

〔論 文〕

Cooling of the Heat Generated during Absorption of Ammonia Vapor into Ammonia/Water Mixtures

Toshiaki INOUE*

Abstract

The heat of mixing is generated near the vapor-liquid interface during absorption of ammonia vapor into ammonia/water mixtures. The effect of the heat on pressure and temperature in a pressure vessel is clarified and it is shown that it is difficult to keep pressure and temperature in the system constant using a cooling pipe located in the vapor area. It is also shown that the heat generated near the vapor-liquid interface can be easily removed and then pressure and temperature in the system can be easily controlled by placing the pipe on the vapor - liquid interface.

Key Words: Absorption, Heat of Dissolution and Dilution, Cooling, Ammonia/Water Mixture

1. Introduction

In mixtures of ammonia/water, each component has a large difference in saturation temperatures and the difference between dew and boiling point is also larger in comparison with other mixtures as shown in Fig.1. Therefore, the temperature of the heat source and the sink vary domestically in the mixtures. Researchers can improve the irreversibility of a heat exchanger for a heat cycle that operates with a small temperature difference by using the mixtures as a working fluid. Furthermore, as ammonia and water are natural substances, the mixtures may be employed for an absorbing refrigerator and the above mentioned heat cycle in the future. Phase equilibrium data in Fig.1 were calculated using modified BWR [1] method for fluorocarbon mixtures and using PROPATH [2] programmed using the Ibrahim and Klein [3] equation for ammonia/water mixtures.

Recently, Inoue et al. [4] clarified that the heat of mixing (heat of dilution and dissolution) is generated near a vapor-liquid interface when

ammonia vapor dissolves into a bulk liquid and the heat fatally affects the pressure and temperature of the mixtures in the system. We must devise a method of removing the heat of

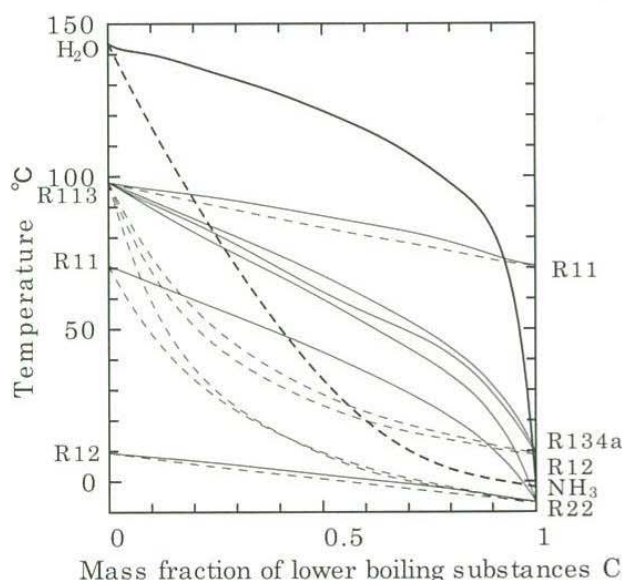


Fig.1 Phase equilibrium diagram of mixtures at
P=0.4MPa

———— Dew point curve
----- Boiling point curve

* 機械システム工学科
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mixing in order to make this trouble vanish in the mixtures.

In the current study, the effect of the heat of mixing on pressure and temperature in the system is clarified. And we proposed an improvement in the cooling device in order to remove the heat generated near the interface more easily. It is shown that pressure and temperature in the system can be easily controlled and the capacity of the cooling pipe can be reduced by installing the heat exchanger on vapor-liquid interface.

Nomenclatures

C	mass fraction of ammonia
h	heat transfer coefficient
P	pressure
q	heat flux
Q_c	heat removed
Q_{dil}	heat of dilution
Q_{in}	heat from surroundings
Q_{sol}	heat of dissolution
T	temperature
ΔT_E	temperature difference between dew and bubble point
ΔT_{sat}	wall superheat
x, y	molar fractions of liquid and vapor, respectively

Subscript

1	more volatile component
2	less volatile component
c	cooling pipe
i	vapor-liquid interface
s	saturation
w	wall

2. Experimental Apparatus and Procedure

2.1 Experimental apparatus

Figure 2 shows a schematic diagram of the experimental apparatus. A platinum wire 2 (diameter 0.3 mm, length 37 mm) employed as a heated surface is horizontally blanketed in a

pressure vessel 1 and is heated by a direct electric current. Wall superheat is measured using the temperature–electric resistance characteristics of the platinum wire, which is determined by a prior experiment. The pressure vessel 1 is immersed in a thermostat bath 8 to isolate it from the surroundings and the temperature in the vessel is kept constant with thermostat liquid through a thermostat with pump 9.

A cooling pipe 6 and a cooling pipe 7 are installed in the vapor area and on the vapor-liquid interface respectively and can be controlled independently with valves 11, though it is common that the cooling pipe is located only in the vapor area. Vapor generated is condensed by cooling pipe 6 and is returned into bulk liquid or is directly absorbed into bulk liquid, while the vapor and bulk liquid are cooled simultaneously in cooling pipe 7 on the vapor-liquid interface. Heat removed can be calculated using temperatures, T_4 and T_5 , measured at the inlet and outlet of the pipes respectively and the mass flow rate through the pipes 6 and 7.

2.2 Experimental procedure

Heat flux to the heated wire 2 was stepwise increased after the test liquid was maintained at a saturation temperature corresponding to the system pressure and then wall superheat, heat flux, temperature (T_1 , T_2 and T_3) and heat removed was measured at each heat flux after the mean temperature of the wire 2 became steady at a given heat flux. The experiment was carried out at pressure of 0.4 MPa before and after the improvements in the cooling pipe.

The temperature T_1 was measured at a location of 7 mm under the vapor-liquid interface and T_2 and T_3 were measured near the wall of the pressure vessel and near the cooling pipe in the vapor area, respectively. The system pressure was kept constant by controlling the supply of cooling liquid to pipes 6 and 7 during the experiment.

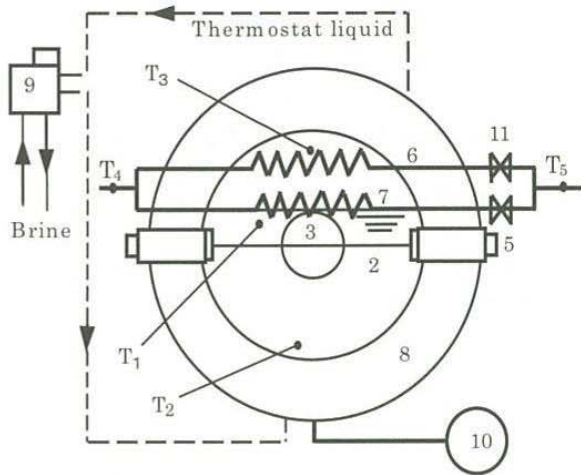


Fig.2 Experimental apparatus

- | | |
|-------------------------|---|
| 1. Pressure vessel | 2. Heated wire |
| 3. View window | 4. Insulator |
| 5. Electrode | 6. Cooling pipe |
| 7. cooling pipe | 8. Thermostat bath |
| 9. Thermostat with pump | 10. Pressure gauge |
| 11. Valve | T_1, T_2, T_3, T_4, T_5 . Thermocouples |

3. Experimental Result

3.1 The effect of heat of mixing on pressure and temperature in the system in cooling using the cooling pipe installed in vapor area

Figure 3 shows changes in pressure and liquid temperatures, T_1 and T_2 , with increases in heat flux, keeping the saturation temperature of vapor, T_3 , constant at ammonia mass fractions of $C = 0.5$ and $C = 1.0$. The system pressure and the liquid temperatures are constant with an increase in heat flux at $C = 1.0$ (ammonia only), while those are increased with the increase in the heat flux at $C = 0.5$. In particular, the liquid temperature, T_1 , near the vapor-liquid interface is dramatically increased, clearly demonstrating that the heat is generated near the liquid surface because of $T_1 > T_2$. This fact supports that the heat of dilution and of dissolution is generated on the vapor-liquid interface. The former is generated when a condensed mixture with a fraction of ammonia that is richer than that of the bulk liquid mixes into the bulk liquid and the latter is generated when ammonia vapor dissolves into the bulk liquid. Therefore the heat generated must be

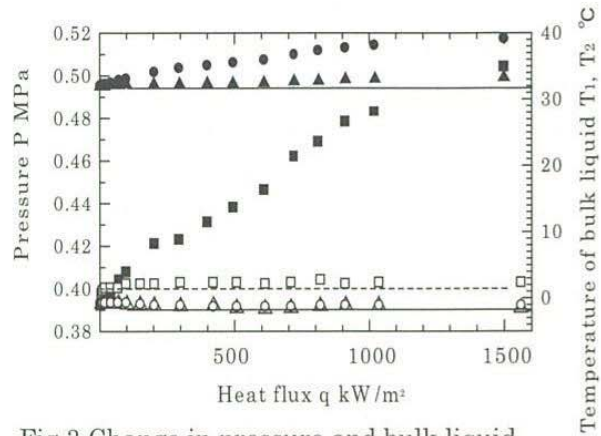


Fig.3 Change in pressure and bulk liquid temperature with heat flux at 0.4 MPa

- Saturation temperature
- - - Saturation pressure
- $C = 0.5, T_3 = 32^\circ\text{C}$
 ■ Pressure, ● Temperature T_1 , ▲ Temperature T_2
- $C = 1.0, T_3 = -1.9^\circ\text{C}$
 □ Pressure, ○ Temperature T_1 , △ Temperature T_2

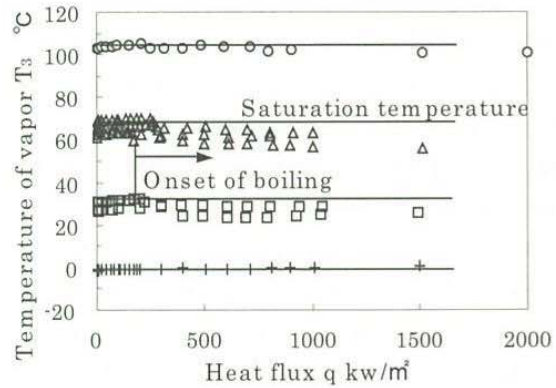
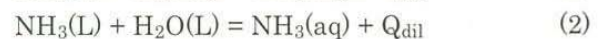
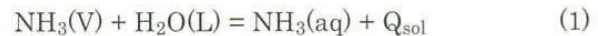


Fig.4 Change in vapor temperature with heat flux at 0.4 MPa

- $C=0.1$, △ $C=0.3$, □ $C=0.5$, + $C=1.0$

removed smoothly to keep the system pressure constant during boiling and absorption.

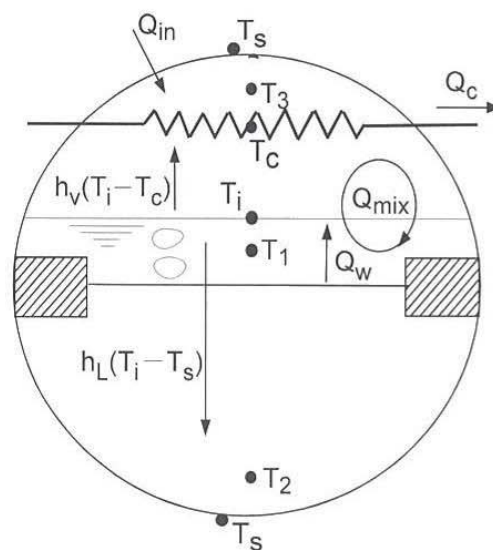
The generated process of the heat of mixing is generally expressed by the following equations (1) and (2).



Where, V, L and aq are vapor, liquid and water solution, respectively, and Q is the quantity of heat generated. Absorption process of ammonia

Figure 4 shows changes in the vapor temperature, T_3 , with increase in heat flux at 0.4 MPa. T_3 does not change with heat flux at $C = 1$, only ammonia and T_3 changes slightly at $C = 0.1$, while T_3 must be decreased after the onset of boiling in order to keep the system pressure constant at $C = 0.3$ and 0.5 . This means that the vapor temperature T_3 must be kept below saturation temperature in order to remove the heat generated near the vapor-liquid interface using the cooling pipe installed in the vapor area. Thus attention must be paid to a unique phenomenon where the heat of mixing is greatly generated in ammonia/water mixtures, differing from mixtures without the heat of mixing.

Figure 6 shows the temperature distribution in the vessel estimated from Figs.3 and 4, during a steady boiling and absorption process in a heat flux. The temperature distribution is tentatively



drawn with a broken line, since the exact distribution is unknown. The temperature distribution for no heat generated during mixing is shown with a dot-dash line for reference. The temperature is highest at the vapor-liquid interface or on the heated wire and becomes lower than the saturation temperature near the cooling pipe, and gradually increases to the saturation temperature of the circumference in the vapor space. Heat is accumulated near a point near the lowest temperature between the heated wire and the interface, some of which seems to be consumed by the creation of vapor bubbles and the remainder of which may be diffused into the surrounding liquid well. The boiling heat transfer coefficients are measured under a dynamic steady state during boiling, condensation and absorption under constant pressure with temperature distribution as shown in Fig.6. Therefore, it should be noted that special attention is needed to control the cooling pipe in order to keep the system pressure constant. It is difficult to control liquid flow rate through the cooling pipe in order to keep the pressure in the vessel constant.

3.2 Position of the cooling pipe and the quantity of heat removed

It was found that it is difficult to keep the system pressure constant by controlling the cooling pipe located in the vapor area, since a large temperature distribution exists in the system, due to the heat of mixing generated during pool boiling in the ammonia/water mixtures. Author added another cooling pipe (7 in Fig.2) on the vapor-liquid interface. The quantity of heat removed, Q_C , was separately measured for two types of cooling pipes.

Figure 7 shows changes in the difference between heat source flow, Q_W , and heat sink flow, Q_C , with change of heat flux and of the position of the cooling pipe in $C = 0.7$ and 0.3 . It is natural that Q_C is equal to Q_W in a pure liquid and in a mixture without the heat of mixing. However Q_C is larger than Q_W in the ammonia/water mixtures as shown in Fig.7. This shows that Q_{in} flows from the surroundings towards the system as shown in Fig.5, because temperature of vapor is under saturation temperature in the ammonia/water system. Namely, heat balance is expressed by Eq. (3).

$$Q_C = Q_W + Q_{in}. \quad (3)$$

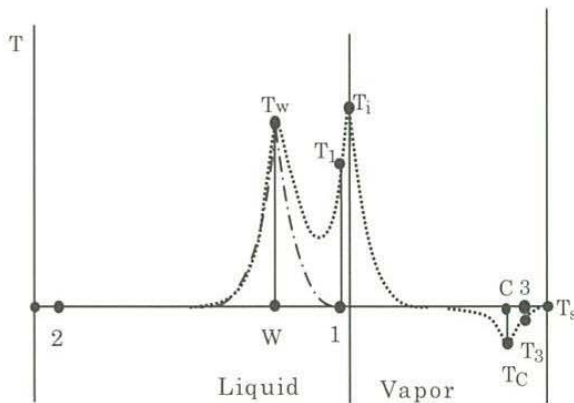


Fig.6 Heat generated and temperature distribution in the system
1,2,3: Position of thermocouples
C : Position of cooling pipe
W: Position of heated wire

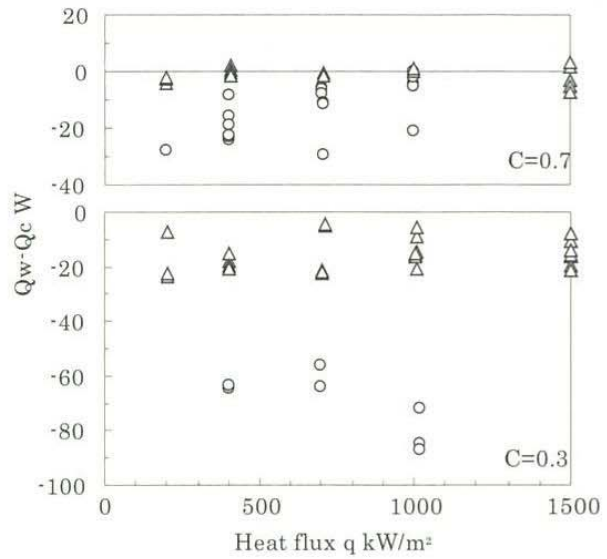


Fig.7 Effect of position of the cooling pipe on $Q_W - Q_C$ at 0.4 MPa

Position of the cooling pipe
○ vapor area, △ vapor - liquid interface

In addition, the heat removed can be reduced by placing the cooling pipe on the vapor-liquid interface, because $Q_C - Q_W = Q_{in}$ becomes small. It is also found that $Q_C - Q_W$ is larger in $C = 0.3$ than in $C = 0.7$. In particular, Q_W becomes equal to Q_C in $C = 0.7$ by using the cooling pipe installed on the interface as shown in Fig.7.

This is attributed to the fact that the heat of mixing is more in $C = 0.3$, because the fraction difference between vapor and liquid, $y_1 - x_1$, is larger in $C = 0.3$ than in $C = 0.7$ as shown in phase equilibrium diagram of Fig.8. The value of $y_1 - x_1$ is 0.64 and 0.29 in $C = 0.3$ and $C = 0.7$, respectively, for reference. I illustrated the phase equilibrium diagram of Fig.7 using PROPATH [2] programmed using the Ibrahim and Klein [3] equation.

4. Conclusion

It was shown that the heat of dilution and dissolution is generated near the vapor-liquid interface during pool boiling and absorption in the mixtures of ammonia/water. It was shown that it is difficult to remove the heat and to control the cooling pipe using one installed in the vapor area.

Finally, it was found that the heat can be easily removed and control of the cooling pipe becomes easy and capacity of the cooling pipe can be reduced by placing it on the vapor-liquid interface.

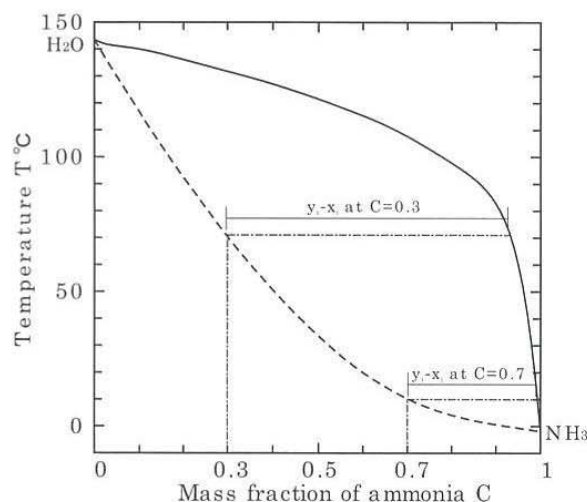


Fig.8 Phase equilibrium diagram of ammonia/water at 0.4 MPa

———— Dew point curve
----- Boiling point curve

Acknowledgement

The author would like to appreciate Mr. M.

Daily, who is a lecturer in Kurume Institute of technology, for his checking English.

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