EXPERIMENTAL AND ANALYTICAL STUDY OF CONDENSATION OF AMMONIA-WATER MIXTURES

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ABSTRACT

The need for more energy efficient power generation and recent environmental issues of CFCs prompted the development of combined steam and Kalina cycle power systems, and advanced ammonia/water absorption heat pumps. However, the working media and associated thermal design aspects require new concepts for maintaining high thermal effectiveness and phase equilibrium for achieving maximum possible thermodynamic advantages. In the present study, a theoretical analysis was carried for the condensation of ammonia/water mixtures on a vertical tube. A set of equations was formulated and a calculation algorithm was developed to predict the local rate of heat and mass fluxes for binary ammonia-water systems. The predicted rate of condensation was compared with the experimental data obtained at Oak Ridge National Laboratory (ORNL) for a mixture of 90% ammonia and 10% water. The role of diffusion in simultaneous heat and mass transfer associated with condensation was analyzed by comparing the results from three limiting cases, which include equilibrium conditions, and liquid-phase diffusion of finite and infinite values. The results showed that the vapor-phase diffusion is a controlling mechanism.

INTRODUCTION

Ammonia-water is a leading candidate for advanced heat-pump cycles and power-conversion systems. Many of the reported investigations [1,2] have focused on the thermodynamic analysis of heat-pump cycles. However, the heat and mass transfer processes in heat pumps could limit their thermodynamic advantages. The regenerative heat exchanger in the generation-absorption exchanger (GAX) heat pump is a critical component for achieving a high coefficient of performance (COP). Similarly, absorption of ammonia in lean aqueous solutions used in the Kalina cycle [3] is a key technical issue for improving the Carnot efficiency. The process of simultaneous heat and mass transfer is a major technical issue for the development of cost-effective and energy-efficient heat pumps. It was stated by Ferreira et al. [4] that the absorption of refrigerant in general limits the overall performance of heat pumps. Examination of the results from the previous investigations [4, 5] show that the mass transfer resistance cannot be ignored; therefore, it is essential to evaluate appropriate heat and mass transfer enhancement techniques to minimize its effects.

Little work has been carried out to develop enhancement for the process of simultaneous heat and mass transfer. Haselden [5] discussed the heat and mass transfer issues for refrigerant mixtures. Machielsen [7] provided an overview of their research work on absorption heat pumps, and showed superior performance for two compact heat exchanger configurations. The local rate of heat and mass transfer for binary mixtures can be calculated with the Colburn-Drew [6] analysis. However, it is not commonly used for designing heat transfer equipment for binary systems. The purpose of the present investigation was to obtain experimental data for condensation of ammonia-water mixture and validate the analytical method based on the Colburn-Drew analysis. The thermodynamics of the ammonia-water system is highly non-ideal and the experimental data are not readily available. Therefore, each set of experimental data is important to validate a theoretical prediction method. The experimental work was carried out at Oak Ridge National Laboratory (ORNL) and the prediction model was developed at Argonne National Laboratory (ANL). The analysis was used for a cooperative project for predicting the thermal performance of the GAX heat exchanger [8] and a plate-fin heat exchanger [9] operating as condenser and evaporator. In this paper, the experimental data obtained at ORNL were analyzed and compared with the ANL theoretical prediction method.

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PREDICTION METHOD

The local heat and mass transfer processes are illustrated by concentration and temperature profiles shown in Figure 1. For the case of absorption of ammonia in a liquid film, the interfacial temperature is expected to be greater than the bulk vapor-phase temperature. The ammonia concentration in the liquid phase is higher at the interface than in the bulk.

Figure 1. Temperature and concentration profiles.

The film theory, based on the Colburn-Drew [6] analysis for analyzing condensation of binary vapor mixtures, is as follows:

\[
N_T = N_1 + N_2 = K_x \ln \left( \frac{Z_1 - Y_{1,b}}{Z_1 - Y_{1,i}} \right) \quad (1)
\]

or

\[
Z_1 = \frac{\exp(\Phi_m) Y_{1,b} - Y_{1,i}}{\exp(\Phi_m) - 1} \quad (2)
\]

where

\[
Z_1 = \frac{N_1}{N_T} \quad (3)
\]

\[
\Phi_m = N_T / K_x \quad (4)
\]

The liquid-phase mass transfer rate should be expressed in terms of component 1 as follows:

\[
N_1 = k_l (X_{1,b} - X_{1,i}) + N_T X_{1,i} \quad (5)
\]

The liquid-phase mass transfer coefficient is difficult to estimate for concentrated solutions; therefore, an analysis of two limiting cases provides the importance of liquid-phase diffusion. In case of perfect mixing, the interfacial concentration is equal to that of the bulk of liquid phase, and the resulting calculation algorithm for interfacial conditions is significantly simplified. For the no-mixing condition, the liquid-phase mass transfer coefficient is assumed to be negligible, and the following relationship can be derived from the film theory:

\[
X_{1,i} = N_1 / N_T \quad \text{and} \quad X_{2,i} = N_2 / N_T \quad (6)
\]

In addition to mass-flux continuity, the following heat-flux equation needs to be satisfied at the interface:

\[
\Phi_T = \frac{N_T (Z_1 C_{p1} + Z_2 C_{p2})}{U_0 (T_i - T_e)} = h_g \left( \frac{H_{v,b} - H_{v,i}}{1 - \exp(-\Phi_T)} \right) \quad (7)
\]

where

\[
\Phi_T = N_T (Z_1 C_{p1} + Z_2 C_{p2}) \quad (8)
\]

In a limiting case of negligible mass transfer resistance, the calculation procedure can follow the design approach discussed by Bogart [10]. The rate of condensation was calculated by a point-wise calculation, in which the local heat and mass fluxes were calculated by solving Equations 1 - 8 in an iterative method. The thermodynamic properties and vapor-liquid equilibrium calculations were carried out using the Peng-Robinson [11] equation of state. The transport properties were calculated from the sources described by Reid et al. [12]. For most cases, the vapor-phase Reynolds number was less than 2000, and the vapor-phase heat transfer coefficient was calculated using the correlation by Chen et al. reported by Knudsen and Katz [13]. The mass transfer coefficient was calculated using the Sherwood et al. correlation [14]. Because it does not include the entrance effects, an entrance-effect correction based on heat transfer results was applied. The condensate film coefficient was calculated using the method of Chen et al. [15].

EXPERIMENTS

A schematic of the test apparatus used for the condensation experiments is shown in Figure 2. The system was designed to operate at 1724 kPa pressure, 43 °C temperature, and the heat load of 5 kW.

Figure 2. Flow schematic of the test facility.
The test apparatus, shown in Figure 3, is a single-tube condenser made of stainless steel and designed to accommodate a tube of 25.4 mm nominal diameter and a length of 1.22 m. Two view ports were used to permit visual and photographic observation of the surface. The test section was a commercial aluminum plain tube with a wall thickness of 0.165 mm.

Figure 3. Schematic of the test section.

The working fluid was vaporized in the boiler and passed through an entrainment separator before entering the condenser test section. Saturated vapor mixture entered at the top of the condenser, and the condensed liquid, collected in the bottom of the test section, was returned to the boiler. The rate of condensation for pure ammonia was measured by a turbine flow meter in the return line as shown in Figure 2. The turbine meter was replaced with a microprocessor-based mass-flow transmitter for ammonia-water experiments. The pressure in the boiler and condenser were measured with precision transmitters with an accuracy of 0.08 kPa. The system was equipped with chromel-alumel thermocouples to obtain temperatures for controlling the loop operation. Themistors, with high level of accuracy, were used for measuring inlet and outlet water temperatures needed for heat balancing.

The system was evacuated with a vacuum pump to eliminate noncondensable gases prior to charging with 30% concentration of ammonium hydroxide. The heat rate was set by controlling the power to the boiler heaters. The coolant temperature and flow rate were maintained in a narrow range of operating conditions for all tests. Vapor and liquid samples were taken for each test run to determine the ammonia concentration using the chemical titration method.

RESULTS AND DISCUSSION

Experimental Results

Initial tests were conducted with pure ammonia to validate the performance by comparing the new data with previous results [16]. The pure ammonia results were in good agreement, and the tests were continued with ammonia-water mixtures. A summary of test conditions is shown in Table 1. A total of seventeen tests were conducted at four flow rates and heat loads. The inlet vapor concentration of water was kept close to 10% by weight for all tests. However, the water concentration gradually increased from about 8.2% by weight to about 12% for the last series of tests. It was most probably due to a slow leak of ammonia during and between the tests. The coolant flow rate was held constant at about 8.5 L/min, with an associated heat transfer coefficient of about 23 kW/m² K. The coolant temperature was about 22.9 °C for all tests, except for Tests 7-10, where the coolant temperature was about 25.2 °C. The change in coolant temperature varied in the range of 0.13 °C and 0.44 °C.

The overall heat transfer coefficient was calculated as follows:

$$ U_0 = \frac{Q}{A_0 \Delta T} $$

where

$$ \Delta T = \frac{(T_{dp} - T_{in}) - (T_{bo} - T_{am})}{\ln ((T_{dp} - T_{in})/(T_{bo} - T_{am}))} $$

Although the log-mean temperature difference for mixtures does not have physical significance, Equation (10) represents the change in saturation temperature between the dew point at inlet and the bubble point at the outlet. The heat transfer coefficient calculated using Equation (9) can be compared with that for pure ammonia, thereby examining the effect of the mass transfer resistance. The Wilson-plot method was used for tests with pure ammonia to determine the individual heat transfer coefficients. The water-side coefficient determined for pure ammonia was used to calculate an effective ammonia-water heat transfer coefficient from the overall coefficient. The overall rate of heat transfer was calculated on the basis of the coolant flow rate and change in the temperature across the test section.

The results expressed as composite, condensing plus wall, heat transfer coefficient for pure ammonia and ammonia-water mixture are shown in Figure 4. The
results show that the effective heat transfer coefficient for the mixture is significantly lower than that for pure ammonia; more than factors of ten and four for low and high heat flux conditions, respectively. The effective heat transfer coefficient increases with an increase in heat flux, while it decreases with increase in heat flux for pure ammonia.

![Heat Transfer Coefficient Graph](image)

**Figure 4.** Average heat transfer coefficient.

These results clearly indicate the effect of the vapor-side mass transfer resistance on the rate of condensation. The increasing trend is due to the higher mass transfer coefficient as the vapor flow rate increases with an increase in heat flux. The results indicate that the development of heat-exchange equipment for ammonia-water mixtures should focus on techniques to enhance the process of simultaneous heat and mass transfer in the vapor phase.

**Analytical Predictions**

The rate of condensation was calculated for the three following mass transfer conditions:

1. vapor and liquid phases are in equilibrium,
2. perfect-mixing condition for the liquid phase, and
3. no-mixing condition for the liquid phase.

The area required for condensing the vapor mixture for the equilibrium calculation was less than one half of that for the perfect-mixing condition half for all tests. As shown in Figure 5, the bulk saturation temperature for the equilibrium condition drops sharply as compared to that for the perfect-mixing condition. The results are plotted for dimensionless test-section length; actual lengths for the equilibrium and perfect-mixing conditions are 0.65 and 1.22 m, respectively. The sharp change in saturation temperature for the equilibrium condition is due to reduction in vapor-phase water concentration as shown in Figure 6. Other test conditions showed similar results. Condensation of water is hindered by the mass transfer resistance that maintains a high bulk saturation temperature. The interface temperature for the perfect-mixing condition is low, thereby leading to a low rate of condensation. The heat flux in Figure 7 is significantly higher at the inlet for the equilibrium condition due to high saturation temperature and film coefficient. The coolant heat transfer coefficient is about 23 kW/m² K, which is relatively high. Therefore, direct use of the experimental data to another system on the basis of the equilibrium condition would introduce significant error.

![Temperature Profiles Graph](image)

**Figure 5.** Axial temperature profiles.

![Vapor Phase Concentration Graph](image)

**Figure 6.** Vapor phase concentration of water.

![Heat Flux Profiles Graph](image)

**Figure 7.** Local heat flux profiles.
The predicted results for Tests 5 were analyzed in detail to quantify the effects of the individual mass transfer resistance. The temperature driving force for the equilibrium condition is the difference between the bulk saturation temperature and coolant temperature. The mass transfer resistance reduces the temperature driving force by lowering the interface temperature as shown in Figure 8. The interface temperatures for perfect- and no-mixing conditions drop sharply as the vapor-phase mass transfer decreases along the length of the tests section due to the entrance effects and the reduction in mass flow rate. The corresponding effects on the local heat flux are seen in Figure 9. Similar results are observed for other test conditions.

![Figure 8. Interfacial temperature profiles for Test 5.](image)

![Figure 9. Heat flux profiles for Test 5.](image)

The rate of condensation for the test section was predicted by the analytical method for all tests and the average heat flux was calculated. The predicted results are then compared with the experimental data as shown in Figure 10. Except for the initial 3 data points, the no-mixing condition predicts lower heat-flux values for the other 3 mass flow rates. The perfect-mixing condition predicts the heat flux for two intermediate mass flow rates with an acceptable accuracy. It underpredicts for the high flow rate and overpredicts for the low-mass-flow-rate tests. Overall, the perfect-mixing condition predicts the experimental data more accurately than the no-mixing condition. It further supports the conclusion derived in the previous analysis [12] that the perfect-mixing condition should be used for designing a heat and mass transfer unit for condensing an ammonia-water mixture, provided the liquid and vapor phases are maintained together.

![Figure 10. Comparison of experimental and predicted average heat fluxes.](image)

**CONCLUSION**

The analysis shows that the mass transfer resistance in condensation of binary vapor mixtures can be represented by the Colburn-Drew analysis based on the film theory. The analysis can be easily incorporated in a design method for the development of enhanced and compact condensers and absorbers. The effects of liquid-phase mass diffusion can be evaluated by considering two limiting conditions of perfect- and no-mixing. It is clearly shown that an unknown level of uncertainty would be introduced when applying experimental data directly to other condenser configurations and operating conditions.

**NOMENCLATURE**

<table>
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<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$A_o$</td>
<td>Heat transfer area $m^2$</td>
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<tr>
<td>$C_p$</td>
<td>Specific heat $J/mol K$</td>
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<td>$H$</td>
<td>Enthalpy $J/mol$</td>
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Subscript
1, 2 Component 1 and 2
i, b Interface and bulk conditions
bp, dp Bubble and dew points
c Coolant
ci, co Coolant in and out
l, v Liquid and vapor phases
T Total

LITERATURE CITED

Table 1. Test Conditions for Condensation Ammonia-Water Mixtures.

<table>
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<tr>
<th>Test Run</th>
<th>Water Concentration mole fraction</th>
<th>Pressure kPa</th>
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