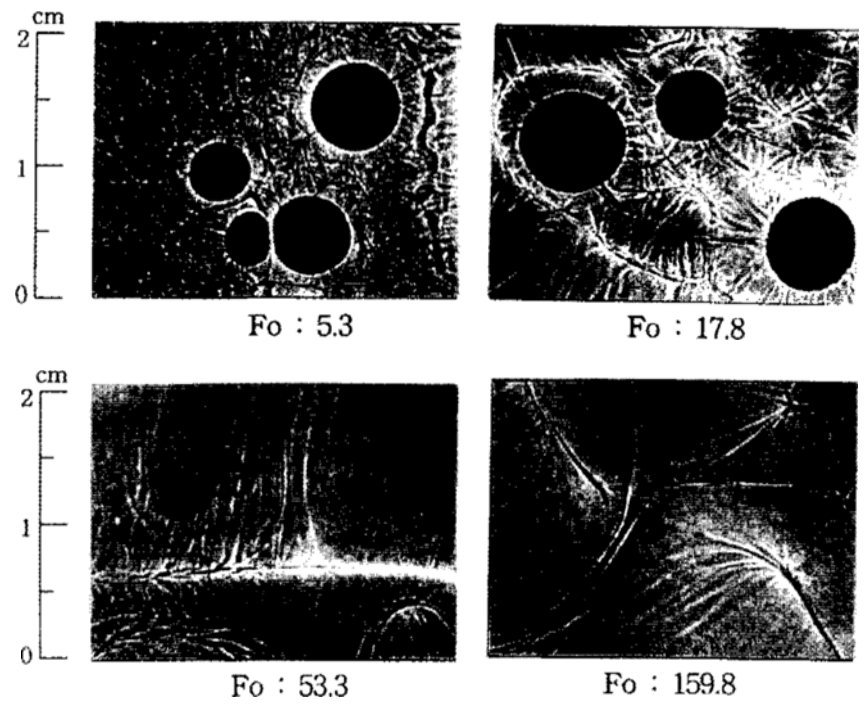


Fig. 6 Visualization of interfacial turbulence, 0.6mass% surfactant addition (with non-absorbable gas, 0.24 volumetric%).

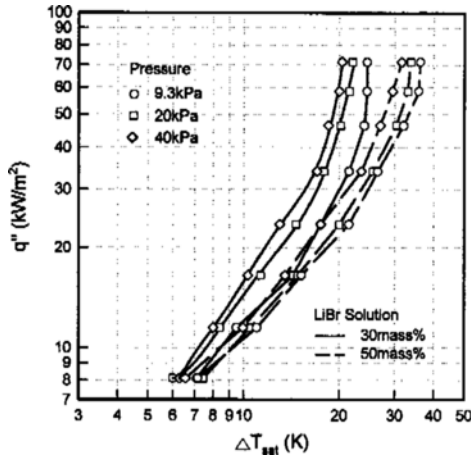


Fig. 7 Change of boiling curves by pressure and concentration.

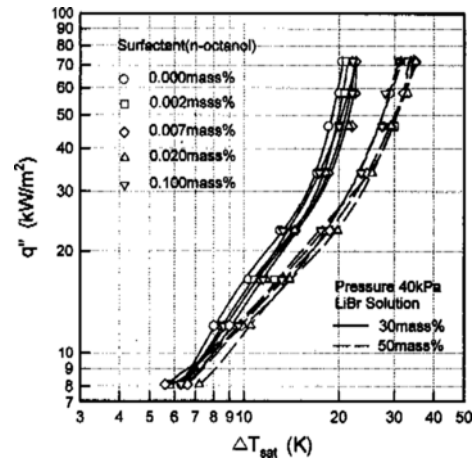


Fig. 9 Variation of boiling curves by concentration and surfactant for the pressure of 40kPa.

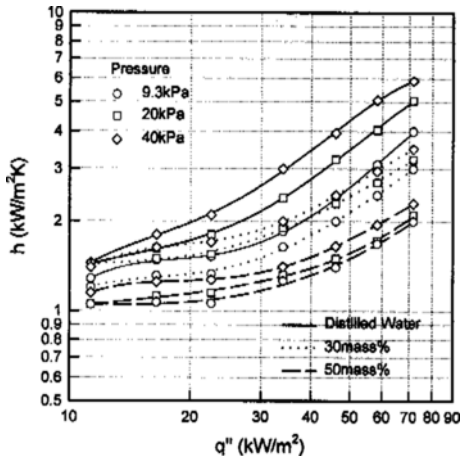


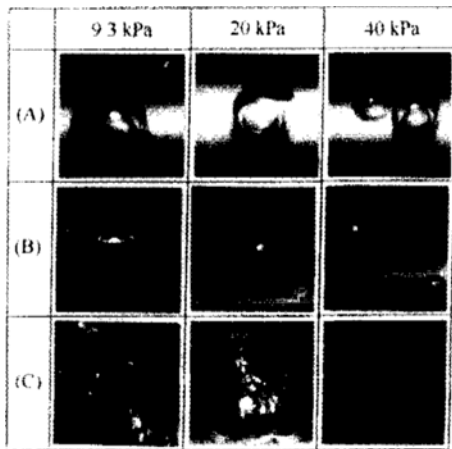
Fig. 8 Change of heat transfer coefficient by pressure and concentration.

generator heat transfer improved as the pressure increased and the concentration decreased; the boiling heat transfer coefficient was shown to be more strongly influenced by the concentration than by the pressure.

The effect of the boiling curve by pressure of LiBr aqueous solution was not remarkable compared to distilled water. The bubble size due to pressure change was larger at a low-pressure than at a high-pressure (Fig. 10). In the asymptotic stage of bubble growth in a pure liquid, liquid evaporated at the liquid-vapor interface due to heating by the superheated liquid surrounding the bubble. For boiling in a LiBr

aqueous solution, the volatile component evaporated at the vapor-liquid interface and thus the LiBr aqueous solution concentration in the liquid immediately adjacent to a bubble increased. The increase in the LiBr aqueous solution concentration resulted in an increase of the solution saturation temperature and a decrease of mass diffusivity. Both effects reduced the bubble growth rate and the transfer performance.

In general, the surfactant addition heat transfer coefficient in the nucleate boiling region was established in literature. With organic liquids, however, Lowery et al. (1957) and Dunskus et al. (1961) found no changes in surface tension but an increase in heat flux with the addition of water active surfactants. The boiling curves arranged with the amount of surfactant as the dependent variable for different concentration are shown in Fig. 9. The present boiling curves lie leftward to all the boiling curves of low concentration; i. e., the boiling heat transfer performance of low concentration is higher than that of high concentration. With surfactant addition, the effect of surfactant amount does not exert the influence on the boiling curve in comparison to without surfactant. Because saturation solubility of the normal octyl alcohol on LiBr solution is only 0.001mass%, most of it is floated on the surface of the solution. In case of 0.02mass% of addition, the shapes of bubble are crushed. The reason is



(A) Without surfactant
 (B) With surfactant (0.002 mass%)
 (C) With surfactant (0.02 mass%)

Fig. 10 Photos of bubbles on the heating surface with the heat flux of 55 kW/m^2 .

assumed to be the unbalance of the concentration difference occurring at the boundary on the upper side of bubbles. It is also assumed that they don't affect the bubble size and the frequency, so the boiling heat transfer is not influenced. It is evident that the influence of surfactant additives on the boiling heat transfer is neither simple nor direct. These additives generally depress surface tensions. The primary effect may be due to other factors which may be independent of, or at best only indirectly related to, changes in surface tension. Such factors may include changes in contact angle or the rate of nucleation.

Fig. 10 shows the bubbles on the heating surface with a heat flux of 55 kW/m^2 and concentration of 50 mass% at various pressures and surfactant amounts, respectively. Much more but relatively smaller in size bubbles were observed at higher pressures. At 9.3 kPa, a wider distribution of bubble departure diameters was observed. At 40 kPa, bubbles with almost the same departure diameter were observed. The number of active nucleation sites at 40 kPa was much more greater than that at 9.3 kPa. When the surfactant amount was 0.02 mass% (Saturation solubility of surfactant, normal octyl alcohol, 0.01 mass%), the bubble shape was distorted, but the bubble size was almost same as without surfactant at low

pressure. This observation is consistent with the theory proposed by Palmer(1972) on the size range of active nucleation cavities. The wide range of bubble size indicates that a larger thermal boundary layer thickness is present. The present observation on the size range of bubbles was also noticed by Ceumern(1977) in the pool boiling of sodium chloride solution. Based on the analytical solution of natural convection on a heated plate(Lienhard, 1981), the thickness of thermal boundary layer at low pressure will be greater than that at high pressure under the identical temperature difference. Thus, the narrow bubble size range observed at pressure of 40 kPa indicated a thinner thermal boundary layer. Heat transfer coefficients at lower pressures are therefore less than those at higher pressures due to a thicker boundary layer thickness as indicated in Fig. 8.

4. Conclusions

For better understanding of the influence of surfactant in the absorption and generation process, where heat and mass transfer coexist, we carried out the experiments on a stationary absorption process and pool boiling process. The main conclusions are:

(1) Water vapor absorption enhancement ratios are less than half of those obtained under the same experimental conditions without non-absorbable gases. In the presence of a non-absorbable gas vapor absorption ratio lie between 1.2 and 2.0 for LiBr aqueous solutions(40 to 50 mass%).

(2) The boiling heat transfer coefficient, h , is influenced by both pressure and concentration.

(3) As concentration increases, the boiling heat transfer coefficient for LiBr aqueous solution decreases.

(4) The result of this study showed that surfactant in absorption heater/chiller made enhanced absorption effect in absorber but it didn't give any influence in generator. Therefore the additive was devoted to helping high performance in the absorption system.

Acknowledgement

This research was supported by the Korea Science and Engineering Foundation (No : 971-1006-037-2). The authors appreciate the support.

Reference

- Calus, F., and Leonidopoulos, D. J., 1974, "Pool Boiling-Binary Liquid Mixtures," *International Journal of Heat and Mass Transfer*, Vol. 17, pp. 249~256.
- Ceumern, W. V., 1977, "Bubble Departure Diameter and Release Frequencies during Nucleate Pool Boiling of Water and Aqueous Sodium Chloride Solutions," *Heat Transfer in Boiling, Hemisphere*, London.
- Dunkus, T., and Westwater, J. W., 1961, "The Effect of Trace Additives on the Heat Transfer of Boiling Isopropanol," *Chem. Engng. Prog. Symp.*, Vol. 57, No. 32, pp. 173~181.
- Hijkata, K., Lee, S. K., and Nagasaki, T., 1992, "Water Vapor Absorption Enhancement in LiBr/H₂O Falling on Horizontal Tubes," *Transactions of JSME (Part B)*, Vol. 58, No. 547, pp. 885~890.
- Hou, M., and Ouyang, D., 1993, "Pool Boiling Heat Transfer in a Horizontal Narrow Annulus of Lithium Bromide/Water Solution Under a Vacuum," *ASHRAE Transactions: Research*, 3685, pp. 661~666.
- Jontz, P. D., and Myers, J. E., 1960, "The Effect of Dynamic Surface Tension on Nucleate Boiling Coefficients," *AIChE Journal*, Vol. 6 No. 1, pp. 34~38.
- Kashiwagi, T., 1985, "The Activity of Surfactant in High-Performance Absorber and Absorption Enhancement," *Refrigeration*, Vol. 60, No. 687, pp. 72~79.
- Kashiwagi, T., 1988, "Basic Mechanism of Absorption Heat and Mass Transfer Enhancement by the Marangoni Effect," *IEA Newsletter*, Vol. 6, No. 4, pp. 2~4.
- Kashiwagi, T., and Yoon, J. I., 1995, "The Effect of Additives in the Absorptive and Regenerative Processes of Lithium Bromide-Water Refrigeration Cycles", *19th International Congress of Refrigeration (IIR/IIF)*, Vol. 1Va, Theme 4, pp. 329~336.
- Kim, B. J., and Kang, I. S., 1995, "Absorption of Water Vapor into Wavy-Laminar Falling Film of Aqueous Lithium-Bromide," *KSME International Journal*, Vol. 9, No. 1, pp. 115~122.
- Lee, K. J., and Kim, W. S., 1990, *Fundamentals of Momentum, Heat and Mass Transfer*, Heejeungdong, Seoul, pp. 363~389.
- Lienhard, J. H., 1981, *Heat Transfer Textbook*, Prentice-Hall, New Jersey, p. 353.
- Lowery, A. J., and Westwater, J. W., 1957, "Heat Transfer to Boiling Methanol—Effect of Added Agents," *Ind. Engng. Chem.*, Vol. 49, No. 9, pp. 1445~1448.
- Ohnishi, M., and Tajima, O., 1974, "On the Pool Boiling Heat Transfer to Lithium Bromide Water Solution," *Refrigeration*, Vol. 49, No. 562, pp. 21~27.
- Palmer, H. J., and Berg, J. C., 1972, "Hydrodynamic Stability of Surfactant Solutions Heated from Below," *Journal of Fluid Mechanics*, Vol. 51, pp. 385~402.
- Takada, S., 1988, *Absorption Refrigerator and Heat Pump*, Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, pp. 29~291.
- Yang, Y. M., and Maa, J. R., 1983, "Pool Boiling of Dilute Surfactant Solutions," *ASME Journal of Heat Transfer*, Vol. 105, No. 2, pp. 190~192.
- Yoon, J. I., Imaizumi, T., Lee, Y. H., and Kashiwagi, T., 1994, "Experimental Investigation of Surfactant Effect on LiBr Solution Pool Boiling Heat Transfer on Absorption Cycle," *Proc. of the 28th Japanese Joint Conference on Air-conditioning and Refrigeration*, Vol. 28, pp. 141~144.