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PREDICTION OF BINARY MIXTURE BOILING HEAT TRANSFER COEFFICIENTS USING ONLY PHASE EQUILIBRIUM DATA

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Abstract—A new method for predicting the variation of nucleate pool boiling heat transfer coefficients with composition for binary liquid mixtures is presented. It is shown that the rise in the local boiling point of the liquid, ΔT_{bp}, adjacent to the heated surface caused by preferential evaporation of the volatile component has a limit at the peak nucleate heat flux. ΔT_{bp} can be determined from knowledge of only the phase equilibrium diagram at the pressure of interest. The resulting equation incorporating ΔT_{bp} accurately predicts published experimental boiling heat transfer coefficients at heat fluxes well below the peak heat flux for six binary liquid mixture systems considered: ethanol–water, acetone–water, ethanol–benzene, nitrogen–argon, nitrogen–oxygen, and nitrogen–methane.

NOMENCLATURE

A, empirical coefficient;
A_0, value of A at 1.0 bar;
c_p, liquid specific heat [J K^{-1} kg^{-1}];
D, liquid mass diffusivity [m^2 s^{-1}];
D_d, bubble departure diameter [m];
f, bubble departure frequency [s^{-1}];
g, acceleration due to gravity [m s^{-2}];
h, heat transfer coefficient [W K^{-1} m^{-2}];
h_{act}, actual heat transfer coefficient [W K^{-1} m^{-2}];
h_{fg}, heat of vaporization [J kg^{-1}];
h_I, ideal heat transfer coefficient [W K^{-1} m^{-2}];
h_{pred}, predicted heat transfer coefficient [W K^{-1} m^{-2}];
K_{st}, empirical coefficient;
k_L, liquid thermal conductivity [W K^{-1} m^{-1}];
N_{Sn}, Scriven number;
Nu, Nusselt number;
n, empirical exponent;
Pr, Prandtl number;
p, pressure [bar];
q, heat flux [W m^{-2}];
T_{bulk}, bulk saturation temperature [K];
T_{local}, local saturation temperature [K];
T_{sat}, saturation temperature [K];
T_w, wall temperature [K];
dT/dx, slope of bubble line [K];
ΔT, wall superheat, $T_w - T_{sat}$ [K];
ΔT_{bp}, maximum rise is local saturation temperature [K];
ΔT_I, ideal wall superheat [K];
x, mass fraction of liquid;
$\tilde{x}$, mole fraction of liquid;
y, mass fraction of vapor;
$\tilde{y}$, mole fraction of vapor.

Greek symbols

α_L, thermal diffusivity of liquid;
β, contact angle [degrees];
η_L, liquid dynamic viscosity [kg m^{-1} s^{-1}];
ρ_L, liquid density [kg m^{-3}];
ρ_v, vapor density [kg m^{-3}];
σ, surface tension [N m^{-1}].

Subscripts

1, single component number one;
2, single component number two;
I, ideal.

1. INTRODUCTION

IT IS a well-established fact from numerous experimental investigations on nucleate pool boiling of binary liquid mixtures that the boiling heat transfer coefficients of the mixtures can be considerably lower than those of an equivalent pure fluid with the same physical properties as the mixture. Figure 1 illustrates this fact for some recent experimental results [1] for an aqueous mixture of ethanol–water at atmospheric pressure. This reduction in the heat transfer coefficient also occurs for organic–organic mixtures [2–4], refrigerant–refrigerant mixtures [5], and liquefied gas mixtures [6–8]. The problem, then, is: (a) to explain physically why the actual heat transfer coefficients are

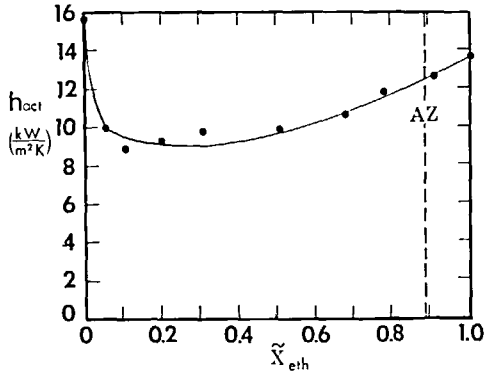

FIG. 1. Variation of boiling heat transfer coefficient with composition as measured by Shakir [1] for ethanol–water mixtures at 1.0 bar and 200 kW m^{-2}.

lower than those expected from single component boiling predictions and (b) to predict the actual variation.

Van Wijk *et al.* [9] gave the first physical explanation for the lower coefficients. They noted that the equilibrium vapor mole fraction, $\tilde{y}$, of the volatile component (i.e. lower boiling point liquid) in the bubbles growing on the heated surface is higher than that of the surrounding bulk liquid, $\tilde{x}$ (Fig. 2). Thus, in order to maintain equilibrium between the phases, more of the volatile component in the liquid must evaporate to provide the additional volatile vapor in the bubble as it grows. This in turn causes a reduction in the local liquid mole fraction of the volatile component and thus a rise in the local boiling point temperature. Consequently, the heated wall temperature has to rise in order to transfer heat at the same rate. Hence, the heat transfer coefficient (which is based on the bulk liquid boiling point) is lowered.

Sternling and Tichacek [10] also attributed the lower heat transfer coefficients in the mixtures to the additional mass diffusion resistance of the volatile component to the vapor bubble. Grigor'ev [11] explained the lower heat transfer coefficients as due to lower boiling site densities caused by higher wall superheats, $T_w - T_{sat}$, required for activation of bubble nuclei in mixtures. Stephan and Körner [12] showed analytically that the reversible isothermal work required for the formation of a bubble in a binary mixture is greater than that for a single component liquid with the same physical properties. They concluded that fewer bubbles are generated in mixtures and that the heat transfer coefficient is thus diminished. Later, Stephan and Preusser [13] attribute part of the reduction in the heat transfer coefficient to the non-linear variation in physical properties with composition. More recently Thome [14] showed that the two principal heat transport mechanisms active in nucleate pool boiling, bubble evaporation and thermal boundary layer stripping, are retarded in mixtures and are therefore partially responsible for the lower heat transfer coefficients.

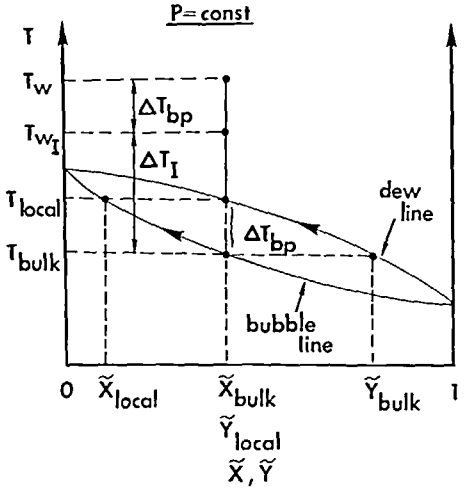

FIG. 2. Vapor–liquid phase equilibrium diagram showing ΔT_{bp}.

The overwhelming conclusion drawn from the many studies on binary liquid mixtures is that their nucleate pool boiling heat transfer coefficients cannot adequately be predicted using single component correlations because of the conditions noted above. Hence, at least seven predictive methods have been developed specifically for binary mixtures. These are reviewed briefly here.

Stephan and Körner [12] developed a correlation based on the explanation given by Van Wijk *et al.* [9] to account for the rise in the local saturation and wall temperatures. Using the excess function formulation that is often utilized for predicting physical properties of binary mixtures, the wall superheat at a given heat flux is given as

$$T_w - T_{sat} = \Delta T_I + \Delta T^E \tag{1}$$

where the ideal mixing law superheat ΔT_I is defined as

$$\Delta T_I = \tilde{x}_1 \Delta T_1 + \tilde{x}_2 \Delta T_2 \tag{2}$$

and the excess superheat ΔT^E is calculated as

$$\Delta T^E = A|\tilde{y} - \tilde{x}|\Delta T_I. \tag{3}$$

The quantities $\tilde{y}$ and $\tilde{x}$ in equation (3) are the mole fractions of the volatile component at bulk conditions. The empirical coefficient A is obtained by fitting equations (1) and (3) to experimental results at a given heat flux and then is used for all heat fluxes. Hence, A is not a function of the heat flux (which it should be) but is dependent on the particular binary mixture system and pressure. To account for the effect of pressure, Körner [15] presented a further empirical relationship valid over the range 1–10 bar as

$$A = A_0(0.88 + 0.12p) \tag{4}$$

with p in bars and A_0 being the value of A at 1.0 bar. He lists values of A_0 for 17 binary mixture systems.

Happel and Stephan [16] presented a similar polynomial empirical relation as

$$\frac{h}{h_I} = \frac{\Delta T_I}{\Delta T} = 1 - K_{st}|\tilde{y} - \tilde{x}|^n \tag{5}$$

where the quantities K_{st} and n need to be determined experimentally for each heat flux, mixture system, and pressure.

An experimental study on bubble departure diameters and frequencies in binary mixtures led Tolubinskiy and Ostrovskiy [17] to propose a correlation based on the vapor mass flux, fD_d. They give the Nusselt number as

$$Nu = \left\{\frac{q}{\rho_v h_{fg}[x_1(fD_d)_1 + x_2(fD_d)_2]}\right\}^{0.7} \times Pr^{-0.2}\left[1 - \frac{(y-x)^2}{y(1-x)}\right]^{1.6}. \tag{6}$$

This correlation is only valid for ethanol–water mixtures and is difficult to utilize since fD_d has to be estimated by some unspecified method.

Calus and Rice [18] developed a semi-empirical correlation based on the assumption that the reduction in the bubble growth rate due to the mass diffusion resistance is directly proportional to the reduction in the heat transfer coefficient in binary mixtures. They arrived at

$$\frac{h}{h_I} = \left[1+|y-x|\left(\frac{\alpha_L}{D}\right)^{1/2}\right]^{-0.7} \quad (7)$$

where h_I is the value given by the Borishanskii–Michenko correlation for single component liquids. The exponent (-0.7) was determined empirically.

Calus and Leonidopoulos [19] later derived the first expression devoid of empirical coefficients for predicting the variation in the wall superheat with composition. They calculated the rise in the local saturation temperature for the growth of a single spherical bubble in an infinite uniformly superheated binary liquid mixture using Scriven's [20] and Van Stralen's [21] solution and assumed this situation was equivalent to that for an actual boiling surface. They thus derived the wall superheat as

$$\Delta T = (x_1\Delta T_1 + x_2\Delta T_2) \times \left[1-(y-x)\left(\frac{\alpha_L}{D}\right)^{1/2}\left(\frac{c_p}{h_{fg}}\right)\left(\frac{dT}{dx}\right)\right] \quad (8)$$

where $(y-x)$ and the slope of the bubble line, (dT/dx), are always of opposite signs and thus ΔT is always predicted to be greater than or equal to ΔT_I.

Stephan and Preusser [13] used dimensional analysis to arrive at the following correlation for multicomponent boiling:

$$\frac{hD_d}{k_L} = 0.100\left(\frac{qD_d}{k_L T_{sat}}\right)^{0.674}\left(\frac{\rho_v}{\rho_L}\right)^{0.156} \times \left(\frac{h_{fg}D_d^2}{\alpha_L^2}\right)^{0.371}\left(\frac{\alpha_L^2}{\sigma D_d}\right)^{0.350}\left(\frac{\eta_L c_p}{k_L}\right)^{-0.162} \times \left[1+\left|\sum_{i=1}^{n-1}(\tilde{y}_1-\tilde{x}_1)(\partial\tilde{y}_i/\partial\tilde{x}_i)_{\tilde{x}_{j,p}}\right|\right]^{-0.0733} \quad (9)$$

where D_d is given as

$$D_d = 0.0146\beta\{2\sigma/[g(\rho_L-\rho_v)]\}^{1/2}. \quad (10)$$

The bracketed term in equation (9) is a measure of deviation from equilibrium concentration.

Thome [22] derived the following analytical expression based on the effect of composition on the thermal boundary layer stripping mechanism for boiling at a heated surface:

$$\frac{h}{h_I} = \frac{\Delta T_I}{\Delta T} = N_{Sn}^{7/5} \quad (11)$$

where ΔT_I is given by equation (2) and the Scriven number, N_{Sn}, is defined as

$$N_{Sn} \equiv \left[1-(\tilde{y}-\tilde{x})\left(\frac{\alpha_L}{D}\right)^{1/2}\left(\frac{c_p}{h_{fg}}\right)\left(\frac{dT}{d\tilde{x}}\right)\right]^{-1}. \quad (12)$$

Since $(\tilde{y}-\tilde{x})$ and $(dT/d\tilde{x})$ are always of opposite signs, h is predicted to be less than h_I except for the single component liquids and at the azeotrope where $(y-x)$ becomes zero.

The empirical equations discussed above suffer from the need for experimental data for every binary mixture system and pressure of interest in order to determine the empirical coefficients and exponents involved. This is a serious limitation since in extending the work to multicomponent boiling, the number of binary mixture pairs involved becomes very large. Some of the correlations take into account the non-linear variation in physical properties with composition by using a single component correlation to define h_I rather than the linear mixing law. However, in practice accurate physical properties for mixtures to be used in the single component correlations are difficult to obtain, especially at elevated pressures.

While the analytical equations presented above are devoid of empirical coefficients, they do include the liquid mass diffusivity, D. Since there is no simple, general equation for predicting D over a wide range of binary mixture systems, it is also difficult to utilize these equations.

The present study has sought to overcome some of the shortcomings of the above predictive methods by approaching the problem from a different point of view. In the next section a very simple model is shown to be very powerful in predicting boiling heat transfer coefficients in binary liquid mixtures using only phase equilibrium data.

2. PHYSICAL MODEL AND ANALYSIS

In postulating the effect of composition on the rise in the local saturation temperature for a binary liquid mixture boiling on a smooth tube or plate, it is evident that the rate of evaporation will control the level of depletion of the volatile component in the liquid adjacent to the heated surface. The problem is complex because not only does the evaporation rate at a characteristic boiling site have to be predicted as a function of composition as was done in [22], but also the rates of diffusion and mixing and the effect of composition on the boiling site density. The problem is bounded at low heat fluxes where only single-phase natural convection occurs and at the peak nucleate heat flux (or departure from nucleate boiling) where all of the liquid arriving at the heated surface is assumed to be evaporated. (For small surfaces, some of the peak heat flux still leaves via convection to the liquid. Thus, the present method will yield a conservative prediction of the heat transfer coefficient.) Thus, the rise in the local boiling point varies from zero at low heat flux up to a maximum at the peak heat flux.

This maximum rise in the boiling point, ΔT_{bp}, at the peak heat flux is easily discernable from a phase equilibrium diagram of $(T-\tilde{x}, \tilde{y})$ at constant pressure. Figure 2 shows a typical phase diagram for a non-azeotropic mixture. If bulk liquid at a composition of $\tilde{x}_{bulk}$ arrives at the heated surface and only saturated vapor leaves, then the local vapor composition, $\tilde{y}_{local}$, must be equal to $\tilde{x}_{bulk}$ for steady-state operating conditions. The boiling point of the liquid adjacent to the wall increases from T_{bulk} to T_{local} but cannot rise past T_{local} without violating the law of conservation of mass. Consequently, there is an upper limit to the increase in the local saturation temperature for nucleate pool boiling of binary mixtures. This increase, ΔT_{bp}, is defined as the temperature difference between the dew line and the bubble line at the bulk liquid mole fraction.

This approach to the problem can be used to calculate the actual wall temperature at the peak heat flux using part of the Stephan and Körner [12] formulation. In equation (13) they approximate the rise in the local saturation temperature, ΔT^E, using the vapor/liquid mole fraction difference and an empirical coefficient, A, which is valid at the heat flux used to determine A. For the present situation, ΔT^E at the peak nucleate heat flux is equal to ΔT_{bp}. Substituting this into equation (1) gives

$$\Delta T = T_w - T_{sat} = \Delta T_I + \Delta T_{bp} \tag{13}$$

or

$$\frac{h}{h_I} = \frac{\Delta T_I}{\Delta T} = \frac{\Delta T_I}{\Delta T_I + \Delta T_{bp}} \tag{14}$$

where h_I at the given heat flux is defined as

$$h_I = \frac{1}{(\tilde{x}_1/h_1) + (\tilde{x}_2/h_2)}. \tag{15}$$

Using the above relationship to predict boiling heat transfer coefficients in binary mixtures should then give a good approximation for intermediate and high heat fluxes. For the case where the heat flux is below the peak nucleate heat flux, the actual rise in the local boiling point will be less than ΔT_{bp}. Thus, using ΔT_{bp} will overpredict the actual overall ΔT, giving a conservative estimate of the actual boiling heat transfer coefficient.

Another option which is available is to use a general purpose single component nucleate pool boiling correlation to predict the ideal heat transfer coefficient, h_I, rather than the linear mixing law as defined in equation (15). While this would allow for non-linear variations in physical properties as in equation (9), for example, the estimation of these physical properties for various mixtures and pressures is not easily achieved since their excess functions are usually only available for the range of 20–40°C. As will be demonstrated in the next section, equation (14) predicts the very non-linear binary mixture systems, i.e. aqueous solutions, quite well using equation (15) to define h_I.

3. COMPARISON WITH EXPERIMENTAL RESULTS

Equation (14) has been compared with experimental pool boiling data obtained from 15 different references. Aqueous solutions are represented by ethanol–water at pressures from 1.0 to 15 bar and acetone–water at 1.0 bar. Organic–organic mixtures are represented by ethanol–benzene at 1.0 bar. Liquefied gases or cryogenic mixture systems are represented by nitrogen–argon and nitrogen–oxygen at 1.0 bar and nitrogen–methane at 2–28 bar. The geometries of the various heated test surfaces represented are given in Table 1.

Eight sets of nucleate pool boiling data for ethanol–water mixtures at 1.0 bar are shown in Fig. 3 at various heat flux levels. Phase equilibrium data were obtained from Kirschbaum [31]. The boiling data from the various studies were normalized by dividing the actual measured heat transfer coefficient, h_{act}, by the ideal heat transfer coefficient, h_I, calculated from the single component heat transfer coefficients for the particular set of data at the heat flux level cited. Note that the mixture behaves as a single component liquid at the azeotrope ($\tilde{x} = 0.89$). Hence, the RHS of equation (2) is divided by 0.89 to normalize $\tilde{x}_1$ and $\tilde{x}_2$ to vary between 0 and 1 between pure water and the azeotrope which affects the values of ΔT_I and h_I in equations (14) and (15).

A wide variation in the reduction in the heat transfer coefficients in the mixtures in Fig. 3 from one study to another is obvious. The results of Preusser [27] show

Table 1. Heated test surface geometries and orientations

Source	Geometry	Orientation
Lyon [6]	70 mm dia. cylinder	vertical
Ackermann *et al.* [7]	19 mm dia. plate	horizontal facing upwards
Thome and Bald [8]	18 mm dia. plate	horizontal facing upwards
Afgan [23]	5 mm dia. cylinder	horizontal
Valent and Afgan [24]	10 × 60 mm plate	horizontal facing upwards
Grigor'ev *et al.* [25, 26]	8 mm dia. cylinder	horizontal
Preusser [27]	14 mm dia. cylinder	horizontal
Tolubinskiy *et al.* [2, 28] Tolubinskiy and Ostrovskiy [17]	4.5 mm dia. cylinder	vertical
Bonilla and Perry [29]	91 mm dia. plate	horizontal facing upwards
Cichelli and Bonilla [30]	95 mm dia. plate	horizontal facing upwards
Happel and Stephan [16]	14 mm dia. cylinder	horizontal
Shakir [1]	25 mm dia. plate	horizontal facing upwards

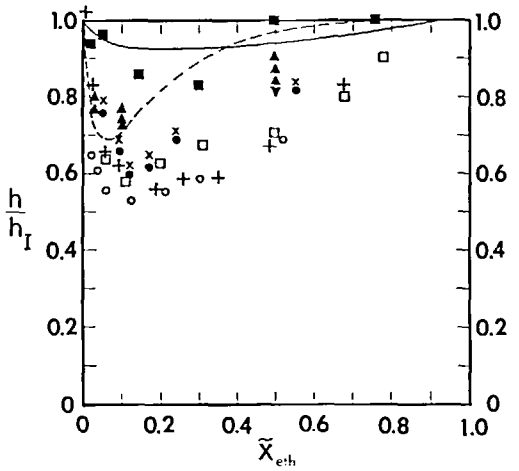

FIG. 3. Normalized boiling heat transfer coefficients for ethanol–water mixtures at 1.0 bar at various heat fluxes. ● Valent and Afgan [24] at 300 kW m^{-2}, × Valent and Afgan [24] at 190 kW m^{-2}, ○ Tolubinskiy and Ostrovskiy [17] at 116 kW m^{-2}, + Grigor'ev *et al.* [25] at 232 kW m^{-2}, ▲ Bonilla and Perry, Fig. 2 [29] at 95 kW m^{-2}, ▼ Cichelli and Bonilla [30] at 221 kW m^{-2}, □ Shakir [1] at 200 kW m^{-2}, ■ Preusser [27] at 200 kW m^{-2}.

much less deterioration in the heat transfer coefficient than the others even though the geometries are similar. While this may be a result of differences in surface finish, it may be due to his use of hot water flowing from 0 to 20 m s^{-1} inside his tube to provide the heat for boiling from its outside surface. This means that the tube wall temperature and heat flux are not uniform along the length of the tube. Using his peak heat flux for water of 1.1 MW m^{-2} and the maximum flow rate of 20 m s^{-1} gives a temperature difference between the tube ends of about 7 K. If this is representative of the axial temperature drop at lower heat fluxes, then part of the test length may be experiencing only single-phase natural convection since Thome *et al.* [32] have measured boiling site deactivation wall superheats in this mixture system to be of the order of 15 K. Of course, there is then no rise in the local saturation temperature of the liquid for this portion of the tube if no boiling occurs. This may explain why the Preusser data are between $h/h_l = 1.0$ and the data of the other researchers.

The solid line shown in Fig. 3 is a comparison of the Stephan–Preusser correlation to the data. Equation (9) was evaluated using mixture physical properties obtained from refs. [27, 33, 34]. To determine h_l, equation (9) was evaluated using linear interpolations between the physical properties of water and the azeotrope at their respective boiling points. While equation (9) of Stephan and Preusser predicts their own data reasonably well, it overpredicts by about 40% most of the other data. Also, the dashed line shown in Fig. 3 is the analytical expression of Thome [22], equation (11). It predicts the more volatile compositions at low $\tilde{x}$ quite well, but at higher $\tilde{x}$ it severely overpredicts the experimental values. This is probably a

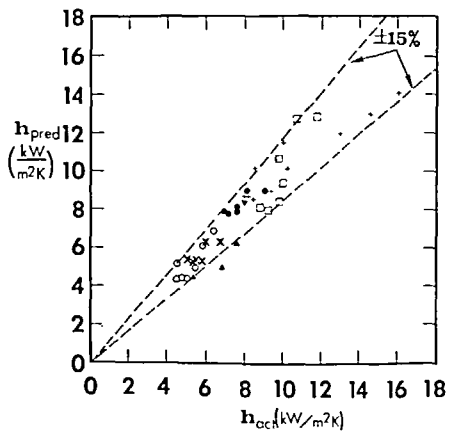

FIG. 4. Comparison of present theory to experiment for ethanol–water mixtures at 1.0 bar (symbols as in Fig. 3).

result of not only a non-linear variation in physical properties but also lower boiling site densities in this aqueous solution than predicted by the linear mixing law used in the analysis, as noted by Thome [32].

The new method presented here, equation (14), predicts the data in Fig. 3 (with the exclusion of the Preusser results) to within about ±15% as shown in Fig. 4 over a heat flux range from 94.6 to 300 kW m^{-2}. The peak nucleate heat flux ranges from about 400 kW m^{-2} for the azeotrope to about 1300 kW m^{-2} for pure water [25]. Thus, equation (14) performs well at heat fluxes much below the peak heat flux.

The most accurate of the other correlations is that of Stephan and Körner using their value of A given as 1.21. The comparison between their correlation, equation (1), and the data is shown in Fig. 5 to be quite good. It is seen, however, that the present method using only readily available phase equilibrium data is more accurate than a correlation with an empirical coefficient determined specifically for this mixture system.

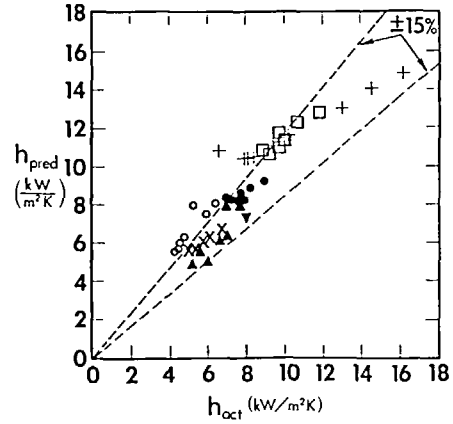

FIG. 5. Comparison of Stephan and Körner correlation [12] to experiment for ethanol–water mixtures at 1.0 bar (symbols as in Fig. 3).

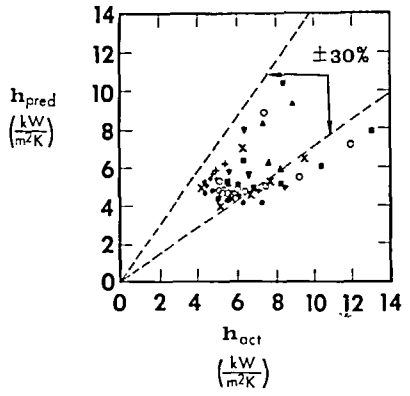

FIG. 6. Comparison of present theory to experiment for ethanol–water mixtures from 1.03 to 15 bar. Symbols: Tolubinskiy *et al.* [28] at 100 kW m^{-2} (● 1.03 bar, + 2.0, × 5.0, ○10.0, ■ 15.0); Afgan [23] at 200 kW m^{-2} (▲ 6.0 bar, ▼ 9.0).

Figure 6 depicts the heat transfer coefficient predicted using equation (14) to the actual experimental values for ethanol–water mixtures from 1.03 to 15.0 bar. The agreement is best for the Afgan [23] data. The Tolubinskiy *et al.* [28] data at 1.03 bar would lie midway between the Preusser results and the others in Fig. 3. The overall scatter is about ±30%.

Three sets of nucleate pool boiling data are available for acetone and water mixtures at 1.0 bar. Phase equilibrium data were obtained from ref. [31]. The ratio of h/h_I vs $\tilde{x}$ is shown in Fig. 7. Significant deviations among the three independent sets of data are again evident. The solid line is equation (14) evaluated using h_I values obtained from the Grigor'ev *et al.* [26] single component data. As shown in Fig. 8, equation (14) predicts the Grigor'ev data quite well. The Preusser [27] heat transfer coefficients are again higher than the

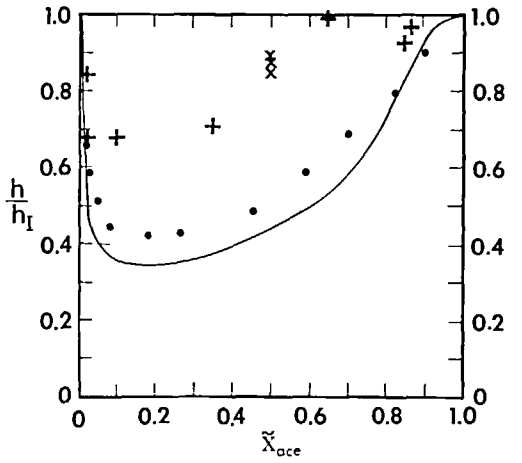

FIG. 7. Normalized boiling heat transfer coefficients for acetone–water mixtures at 1.0 bar. Symbols: ● Grigor'ev *et al.* [26] at 233 kW m^{-2}, × Bonilla and Perry [29] at 63, 158, and 315 kW m^{-2}, + Preusser [27] at 200 kW m^{-2}.

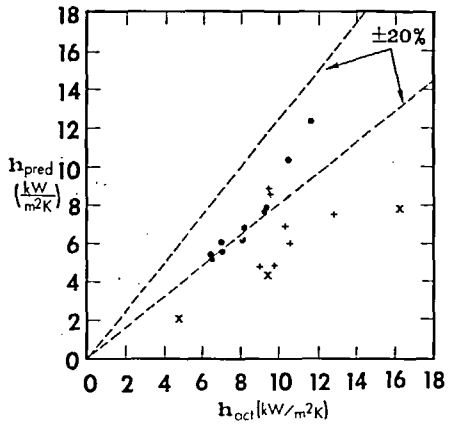

FIG. 8. Comparison of present theory to experiment for acetone–water mixtures at 1.0 bar (symbols as in Fig. 7).

Grigor'ev data to about the same relative extent as in Fig. 3.

Five published sets of experimental results for the organic binary mixture system of ethanol–benzene at 1.0 bar are compared to equation (14) in Fig. 9 using phase equilibria from [35]. There is good agreement from one data set to another and to their predicted values. This mixture system forms an azeotrope at $\tilde{x} = 0.44$. The peak nucleate heat flux is in the neighborhood of 400 kW m^{-2}.

Three cryogenic binary mixture systems have been studied experimentally. Figure 10 illustrates agreement to within about ± 15% for the Thome and Bald [8] data at 1.0 bar for liquid nitrogen–liquid argon mixtures. The peak nucleate heat flux is of the order of 200 kW m^{-2}. Hence, equation (14) is applicable to heat

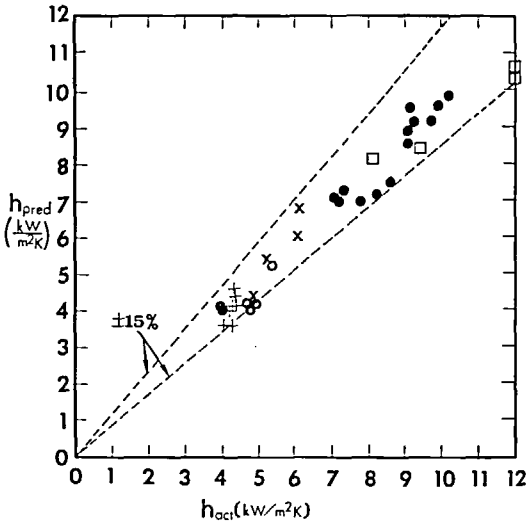

FIG. 9. Comparison of present theory to experiment for ethanol–benzene mixtures at 1.0 bar. Symbols: ● Grigor'ev *et al.* [25] at 232 kW m^{-2}, × Happel and Stephan [16] at 100 kW m^{-2}, ○ Tolubinskiy *et al.* [2] at 100 kW m^{-2}, + Tolubinskiy and Ostroviskiy [17] at 116 kW m^{-2}, □ Shakir [1] at 170 kW m^{-2}.

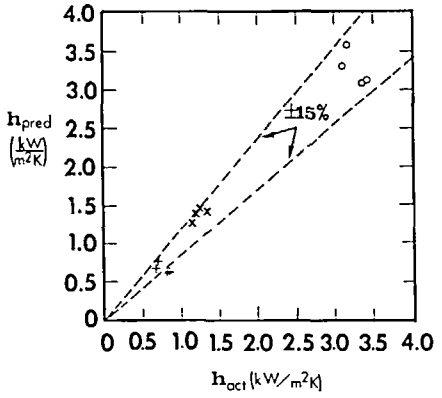

FIG. 10. Comparison of present theory to experiment for liquid nitrogen–liquid argon mixtures at 1.0 bar. Symbols: Thome and Bald [8] (+ 4.5 kW m^{-2}, × 10 kW m^{-2}, ○ 30 kW m^{-2}).

fluxes an order of magnitude below the peak nucleate heat flux. Phase equilibrium data were obtained from Thorpe [36].

The nucleate pool boiling data of Lyon [6] are tested against equation (14) in Fig. 11 for liquid nitrogen–liquid oxygen mixtures common to the air separation industry. Phase equilibrium data were drawn from Kirschbaum [31]. The agreement between theory and data is quite good even at heat fluxes far removed from the measured peak heat fluxes of about 150 kW m^{-2}. The actual heat transfer coefficient drops as much as 40% below h_l at the more volatile compositions.

Ackermann *et al.* [7] studied the boiling characteristics of liquid nitrogen–liquid methane mixtures, i.e. liquid natural gas (LNG) without the minor components present, up to reduced pressures of 0.6. The phase equilibrium diagrams at the various pressures were pieced together from a number of sources [37–41]. Figure 12 shows the comparison of the present theory to their experimental results at 5.0 bar. The decrease in the heat transfer coefficients in this mixture system are severe as noted by values of h being only one quarter of h_l at the more volatile compositions. Even so, the present theory shows that

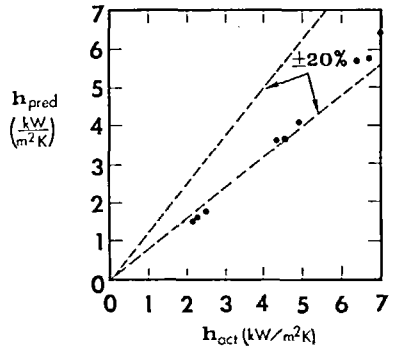

FIG. 11. Comparison of present theory to experiment for liquid nitrogen–liquid oxygen mixtures at 1.0 bar. Symbols: Lyon [6] at 10.7, 31.5, and 54.9 kW m^{-2}.

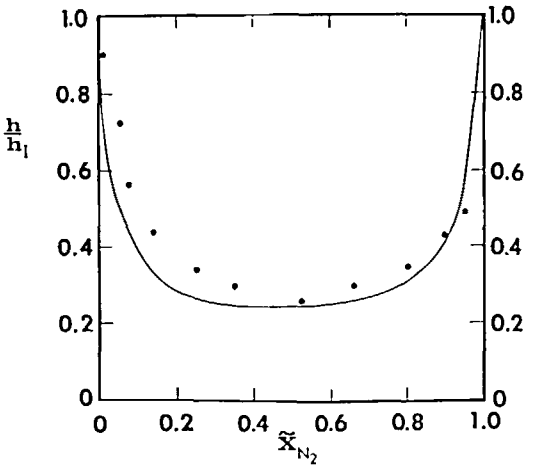

FIG. 12. Normalized boiling heat transfer coefficients of Ackermann *et al.* [7] for liquid nitrogen–liquid methane mixtures at 5.0 bar and heat flux of 210 kW m^{-2}. Solid line is present theory.

this large decrease is expected from thermodynamic considerations. Figure 13 depicts the comparison of h_{pred} to h_{act} over the whole pressure range. Agreement to within ±30% is found for 88% of the data points. Also, it predicts the heat transfer coefficients to within about ±20% for the range of composition of interest to the LNG industry. The measured peak heat fluxes for this mixture system ranged from about 250 kW m^{-2} for liquid nitrogen up to 600 kW m^{-2} for liquid methane.

4. DISCUSSION

Several additional points can be made about the present method for predicting boiling heat transfer coefficients in binary liquid mixtures.

First, equation (14) works well without taking into account non-linear variations in the pertinent physical properties. This is convenient because often a single component correlation which works well for one of the

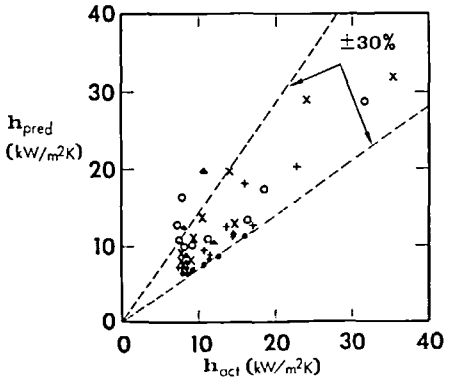

FIG. 13. Comparison of present theory to Ackermann *et al.* [7] data for liquid nitrogen–liquid methane mixtures at 210 kW m^{-2} from 2 to 28 bar. Symbols: ● (2 bar), + (5), × (16), ▲ (21), ○ (28).

single components, such as water, does not always work well for the other pure liquid, such as acetone. The Stephan and Preusser [13] results confirm this in that the coefficient of 0.100 in equation (9) best represents all of their data while a value of 0.0871 best represents the data for pure water alone. With the present formulation, different correlations can be used to calculate h_1 and h_2 in equation (15) which best suit the individual single components.

A second important consideration is that equation (14) is strictly only true at the peak heat flux. Yet, it has been demonstrated that it is still quite accurate for heat fluxes far below the peak heat flux (perhaps because microlayer evaporation may be the dominant heat transfer mechanism). This is important in the actual application of equation (14) since heat exchangers are designed to operate at heat fluxes safely below the peak heat flux. Further work is suggested to modify the method by including the heat flux dependency on the mixture correction factor such that very low heat fluxes can be accurately predicted.

The new method for predicting heat transfer coefficients in binary mixtures is easily extendable to multicomponent mixtures. ΔT_{bp} is then evaluated from the multicomponent phase equilibrium diagram again using the dew point and bubble point lines and matching the vapor composition to that of the liquid. Equation (2) is extended to be a summation over all the components present.

5. CONCLUSIONS

(1) A new method for predicting nucleate pool boiling heat transfer coefficients for binary liquid mixtures is presented based on the maximum rise in the local boiling point, ΔT_{bp}, allowed thermodynamically.

(2) Using only phase equilibrium data, the equation $(h/h_l) = \Delta T_l/(\Delta T_l + \Delta T_{bp})$ is shown to more accurately predict published binary mixture boiling heat transfer coefficients for the systems ethanol–water, acetone–water, ethanol–benzene, nitrogen–argon, nitrogen–oxygen, and nitrogen–methane than other methods. It seems to be quite universal in applicability with an accuracy of about $\pm 30\%$.

(3) The new method has been shown to be suitable for pressures ranging from atmospheric up to 28 bar and for single component boiling points within a binary mixture system which differed by up to 60 K (nitrogen–methane).

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APPENDIX

An additional correlation has been brought to the author's attention. Palen and Small ["A new way to design kettle and internal reboilers", *Hydrocarbon Processing* 43(11), 199–208 (1964)] give a correlating equation using the boiling range of the mixture, ΔT_{bp}, as

$$\frac{h}{h_I} = \exp(-0.027\Delta T_{bp}). \quad (1)$$

For ethanol-water mixtures at 1.0 bar, this correlation predicts the results in Fig. 3 (excluding Preusser's data) with about twice the error shown in Fig. 4.

PREVISION DU TRANSFERT THERMIQUE PAR EBULLITION D'UN MELANGE BINAIRE, A PARTIR DES DONNEES D'EQUILIBRE DE PHASE

Résumé—On présente une nouvelle méthode pour prédire la variation des coefficients de transfert thermique par ébullition nucléée en réservoir, en fonction de la composition des mélanges liquides binaires. On montre que l'élévation du point d'ébullition local ΔT_{bp}, adjacent à la surface chaude, causée par l'évaporation préférentielle du composant volatil a une limite au pic de flux thermique nucléé. ΔT_{bp} peut être déterminé par la connaissance du diagramme d'équilibre de phase à la pression considérée. L'équation résultante qui introduit ΔT_{bp} prédit avec précision les coefficients expérimentaux à des flux inferieurs au pic de flux thermique pour six systèmes de mélanges binaires: éthanol–eau, acétone–eau, éthanol–benzène, azote–argon, azote–oxygène et azote–méthane.

BERECHNUNG VON WÄRMEÜBERGANGSKOEFFIZIENTEN BEIM SIEDEN BINÄRER GEMISCHE UNTER ALLEINIGER VERWENDUNG VON PHASENGLEICHGEWICHTSDATEN

Zusammenfassung—Es wird eine neue Methode zur Vorausberechnung der Abhängigkeit des Wärmeübergangskoeffizienten beim Behältersieden von der Zusammensetzung binärer Flüssigkeitsgemische vorgestellt. Es wird gezeigt, daß die Erhöhung des lokalen Siedepunktes der Flüssigkeit, ΔT_{bp}, an der beheizten Oberfläche, verursacht durch überwiegende Verdampfung der leichtersiedenden Komponente, bei der maximalen Wärmestromdichte der Blasenverdampfung eine obere Grenze erreicht. ΔT_{bp} kann bei dem interessierenden Druck allein aus der Kenntnis des Phasengleichgewichtsdiagramms bestimmt werden. Die resultierende Gleichung, welche ΔT_{bp} enthält, gibt veröffentlichte, experimentell ermittelte Wärmeübergangskoeffizienten beim Sieden mit Wärmestromdichten, die genügend weit unterhalb der maximalen Wärmestromdichte liegen, von sechs binären Flüssigkeitssystemen sehr gut wieder. Die untersuchten Systeme sind: Äthanol–Wasser, Azeton–Wasser, Äthanol–Benzol, Stickstoff–Argon, Stickstoff–Sauerstoff und Stickstoff–Methan.

РАСЧЕТ КОЭФФИЦИЕНТОВ ТЕПЛОПЕРЕНОСА ПРИ КИПЕНИИ БИНАРНЫХ СМЕСЕЙ, ИСХОДЯ ТОЛЬКО ИЗ ДАННЫХ О РАВНОВЕСИИ ФАЗ

Аннотация—Предложен новый метод расчета изменения коэффициентов теплопереноса при пузырьковом кипении в большом объеме при изменении состава бинарных смесей жидкостей. Показано, что при пузырьковом кипении увеличение температуры локального кипения жидкости, ΔT_{bp}, вблизи нагреваемой поверхности из-за преобладающего испарения летучего компонента при максимальной плотности теплового потока происходит только до определенного предела. Величину ΔT_{bp} можно определить, используя только диаграмму фазового равновесия смеси при заданном давлении. Получено уравнение, учитывающее ΔT_{bp}, позволяющее рассчитывать коэффициенты теплопереноса при кипении, которые хорошо согласуются с известными экспериментальными данными, когда значения плотности теплового потока намного ниже значений максимальной тепловой нагрузки для шести рассмотренных систем бинарных жидких смесей: этанол – вода, ацетон – вода, этанол – бензол, азот – аргон, азот – кислород и азот – метан.