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Condensation of binary vapors of immiscible liquids

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Abstract—Measurements were made of condensation heat transfer coefficients of binary vapors of water and hydrocarbon such as n-octane and n-heptane on the vertical flat plate, vertical tube and horizontal tube. The result indicates that the heat transfer coefficients of the binary vapors of azeotropic composition are larger than those of the pure organic vapors. A model assuming that the heat transfer resistances of pure water and organic condensates are parallel predicts the measured values of heat transfer coefficients.

1. INTRODUCTION

A HYDROCARBON or a halogenated hydrocarbon of low boiling temperature is used in general as a working fluid in a heat engine or a heat-pump cycle for recovery of energy from a low temperature heat source. However, such compounds have some drawbacks that the latent heat is low, which requires a high circulation rate of the fluid, and the thermal conductivity in the liquid state is small, which causes low heat transfer coefficients in condensation. These drawbacks would be eliminated by employing a mixture of the organic compound with water as a working fluid because water has a higher latent heat and a higher thermal conductivity in the liquid.

The condensation of mixed vapors of immiscible liquids such as hydrocarbon and water has been the subject of many experimental studies [1–9]. However, the data obtained so far do not agree with one another. This is due primarily to the fact that most of the data have been obtained for the mixture of non-azeotropic composition. When the vapor composition is non-azeotropic, only one vapor condenses and the other behaves as a non-condensing gas. An analysis has been given of the vapor phase diffusional resistance during condensation of vapors of immiscible liquids by Sardesai and Webb [10]. They have used the film model of Colburn and Hougen [11] to calculate the molar flux in the vapor phase. More detailed investigation will be necessary on this aspect of condensation.

When the vapor composition is azeotropic, two vapors condense simultaneously on the condensing surface. Visual observations of the condensate flow patterns have been made by Bernhardt *et al.* [9] and Polley and Calus [13]. The results have shown that the mechanism of the dual-phase condensation is highly complex. Therefore, the correct theoretical treatment of condensation of immiscible mixtures is not available at present.

A number of empirical or semi-empirical equations have been proposed based on simplified models of the condensate flow. Notable among these are the models of Akers and Turner [8], Bernhardt *et al.* [9] and recently of Polley and Calus [12, 13]. The models of Akers and Turner and of Bernhardt *et al.* are purely empirical. Akers and Turner proposed the Nusselt equation with physical properties weighted in terms of the composition of the two-phase condensate. Bernhardt *et al.* assumed that each liquid species occupy a fraction of the area equal to its volume fraction in the mixed condensate. Polley and Calus proposed a standing-drop model [12] and channeling-flow model [13]. The channeling-flow model was an extension of that of Bernhardt *et al.*, but the fraction of the area covered by each phase was not formulated.

The purpose of the present investigation is to obtain reliable condensation heat transfer coefficients of the binary mixture of azeotropic composition. Comparison is also made between the experimental result and the prediction by an improved model.

2. AZEOTROPIC MIXTURE

The essential feature of an immiscible system is that each liquid phase exerts its own vapor pressure regardless of the quantity of the other liquid present.

The phase characteristics of such a system are well illustrated on the temperature–composition diagram. The diagram for a binary system of n-heptane and water at atmospheric pressure is shown in Fig. 1.

Suppose initially the mixture is entirely in the vapor phase at a composition. This would be represented by point A in Fig. 1. Upon cooling at constant pressure, point B is reached such that the vapor pressure of pure n-heptane is equal to the partial pressure of n-heptane in the vapor. With continued cooling, pure liquid n-heptane will be condensed and the vapor composition will decrease in n-heptane along the line BC. When the temperature T_a is reached, the partial pressure of the water in the vapor will have become equal to the vapor pressure of pure water, that is, the sum of the vapor pressures of the two liquids will

NOMENCLATURE

g	gravitational acceleration [m s^{-2}]
h	heat transfer coefficient [W m^{-2} K^{-1}]
ΔH	heat of vaporization [J kg^{-1}]
k	thermal conductivity [W m^{-1} K^{-1}]
L	length of the condensing surface [m]
q	heat flux [W m^{-2}]
T	temperature [K]
W	width of the condensate [m]
x, y, z	coordinate.

Greek symbols

Γ	flow rate of condensate per unit perimeter [kg s^{-1} m^{-1}]
δ	thickness of condensate film [m]
μ	viscosity [Pa s]
ρ	density [kg m^{-3}]
ω	mass fraction.

Subscripts

a	azeotropic
v	vapor
w	condensing surface
1	organic component
2	water component.

become equal to the total pressure. At this temperature, there will be three phases in equilibrium, pure liquid n-heptane, pure liquid water, and vapor of composition C. Upon further heat removal, both components will condense from the vapor mixture and the temperature and the vapor composition will remain constant until the vapor phase disappears, that is, the composition of the condensate is the same as that of the vapor.

The mixture at composition C can be called the azeotropic mixture although this term is used in general for miscible systems.

3. EXPERIMENT

3.1. *Experimental apparatus and procedure*

A schematic diagram of the apparatus is shown in Fig. 2. A stainless steel evaporator was used to vaporize the liquid mixture. The electric heater was immersed in the lower phase so that bubbles generated on the heater rose through the less dense liquid phase. A thermometer in the vapor showed that the azeotropic mixture was obtained. The mixed vapor passed from the evaporator into a rectangular duct, 150 mm high and 150 mm wide, in which a copper tube, 20 mm o.d. and 140 mm long was mounted vertically or horizontally. Cooling water flowed through the tube. The vapor mixture condensed in part on the copper tube and the remainder was handled by a total condenser. Condensate on the vertical tube ran down into a cup at the bottom of the tube and that on the horizontal one into a trough below the tube.

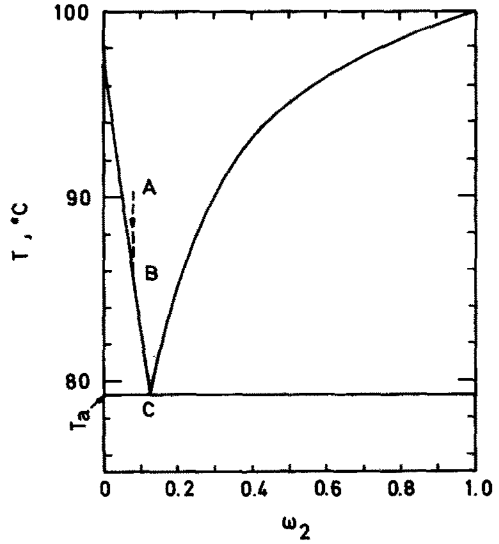

FIG. 1. Temperature–composition diagram for binary system of n-heptane and water.

When a flat condenser surface was used, the rectangular duct was replaced by a condenser shown in Fig. 3, which consisted of a vertical copper plate, 20 mm wide and 45 mm high. Cooling water flowed through the jacket behind the condensing surface and a condensate collector was provided below the condensing surface.

During the experiment the condensing surface could be viewed from windows equipped with the condensers for both cases of tube and flat plate.

The average heat flux was calculated from the measurement of the condensate flow rate. The temperature of the condensing surface for the vertical and horizontal tube was determined by using the heat transfer coefficient of cooling water which was confirmed to be in good agreement with the equation of Sieder and Tate [14] in their preliminary experiment. The temperature of the flat plate surface was determined from the temperature measured by a thermocouple B imbedded in the copper plate and the measured heat flux. The effect of the velocity of vapor on the condensation heat transfer coefficient could be neglected in the present experiment.

Experiments were made on three immiscible systems: n-heptane–water, isooctane–water and n-octane–water. The azeotropic compositions of these systems are $\omega_1 = 0.871$, 0.885 and 0.751, and the saturation temperatures 79.2, 79.4 and 89.4°C, respectively.

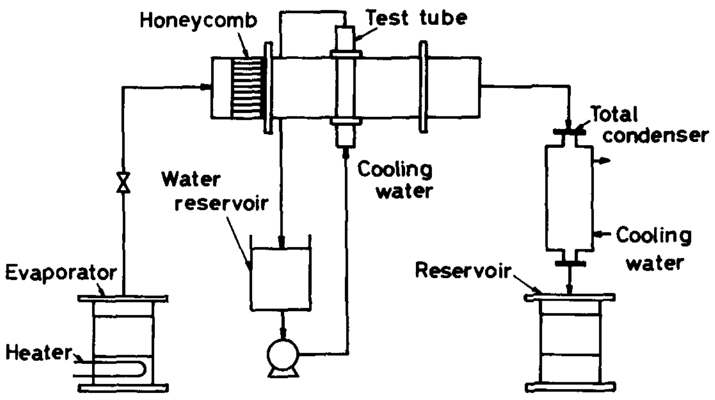

FIG. 2. Schematic diagram of experimental apparatus for condensation.

3.2. *Experimental result*

The results obtained for the condensation of azeotropic mixtures of n-heptane–water and n-octane–water on the flat surface are presented in Figs. 4 and 5. The data obtained for the condensation of pure water and pure organic compounds are also depicted in these figures.

The heat transfer coefficients of pure water and organic compounds are in good agreement with the calculated values by the Nusselt equation shown by the dot-dashed line for water and the solid line for the hydrocarbons. The values of the heat transfer coefficient of the azeotropic mixtures are remarkably larger than those of the pure organic compounds. They exhibit a Nusselt-type dependence upon temperature difference. Similar results were obtained for

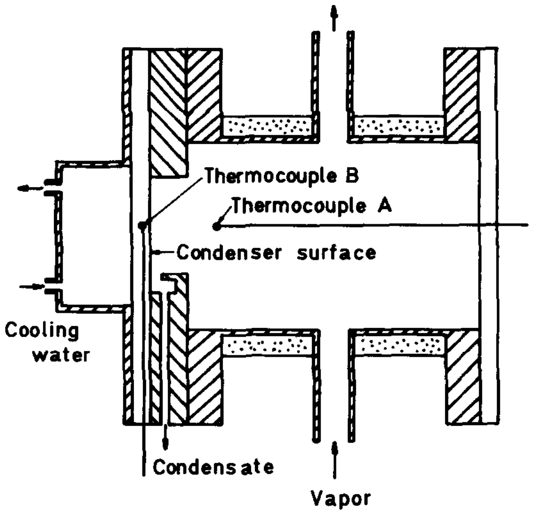

FIG. 3. Sketch of condenser with vertical flat plate.

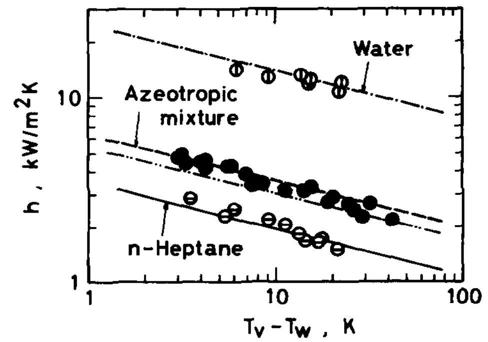

FIG. 4. Condensation heat transfer coefficients of an n-heptane–water azeotropic mixture on a vertical flat plate: ⦶, water; ⊖, n-heptane; ●, azeotropic mixture; ————, equation (8); —··—··—, Bernhardt *et al.*

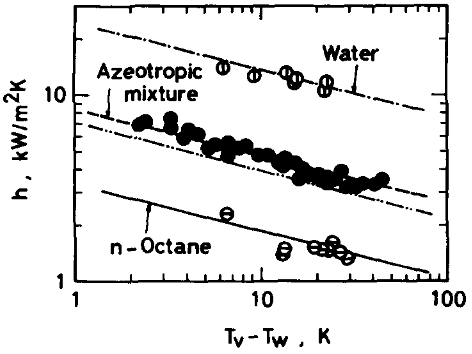

FIG. 5. Condensation heat transfer coefficients of an n-octane–water azeotropic mixture on a vertical flat plate: ⦶, water; ⊖, n-octane; ●, azeotropic mixture; ————, equation (8); —··—··—, Bernhardt *et al.*

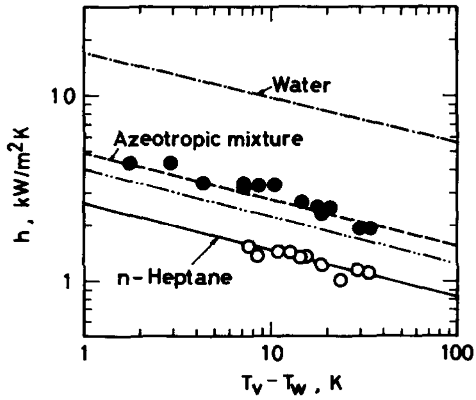

FIG. 6. Condensation heat transfer coefficients of an n-heptane–water azeotropic mixture on a vertical tube: ○, n-heptane; ●, azeotropic mixture; ————, equation (8), —··—··—, Bernhardt *et al.*

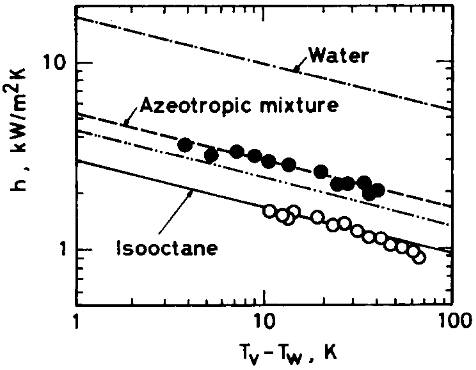

FIG. 7. Condensation heat transfer coefficients of an isooctane–water azeotropic mixture on a vertical tube: ○, isooctane; ●, azeotropic mixture; ————, equation (8); —··—··—, Bernhardt *et al.*

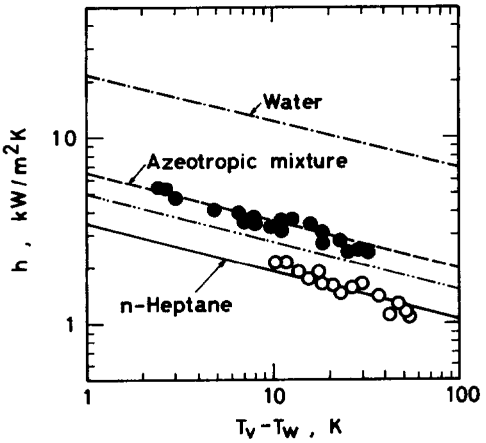

FIG. 8. Condensation heat transfer coefficients of an n-heptane–water azeotropic mixture on a horizontal tube: ○, n-heptane; ●, azeotropic mixture; ————, equation (8); —··—··—, Bernhardt *et al.*

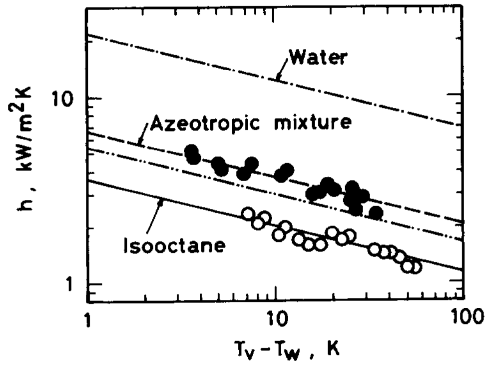

FIG. 9. Condensation heat transfer coefficients of an isooctane–water azeotropic mixture on a horizontal tube: ○, isooctane; ●, azeotropic mixture; ————, equation (8); —··—··—, Bernhardt *et al.*

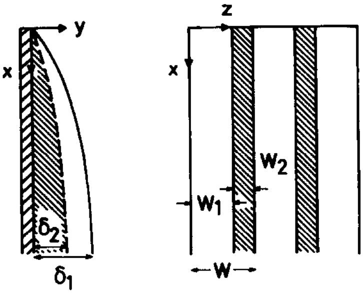

FIG. 10. Model for condensation of an azeotropic mixture.

the condensation of n-heptane–water and isooctane–water azeotropic mixtures on the vertical and horizontal tubes as shown in Figs. 6–9.

4. DISCUSSION

The behavior of the two liquid phases on the condensing surface can generally be considered to be characterized by one of three ideal types; film-drop pattern, standing drop pattern and channeling flow [13].

The film-drop pattern consists of a continuous organic liquid film with droplets of water embedded within the film and flowing with it. The model of Akers and Turner is based on this flow pattern.

The standing drop pattern consists of water droplets attached to the cold surface and surrounded by an organic liquid film. These standing drops remain on the cold surface, grow to a large size, and offer a relatively large resistance to heat transfer. Polley and Calus [12] presented a model of this flow pattern.

A channeling flow pattern consists of distinct separate areas of the condenser surface occupied by flowing films or rivulets of the individual liquids.

Although it is not clear which pattern appears in what condition, the channeling flow often occurs at high condensate flow rates. Hence, it is practically the most important of the three ideal condensate patterns. The principal feature seen in the present experiment is the channeling flow pattern like that given by Polley and Calus [13].

A parallel condensation shown in Fig. 10 can be assumed as a model for channeling. The analysis is a modification of the Nusselt approach to laminar film condensation and similar assumptions apply.

The mass flow rate of the condensate per unit perimeter is given by

$$\Gamma_i = \frac{\rho_i^2 g}{3\mu_i}\left(\frac{4k_i(T_v - T_w)\mu_i L}{\rho_i^2 g \Delta H_i}\right)^{3/4} \qquad (1)$$

where i indicates the liquid under consideration.

The condensate mass flow rate is related to the composition of the condensate by

$$\omega_i = \Gamma_i W_i/(\Gamma_1 W_1 + \Gamma_2 W_2) \qquad (2)$$

where W_i is the width of the condensate of component i, as shown in Fig. 10. Rearrangement of equation (2)

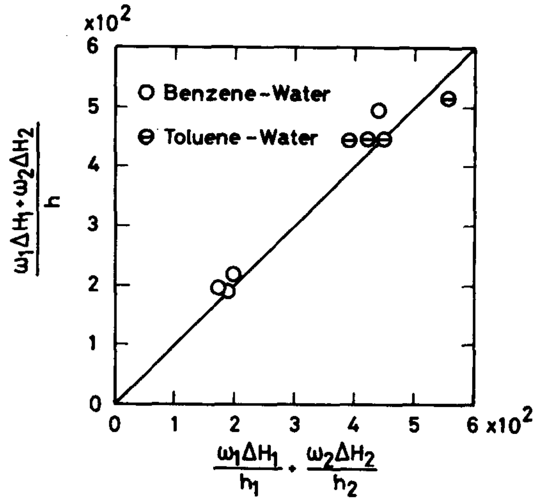

FIG. 11. Comparison of the prediction with experimental results of other azeotropic systems.

gives

$$W_1/W = \omega_1\Gamma_2/(\omega_2\Gamma_1+\omega_1\Gamma_2) \tag{3}$$

$$W_2/W = \omega_2\Gamma_1/(\omega_2\Gamma_1+\omega_1\Gamma_2) \tag{4}$$

where $W = W_1 + W_2$.

The total heat transferred from the vapor to the cold surface can be expressed by

$$qWL = \Gamma_1 W_1 \Delta H_1 + \Gamma_2 W_2 \Delta H_2. \tag{5}$$

The heat transfer coefficient is

$$h = \frac{W_1}{W}\frac{\Gamma_1\Delta H_1}{L(T_v-T_w)} + \frac{W_2}{W}\frac{\Gamma_2\Delta H_2}{L(T_v-T_w)}. \tag{6}$$

If we assume that W_i/W is equal to the volume fraction of component i in the mixed condensate and take account of the following relation:

$$h_i = \frac{\Gamma_i\Delta H_i}{L(T_v-T_w)} = \frac{4}{3}\left[\frac{k_i^3\rho_i^2 g\Delta H_i}{4\mu_i(T_v-T_w)L}\right]^{1/4} \tag{7}$$

equation (6) gives the model of Bernhardt *et al.*

Substitution of equations (1), (3), (4) and (7) into equation (6) gives

$$h = \frac{\omega_1\Delta H_1+\omega_2\Delta H_2}{\omega_1\Delta H_1/h_1+\omega_2\Delta H_2/h_2}. \tag{8}$$

The same equation can be derived for the horizontal tube.

Predictions by equation (8), broken lines, are compared with the experimental results in Figs. 4–9. The agreement between the predictions and the experimental data is very good not only for the flat surface but also for the vertical and horizontal tube. For comparison the calculated values from Bernhardt *et al.*'s model are shown in Figs. 4–9 by double-dot-dashed lines. The calculated values are smaller than the measured values.

Figure 11 shows the comparison between the prediction and experimental results of Akers and Turner [8] and Hazelton and Baker [5]. Only the tabulated azeotropic data are included. The ordinate shows the measured values and the abscissa the calculated ones. Equation (8) can also apply to benzene–water and toluene–water systems.

5. CONCLUSION

(1) The condensation heat transfer coefficient of the azeotropic mixture of organic compound and water is larger than that of the pure organic vapor.

(2) A model assuming that the heat transfer resistances of water and organic condensates are parallel predicts the measured values of heat transfer coefficients.

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CONDENSATION DE VAPEUR BINAIRE DES LIQUIDES NON MISCIBLES

Résumé—On fait des mesures de coefficient de transfert thermique par condensation pour des vapeurs binaires d'eau et d'hydrocarbures, tels que n-octane et n-heptane, sur une plaque plane verticale, un tube vertical et un tube horizontal. Les résultats montrent que les coefficients de transfert de chaleur sur les vapeurs binaires de composition azéotropique sont plus grands que ceux de la vapeur pure organique. Un modèle supposant que les résistances de transfert thermique de l'eau pure et des condensats organiques sont en parallèle prédit les valeurs mesurées des coefficients de transfert thermique.

KONDENSATION VON BINÄREN DÄMPFEN NICHT-MISCHBARER FLÜSSIGKEITEN

Zusammenfassung—Die Wärmeübergangskoeffizienten bei der Kondensation von binären Dämpfen von Wasser und Kohlenwasserstoffen wie z. B. n-Oktan and n-Heptan, auf einer vertikalen ebenen Platte, in einem vertikalen und horizontalen Rohr wurden gemessen. Das Ergebnis zeigt, daß die Wärmeübergangskoeffizienten der binären Dämpfe azeotroper Zusammensetzung größer sind als diejenigen der reinen organischen Dämpfe. Ein Modell mit der Annahme, daß die Wärmeübergangswiderstände von reinem Wasser und organischen Kondensaten parallel anzusehen sind, erlaubt es, die gemessenen Werte der Wärmeübergangskoeffizienten zu berechnen.

КОНДЕНСАЦИЯ БИНАРНЫХ ПАРОВ НЕСМЕШИВАЮЩИХСЯ ЖИДКОСТЕЙ

Аннотация—Измерены коэффициенты теплообмена при конденсации бинарных паров воды и углеводорода (*н*-октан и *н*-гептан) на вертикальной плоской поверхности, вертикальной и горизонтальной трубах. Результаты показывают, что коэффициенты теплообмена бинарных паров азеотропного состава выше, чем чистых органических паров. Модель, предполагающая, что тепловые сопротивления чистой воды и органических конденсатов аддитивны, позволяет рассчитывать измеренные значения коэффициентов теплопереноса.