Pergamon

Int. J. Heat Mass Transfer. Vol. 40, No. 4, pp. 765–772, 1997

0017-9310/97 $17.00+0.00

PII: S0017-9310(96)00178-0

Augmentation of steam condensation heat transfer by addition of ammonia

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(*Received* 22 *February* 1996 *and in final form* 21 *May* 1996)

Abstract—In all previous publications concerning the condensation of binary mixtures of vapours, the condensation rates are reported to be less than for pure mixtures. It is reported in this paper that for the condensation of weak binary vapours on a horizontal tube, where the vapour concentration of ammonia in steam is in the range 0.23–0.88 wt%, condensation heat transfer is enhanced by as much as 13%. This enhancement is due to the Marangoni effect which causes a 40% increase in heat transfer through the condensate film. This effect is moderated, however, by the increasing heat transfer resistance of the vapour film. The mechanism by which the heat transfer process is enhanced is an inherent feature of these weak binary mixtures and occurs over the entire condensing surface without promotion. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION—A REVIEW OF BINARY CONDENSATION

There has been considerable research on the condensation of multi-component vapours. The most recent motivation for this has been the development of new thermodynamic cycles such as the Kalina cycles which employ ammonia–water mixtures as working fluids. The following section provides a brief overview of research on the condensation of binary vapours and concludes with more recently published work on Marangoni films in binary vapour condensation. This information is then used to interpret the experimental results presented in this paper.

It has been widely reported that vapour mixtures generally condense at a slower rate than pure mixtures. This lower heat transfer is generally attributed to there being a mass diffusion layer between the bulk vapour and the surface of the condensate film. This vapour film, shown in Fig. 1, creates an additional resistance to the condensation process.

The first rigorous theoretical analysis of the problem of condensing vapours of mixed, miscible liquids was presented by Colburn and Drew [1]. They assumed that the concentrations in the liquid and vapour phases at the condensate–vapour interface could be approximated by static equilibrium. Using this assumption, they equated the mass diffusion through the vapour film to the heat transfer through the liquid film, and the latent heat of condensation. This analysis proved to accurately describe several aspects of mixed vapour condensation.

The existence of the vapour diffusion layer was shown in this analysis to result in the condensation heat transfer for a binary mixture always being less than that for a pure mixture. They also observed that the fraction of the volatile component in the condensate was generally lower than in the vapour. This difference is indicated in Fig. 1, and is a function of the phase equilibrium behaviour and the interfacial temperature. At high cooling rates, however, the interfacial temperature approached the bubble point temperature for the bulk vapour. Under such conditions, the equilibrium concentration of the condensate therefore approached that of the bulk vapour, resulting in 'local total condensation'. Van Es and Heertjes [2] reported an experimental investigation into the condensation of methanol–water mixtures which confirmed these findings.

A later study by Sparrow and Marschall [3], based on a boundary-layer analysis of methanol–water vapour condensation, again demonstrated that the condensation heat transfer for the binary mixture was always less than that of a pure vapour. The ratio between the two was observed to approach unity only as the vapour concentration approached zero or unity, and where the vapour to cooling surface temperature difference was very large. The minima for the methanol–water system occurred at a mass concentration of 45% with a temperature difference of 10°C where the ratio was 0.1. Marschall and Hall [4] conducted experiments to verify this analysis, but although they found the theory to be generally consistent with their results, some variation was observed at low heat transfer rates. They attributed this discrepancy to difficulties in taking accurate measurements at these conditions.

The effect of vapour velocity was investigated by Denny and South [5] who also used a boundary-layer analysis to model the condensation at the forward stagnation point of a cooled cylinder in a down-flowing vapour. Their results were consistent with the general findings of Sparrow and Marschall [3], but in addition showed that the effect of higher vapour vel-

NOMENCLATURE

A	area
D	diameter
g	gravitational acceleration
h	heat transfer coefficient
$h_{l,Nu}$	heat transfer coefficient of the condensate film using equation (7)
h_{lv}	latent heat of condensation
h_{Nu}	heat transfer coefficient according to Nusselt's theory [equation (5)]
k_l	thermal conductivity
m	mass flow
q	heat flux
$q_{l,Nu}$	heat flux calculated by equation (8)
P	pressure
Q	total heat transfer
R	thermal resistance
Re	Reynold's number ($\rho U_\infty D/\mu$)
T	temperature
U	velocity
x	mass concentration [%].

Greek symbols

σ	surface tension
δ	film thickness
μ	viscosity
ρ	density.

Subscripts

BP	bubble point
i	interface
l	condensate film
o	external
tc	thermocouple
v	vapour
w	tube surface
∞	bulk condition.

ocities and thermal driving forces in the vapour film was to improve mass transfer in the vapour film and therefore lower the vapour film resistance to condensation. This result was further confirmed by the experimental work of Hijikata *et al.* [6] who studied the condensation of a horizontally flowing R113–R114 vapour on a short vertical tube. At low vapour Reynold's numbers ($Re_v = 1300$) and with a mole fraction of 10% R114 in R113, the reduction in heat transfer was approximately 50%. However, at Reynold's numbers of 8900, the heat transfer slightly exceeded the prediction for condensation of a pure, stagnant vapour. This can be compared with their results for the condensation of pure R113 where the enhancement of a similar magnitude was achieved at $Re_v = 3500$.

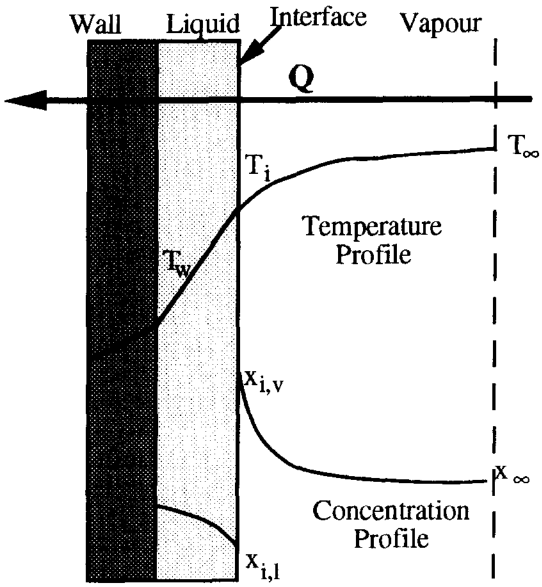

Fig. 1. General features of the binary vapour condensation process.

The general conclusion of the studies described above is that binary vapour mixture condensation characteristically occurs at a lower heat transfer rate than pure vapour condensation. Although this effect can be ameliorated by high thermal driving forces, vapour velocities and finned tubes [6], the reduction nevertheless appears unavoidable. This conclusion must, however, be limited to studies where the condensate film is smooth and laminar. While such a condition readily facilitates modelling of the binary condensation problem, it ignores the potential of binary vapours to have different condensation behaviours not possible with pure vapours.

The condensation of binary vapours may also be influenced significantly by the Marangoni effect. This effect describes the influence of surface tension gradients, which may occur in liquid mixtures where there are local perturbations in concentration and temperature. In particular, the Marangoni effect manifests itself when a process reinforces these local perturbations so that they become significant.

The Marangoni effect has been observed in several heat and mass transfer processes such as distillation and condensation. Zuiderweg and Harmens [7] reported the effect of surface phenomena on distillation columns where the destabilisation and breakup of liquid films into rivulets was linked to the direction of mass transfer and the magnitude of the surface tension gradient developing in the reflux. However, Bainbridge and Sawistowski [8] later concluded that the destabilisation of liquid films was due to local perturbations in surface tension within the film. Subsequent to this finding, a general criteria for the Marangoni effect was developed by Ford and Missen [9]. Their work evolved from earlier studies on the condensation of binary mechanisms where non-filmwise condensation was reported. In particular, Mirkovich and Missen [10, 11] had observed the condensate films for pentane–methanol and pentane–methylene dichloride to be irregular, streaked and even dropwise.

Ford and Missen [9] demonstrated that the criteria for film instability could be expressed simply by the inequality given in equation (1). This expression states that if local surface tension tends to increase with an increase in film thickness, then the film will be unstable. This conclusion is self-evident when considering that if a local region of relatively thick liquid film has a relatively high surface tension it will tend to draw liquid from adjacent thin film regions with lower surface tension. Furthermore, it is worth considering equation (2) which describes the dependence of surface tension on film thickness as a function of temperature

$$\frac{\partial \sigma}{\partial \delta} > 0 \tag{1}$$

$$\frac{\partial \sigma}{\partial \delta} = \left(\frac{\partial \sigma}{\partial T}\right)_{\mathrm{sat}} \cdot \frac{\partial T}{\partial \delta}. \tag{2}$$

For condensation, the derivative $\partial T/\partial \delta$ is always positive. Therefore, the stability of the condensate film depends on the thermodynamic properties of the mixture. If the more volatile component has the lower surface tension, then the condensate film will tend to be unstable.

A recent theoretical study by Hijikata *et al.* on the 'pseudo-dropwise' condensation of a binary vapour mixture on a flat condensing surface [12] has indicated that the growth of instabilities in the condensate film is dependant on the wavelength of the instability and a modified Marangoni number which describes the dimensionless surface tension gradient in the film. They concluded that a perturbation will only grow if the wavelength and Marangoni number are sufficiently high.

Finally, to quantify the effect of non-filmwise condensation on the heat transfer resistance of the condensate film, Goto and Fujii [13] investigated the condensation of R114–R113 vapour mixtures on a horizontal tube. They observed 'ring-wise' and 'turbulent ring-wise' condensate films. While the overall heat transfer was found to be less than for a pure mixture, the tests where non-filmwise condensation occurred nonetheless exhibited a 50% higher than predicted heat transfer. This was equated to an effective 40% increase in the condensate film heat transfer coefficient. Mirkovich and Missen [11] made similar observations regarding dropwise condensation on a vertical surface. They compared the actual heat transfer with a liquid film heat transfer coefficient calculated using equation (3), where the interface temperature was evaluated as the bubble point temperature of the condensate. They found the condensate film heat transfer coefficient to be twice that for a smooth film. This contrasts with pure vapour droplet condensation where heat transfer is enhanced by a factor of 10. This discrepancy between true droplet condensation and pseudo-droplet condensation was attributed to the different mechanisms involved in the two processes.

$$h_{\mathrm{l}} = \frac{Q}{A(T_{\mathrm{i}} - T_{\mathrm{w}})} \tag{3}$$

To summarise, binary vapour condensation generally occurs at a slower rate than pure vapour condensation. This is due to a vapour diffusion layer which creates an additional resistance to heat transfer. However, it is possible for the condensation heat transfer of certain binary mixtures to be enhanced by instabilities in the liquid film. These instabilities are a manifestation of the Marangoni effect, caused by surface tension gradients within the condensate film, and are inherent in the process. However, none of the papers reviewed here have shown the enhancement of heat transfer by this effect to be of a similar order to the reduction due to the additional vapour resistance.

2. THE CONDENSATION OF AMMONIA–WATER VAPOURS—EXPERIMENTAL METHOD

The research presented here concerns the external condensation of down-flowing ammonia–water vapours on a 145 mm long cooled horizontal tube of 25 mm external diameter. The tube, which could be rotated through 360°, was fabricated from 316 stainless steel with a 1 mm sheathed K-type thermocouple probe embedded in its surface. The overall heat transfer was measured from a heat balance on the cooling water which employed a 32-point K-type differential thermopile device integrated into a spiral insert inside the tube. The spiral insert ensured thorough mixing of the temperature controlled cooling water and also a high internal heat transfer coefficient. The arrangement of this apparatus is shown in Fig. 2. It should be noted that all thermocouple devices used in the instrumentation were calibrated in a New Zealand Standard approved facility. A further feature of the equipment was sight glasses in the wall of the test section for viewing the condensing tube surface. Hence, it was possible to observe and photograph the mode of condensation. The vapour was generated with an in-tube vaporiser. This made it possible to generate vapours at near-atmospheric conditions with very low concentrations of ammonia.

The tube surface temperature was determined by rotating the tube through 360° and measuring the embedded thermocouple temperature at intervals of 30°. The tube surface temperature was then calculated by using the overall heat transfer and the thermal

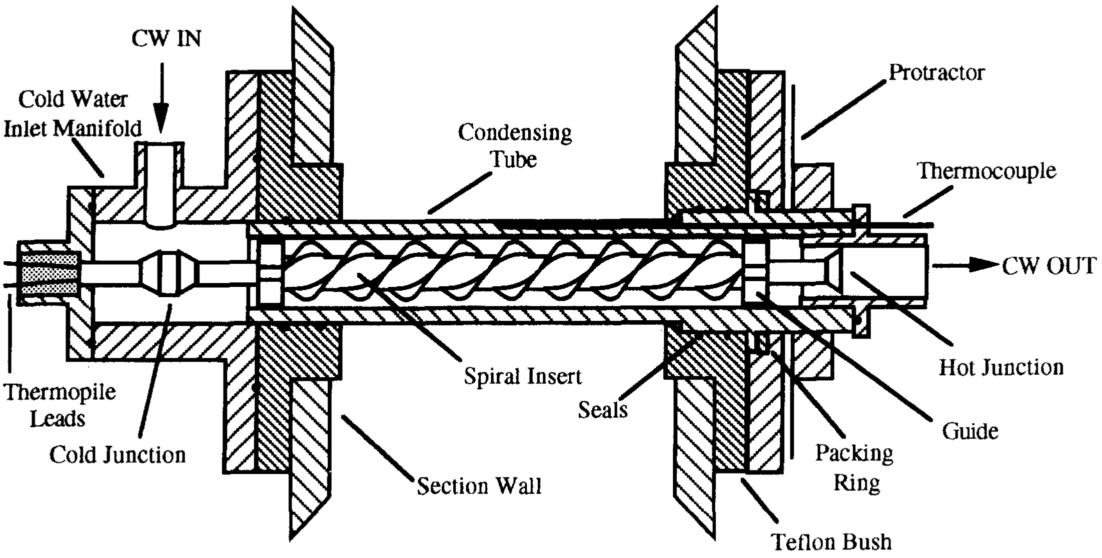

Fig. 2. The condensing tube assembly.

resistance between the thermocouple and the tube surface (equation (4)). The thermal resistance was estimated from the dimensions of the thermocouple probe and the materials of its construction. The accuracy of this method was verified by the excellent agreement of experimental results for steam condensation with theory as described later in this section. The average surface temperature was then used to calculate the condensing heat transfer coefficient as shown in equation (5).

$$\bar{T}_{w,o} = \bar{T}_{tc} + \frac{Q}{R} \tag{4}$$

$$h_{w,o} = \frac{Q}{A_{w,o}(T_{v,\infty} - \bar{T}_{w,o})}. \tag{5}$$

To provide a comparison with the experiments, two simple theoretical models were employed. In the first case, a theoretical condensation heat transfer coefficient was calculated from Nusselt's theory of condensation (equation (6)).

$$h_{Nu} = 0.728\left[\frac{k_l^3 \cdot g \cdot \rho_l \cdot (\rho_l - \rho_v) h'_{lv}}{\mu_l \cdot (T_v - \bar{T}_{w,o}) D_o}\right]^{0.25} \tag{6}$$

This calculation was based on steam condensing on the tube, with the vapour at the same saturation temperature as that of the binary vapour, and a uniform wall temperature equal to that measured in the experiments.

Furthermore, a second calculation scheme was developed which isolated the thermal resistances of the vapour and condensate films. In the case where total local condensation occurred, the mass flow rate of condensate was calculated using equation (7). The condensate–vapour interface temperature was assumed to be at the bubble point temperature for the vapour and the film properties were evaluated accordingly at an average film temperature. Then the condensate film heat transfer resistance was estimated using equation (8), derived from Nusselt's theory. This calculation scheme assumed a smooth, laminar condensate film. Finally, the total heat flux was calculated using equation (9). This calculation represented the heat transfer which could be expected to occur in the absence of a vapour film where the condensate film is smooth and laminar.

$$\dot{m}_l = \frac{Q}{h_{lv} \cdot 2 \cdot L} \tag{7}$$

$$h_{l,Nu} = 0.762 \cdot k_l \cdot \left[\frac{\rho_l \cdot (\rho_l - \rho_v) \cdot g}{\mu_l \cdot \dot{m}_l}\right]^{1/3} \tag{8}$$

$$q_{l,Nu} = h_{l,Nu} \cdot (T_{BP} - \bar{T}_{w,o}). \tag{9}$$

The estimates represented by h_{Nu} and $q_{l,Nu}$ are used in the following section for comparison with the experimental values.

Before applying the method described above, it was important to verify that LTC conditions were satisfied. To do this, the bubble point temperatures for the vapour were compared with the measured tube surface temperature. For the ammonia–water tests where the surface temperature was found to be considerably less than the bubble point temperature, it was reasonable to assume that 'local total condensation' occurred.

3. RESULTS AND DISCUSSION

Table 1 contains the results from fifteen condensation tests: seven were conducted with pure steam and the remaining eight were conducted with binary ammonia–water vapours having low concentrations of ammonia. The table also lists the ratio of the measured heat transfer coefficient to the value for pure steam calculated using equation (6). Figure 3 demonstrates the ammonia–water test results graphically.

Table 1. The test conditions and results for the ammonia–water vapour condensation

Test	x_v [wt%]	Re_v	P_v [kPa]	$T_{v,\infty}$ [°C]	$T_{w,o}$ [°C]	ΔT_v [°C]	Film type	q [W m^{-2}]	$h_{w,o}$ [W m^{-2} K^{-1}]	h/h_{Nu}	Estimated error [%]
1S	0.00	588	100.2	99.7	82.3	17.4	S	184839	10629	0.98	5
2S	0.00	577	100.6	99.8	79.6	20.2	S	205562	10161	0.97	5
3S	0.00	588	101.3	100.0	86.3	13.7	S	154282	11270	0.97	5
4S	0.00	471	100.6	99.8	91.1	8.7	S	110025	12690	0.97	6
5S	0.00	455	146.5	110.7	97.1	13.6	S	162009	11930	1.00	5
6S	0.00	455	146.7	110.7	93.8	16.9	S	186069	10991	0.97	5
7S	0.00	4.08	69.1	89.6	73.6	16.1	S	172634	10736	1.01	5
1A	0.10	553	43.0	77.6	63.1	14.5	S	132164	9123	0.86	6
2A	0.23	537	64.5	87.9	72.7	15.2	SR	171317	11289	1.04	5
3A	0.39	537	63.9	87.6	73.0	14.6	RB	173252	11881	1.09	5
4A	0.52	535	67.6	89.0	74.0	15.0	RB	175228	11692	1.07	5
5A	0.71	536	66.6	88.6	73.7	14.9	R	184191	12365	1.13	5
6A	0.88	535	66.9	88.7	73.9	14.8	R	178608	12053	1.10	5
7A	2.05	535	67.2	88.7	70.4	18.3	R	168645	9197	0.89	5
8A	2.20	181	109.0	101.9	86.9	15.0	B	127617	8519	0.75	6

Film types: S = smooth, B = banded, R = rippled.

Furthermore, the nature of the condensate film is listed and this is discussed in detail later. It should be noted that the binary ammonia–water tests were all conducted under conditions of local total condensation.

The values of the pure steam tests are in good agreement (error < 3%) with the theoretical values calculated using equation (6). Tests 1S–6S were conducted prior to the ammonia–water tests, while 7S was conducted once the ammonia–water tests had been completed. This suggests that the accuracy of the experimental values was well within the estimated 5–6% error based on the precision of the heat balance and temperature measurements.

The results for the binary ammonia–water vapours show that the condensation heat transfer was initially less than the Nusselt prediction at the lowest concentration (0.1%), but exceeded the Nusselt prediction by as much as 13% over the range 0.23–0.88 wt% before decreasing again. For concentrations over 2 wt%, it was observed that the condensation heat transfer coefficient continued to decrease significantly, and, at a concentration of 27.0 wt%, was only 12% of the value estimated for pure steam condensation

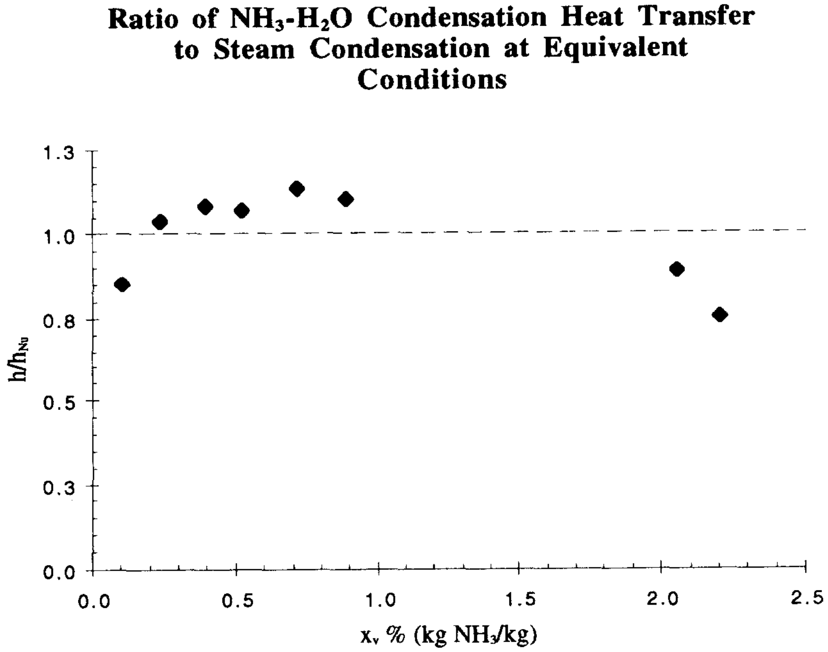

Fig. 3. The ratio of measured condensation heat transfer coefficient to the equivalent coefficient for pure steam condensation vs wt% ammonia concentration in the vapour.

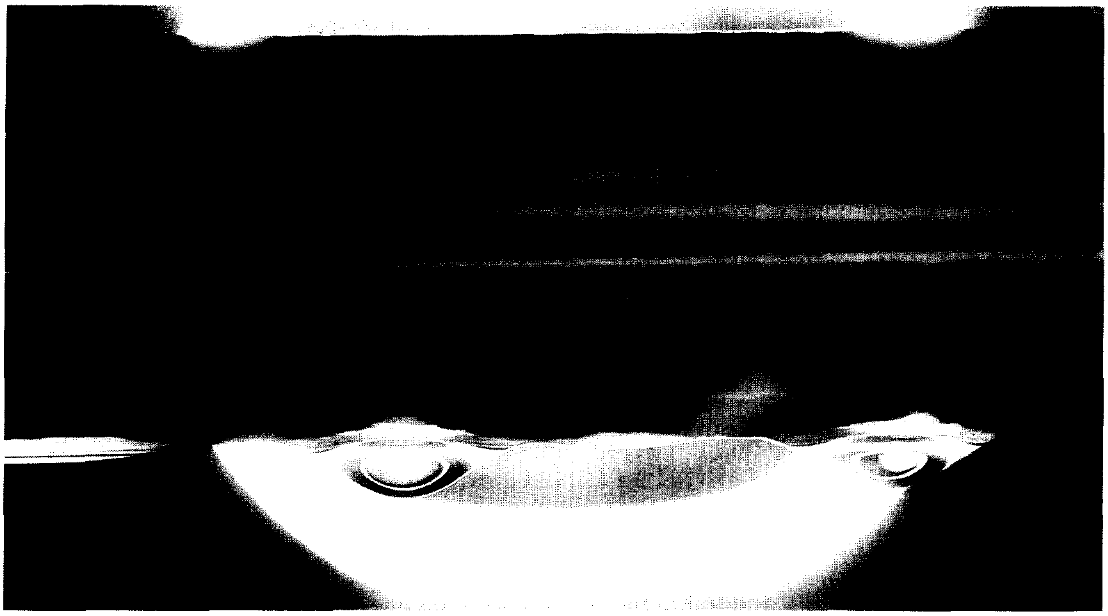

Fig. 4. 'Rippling' condensation of binary NH_3–H_2O vapour on a 25 mm tube.

under the same conditions. This value is of the order expected from the findings of earlier studies of binary vapour condensation.

The characteristics of the condensate film in the region 0.23–0.88 wt% are described in Table 1. For the test at 0.1 wt%, the film was observed to be smooth. The film surface for the test at 0.23 wt% was also mostly smooth, but was disturbed by intermittent, random ripples occurring on it. The condensate films in the tests from 0.39 to 2.05 wt% (Fig. 4) displayed considerably more vigorous disturbances. These ripples, unlike conventional turbulence, were initiated at the top of the tube where ridges were observed to rise before 'falling' down the film. This phenomenon is consistent with the observations made by Ford and McAleer [14] who observed Marangoni film disturbances on a vertical surface where perturbations in a smooth film formed waves which then contracted to form ridges and finally droplets.

Figure 4 is a photograph of this 'rippling' condensation mode. Small ridges are apparent at the top of the tube. These ridges were generally stationary for the 0.39–0.52 wt% tests, so that the film appeared 'banded'. It is remarkable that they can be observed at all given the very small average film thickness which would normally occur at this point. The photograph also shows the approximately horizontal ripples moving down the tube surface. The tests in the 0.71–2.05 wt% region displayed similar behaviour, but the position of the disturbances along the tube was unstable and thus the rippling behaviour was generally uniform. The condensate film of the last test, at 2.2 wt%, had very stable bands, but no noticeable ripples.

It is likely that the increased heat transfer for the tests is due to the non-laminar behaviour of the condensate film which probably promotes both heat and mass transfer through the film. However, in order to understand the exact nature of the problem, it is necessary to compare the overall heat transfer with a value predicted for the condensate film assuming that it is smooth, laminar and has no vapour film. This comparison is made in Fig. 5 using the experimental values and the results from equation (9). It should be noted that the tube surface temperature was over 10°C below the bubble point temperature for the vapour for all these tests, confirming the validity of the analysis.

The results in Fig. 5 graphically demonstrate the increased heat transfer due to the disturbances in the condensate film. This increase is shown to be of the order 32%, which is consistent with the findings of Hijikata *et al.* [6]. The results given in both Figs. 3 and 5 can be combined to show that the vapour film resistance increases rapidly in the region 0–2.2 wt%. The overall increase in heat transfer in the 0.23–0.88% region is then due only to the nature of the condensate film, and is in fact moderated by the increasing vapour film resistance.

Proof of the Marangoni effect being responsible for the non-laminar film behaviour requires further consideration of the criteria given in equations (1) and (2). In as far as ammonia has a significantly lower surface tension and greater volatility than water, it is most likely that the necessary surface tension gradients did exist for this effect to occur during ammonia–water mixture condensation. However, exact proof requires experimental data on the surface tension of low-concentration ammonia–water solutions. This data is not available and cannot be reliably generated from interpolation of the pure component data given the polar nature of both components. Given the absence of mathematical proof for the Marangoni effect, it is important to refute the possibility of surface

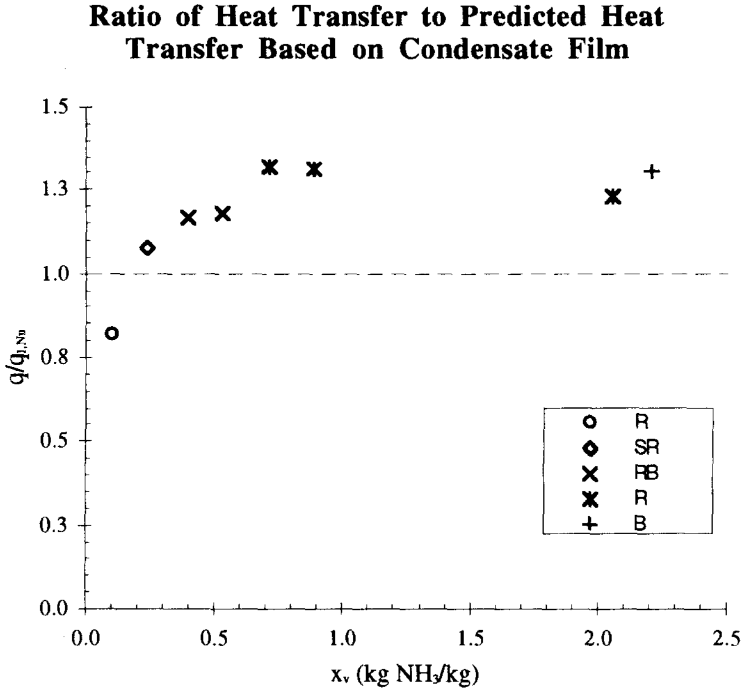

Fig. 5. Film characteristics and relative heat transfer enhancement.

contamination being responsible for the non-laminar condensate film behaviour. In the first instance, the tube surface was observed to be completely wettable when the rig was not being operated. Secondly, the condensate film behaviour was smooth and laminar for the steam tests and the 0.1 wt% ammonia test. If any surface contamination was responsible for the non-laminar condensate film behaviour, it would have manifested during all the tests. Consequently, it is reasonable to assume that the most likely cause for the behaviour was the existence of surface tension gradients at the vapour–liquid interface: the Marangoni effect.

4. CONCLUSIONS

The results presented in this paper show that for the condensation of binary ammonia–water vapours at low concentrations, surface tension effects generate significant disturbances in the film. These disturbances cause the heat transfer coefficient of the condensate film to increase by as much as 32%. This heat transfer enhancement is inherent in the process itself and occurs over the entire condensation surface without promotion. The results also show that with further increase of the ammonia concentration in the vapour, the vapour film resistance to condensation becomes more dominant. In previous literature concerning binary vapour condensation, the vapour film resistance has been reported to dominate the process such that the condensation heat transfer is always less than for pure vapours. However, for ammonia–water vapours of 0.23–0.88 wt% ammonia, the overall effect on condensation heat transfer is a positive enhancement of the order 13%.

Acknowledgements—The authors would like to acknowledge Chris Philpott and Stefan Fiedler who assisted in the operation of the experimental equipment.

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