공냉형 흡수식 열펌프를 위한 작동유체의 개발

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Development of New Working Fluid for Air-Cooled Absorption Heat Pump

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Introduction

The increasing energy cost and environmental problems have made the heat-powered absorption heat pump more attractive. Recently, much efforts have been made to develop an air-cooled absorption heat pump (chiller) because of the high equipment cost of the existing water-cooled absorption unit. The air-cooled operation of an absorption unit can be accomplished by the development of new working fluids which have a broad operation range.

Theory

A simple absorption heat pump (chiller) consists of the following four major functional steps and one heat exchanger.

Evaporator *Absorber* *Generator* *Condenser*

The evaporator and the absorber operate under the low pressure which corresponds to the evaporating temperature. The generator, the condenser, and the heat exchanger operate under high pressure, the level of which corresponds to the condensing temperature. The major energy input is conducted in the generator, and the refrigeration (cooling) is done in the evaporator. Additional cooling towers are needed in the absorber and the condenser for a water-cooled system, but for an air-cooled system the cooling source in this two step is the air supplied by a fan. The conditions required for the air-cooled operation are those below.

- A large difference between the cooling air temperature and the absorber temperature (>15°C) is required. Thus the solution concentration must be high to have a low pressure at the absorber. So the operation range of the new working fluid must be considerably broadened compared with the lithium bromide + water system.
- The working fluid must not excessively corrode metals, such as Fe, Cu, SUS, etc.
- The working fluid must be nontoxic and nonflammable.

In order to develop a new working fluid and to know whether its operation characteristics satisfy a specific condition, at least four thermodynamic properties, solubility, vapor pressure, heat of mixing, and heat capacity of the working fluid, should be accurately measured over the operation range (the heat of mixing was estimated). In this study, experimental apparatuses for the measurement of these properties were constructed first, and several candidates of high boiling organic compounds which could broaden the operation range of the absorption cycle were selected. The fluids containing these organic compounds were analyzed experimentally with respect to the solubility enhancement of salt, and then one organic liquid, ethanol amine ($H_2N(CH_2)_2OH$), was selected. The selected organic compound was added to the lithium bromide + water system system by an appropriate ratio and several thermodynamic properties were accurately measured. Each experimental data was correlated with a proper model equation, and finally the theoretical absorption cycle analysis was carried out.

Experiment

Solubility The visual polythermal method [1] was used to measure the solubility of each sample. A sample solution (approximately 40 cm^3) of a desired absorbent concentration at the given mixing ratio was placed in the vessel and was stirred well. The sample solution was first incrementally heated to dissolve all the crystals and agitated at a temperature at least 5 K higher than the crystallization temperature. Then, the solution temperature was lowered slowly to nucleate a small amount of crystals. The temperature of the solution was lowered and raised at a very slow rate (less than 0.1K/min) using the constant temperature bath and circulator. The temperature at which the last crystal disappeared was taken as the crystallization temperature for the given absorbent solution in this polythermal methods.

Vapor Pressure The vapor pressure measurement was carried out using the boiling point method [2]. A sample with approximate volume of 250 cm^3 was placed in the vessel and it was then stirred well with magnetic stirrer to prevent superheating. At the thermal equilibrium, the pressure in the apparatus and the temperature of the sample solution were measured. The condenser was worked with sufficiently cooled water (< 4°C) to minimize the amount of condensed vapor because this water-rich vapor can vary the initial concentration of the sample solution.

Heat Capacity The heat capacities of a sample solution was measured by a differential scanning calorimeter (Du Pont Co., Ltd., Thermal Analyzer 9900). Accurately weighted sample solution (approximately 30mg) was placed in a small cell, and was heated at a constant rate of temperature elevation. During the heating process the rate of heat transfer was accurately recorded, and thus the heat capacity of sample solution could be calculated through a simple mathematical manipulation.

Results and Discussion

Duhring Chart Duhring chart is a *P-T-X* diagram which gives the relations between the solution temperature and the vapor pressure at various concentrations including the crystallization line of the solution. So the operation range of an absorption cycle can be known from this chart. For the lithium bromide + ethanol amine + water (3.5:1 ratio) system the Duhring chart was constructed using the correlation results of the solubility and vapor pressure. From the Duhring chart shown in Fig.1, it is known that the system can be operated at the high absorber temperature (above 45 °C) and at the low pressure allowing appropriate concentration difference (about 5 %), which is essential for the construction of an air-cooled absorption chiller.

Enthalpy – Concentration Chart The enthalpy - concentration chart (*H-T-X* diagram of solution) was constructed for the new system. This chart is important for the energy balance in a performance calculation. The measured vapor pressure and heat capacity were used to obtain the relative enthalpy of the solution. Duhring line slope was used to obtain the latent heat of the refrigerant (water) in the solution. Then using known properties of the water and standard thermodynamic manipulations, the desired solution enthalpy could be obtained. The calculated relative enthalpy isotherms are shown in Fig.2 as a function of concentration.

Theoretical Coefficient of Performance (Single Effect Cycle) Fig.3 shows the relations between the theoretical COP and the generator temperature (T_g) at different three absorber temperatures. Three working fluid systems were considered in this analysis. The lithium bromide + water system is the most widely used working fluid for the water-cooled system, and the lithium bromide + LB621 system (lithium bromide/organic compound in LB621

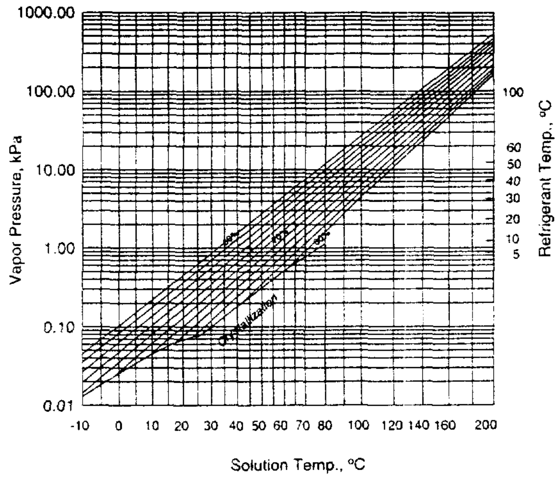

Fig. 1 Dudring Chart of the LiBr + $H_2N(CH_2)_2OH$ + H_2O (LiBr/$H_2N(CH_2)_2OH$ mass ratio 3.5:1) System.

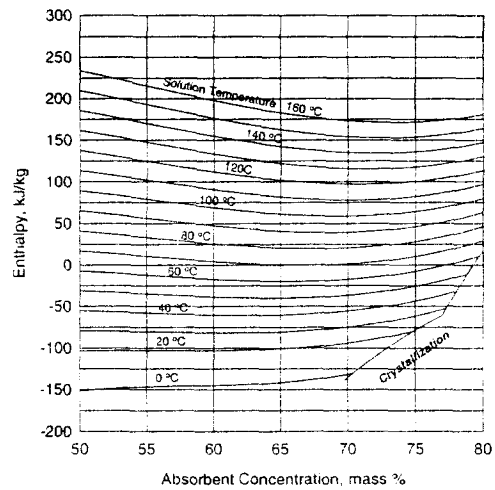

Fig. 2 Enthalpy - Concentration Chart of the LiBr + $H_2N(CH_2)_2$ OH + H_2O (LiBr/$H_2N(CH_2)_2OH$ mass ratio 3.5:1) System.

mass ratio 3.5:1) is one of the new working fluids for the air-cooled system suggested by GRI [3], and the other lithium bromide + ethanol amine + water (3.5:1 ratio) the new system developed in this study. Through all the calculations, the following operation conditions were fixed.

$$T_e = 5\ ^{\circ}\mathrm{C} \quad ; \quad T_a = T_c \quad ; \quad e = 0.8$$

where T_e is the evaporator temperature, T_a the absorber temperature, T_c the condenser temperature, and e the efficiency of the heat exchanger.

From the Fig.3, it can be known that the theoretical COP increase as the generator temperature increase at the same absorber temperature, and it decrease as the absorber temperature increase at the same generator temperature for all systems considered. The figure also shows that the lithium bromide + ethanol amine + water system gives the highest COP value among three systems at the same condition. Moreover, this new system is found to have high degree of COP value at the high absorber temperature without the danger of crystallization.

A more detailed analysis results at the high absorber temperature is shown in Fig.4. In this figure, two additional cycle characteristics, the crystallization temperature and the concentration difference, are also shown as a function of the generator temperature. These results are calculated at a fixed absorber temperature 45 °C (If the temperature of the open air is about 15 °C, the temperature difference between the open air and the absorber will be about 15 °C, which is suitable for air-cooled cycle operation). The crystallization temperature of which corresponding concentration is the value at the generator can be a safety factor of the cycle, and the concentration difference between the inlet and outlet stream in the absorber gives the cooling capacity of the cycle. For a safe air-cooled cycle operation, low crystallization temperature is required, but the crystallization temperature of the lithium bromide + water system is too high to guarantee a safe operation. On the other side, the lithium bromide + ethanol amine + water (3.5:1 ratio) system can be operated safely without the danger of crystallization at an appropriate concentration difference. The figure also shows that the system have higher value of COP and cooling capacity than the lithium bromide + LB621 (3.5:1 ratio) system at the same condition.

Therefore, the new working fluid, the lithium bromide + ethanol amine + water (3.5:1 ratio) solution, can be successfully applied to the air-cooled absorption heat pump (chiller).

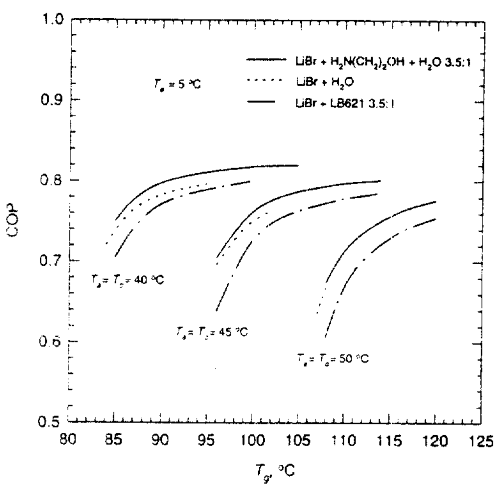

Fig. 3 COP versus Generator Temperature in a Single Effect Absorption Chiller.

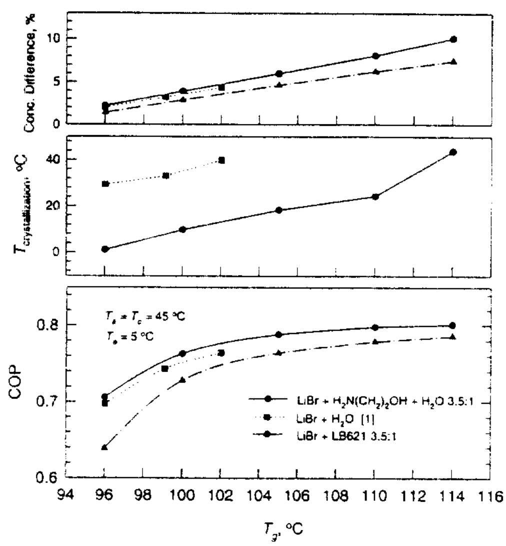

Fig. 4 Crystallization Temperature, Concentration Difference, and COP versus Generator Temperature in a Single Effect Absorption Chiller.

References

1. Iyoki, S., Iwasaki, S., and Uemura, T. *J. Chem. Eng. Data* 1993, **38**, 396.
2. Iyoki, S., Iwasaki, S., and Uemura, T. *J. Chem. Eng. Data* 1990, **35**, 429.
3. Gas Reserach Institute, Aqueous Absorption Fluids, Annual Reports, 1987-1990. Chicago.