

PERGAMON

International Journal of Heat and Mass Transfer 41 (1998) 3679-3683

Technical Note Augmentation of steam condensation heat transfer by addition of methylamine

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(Received 15 April 1997; in final form 20 October 1997)

Nomenclature

A area

- D diameter
- g gravitational acceleration
- *h* heat transfer coefficient
- $h_{\rm lv}$ latent heat of condensation
- h_{Nu} heat transfer coefficient according to Nusselt's the-
- ory
- k_1 thermal conductivity
- q heat flux
- P pressure
- Q total heat transfer
- *R* thermal resistance
- *Re* Reynold's number $(\rho U' \Delta D / \mu)$
- T temperature
- x mass concentration (%).

Greek symbols

- δ film thickness
- μ viscosity
- ρ density
- σ surface tension.

Subscripts

- 1 condensate film
- o external
- tc thermocouple
- v vapour
- w tube surface
- ∞ bulk condition.

1. Introduction

The general conclusion of previous binary condensation studies has been that binary vapour mixture condensation characteristically occurs at a lower heat transfer rate than pure vapour condensation. This lower heat transfer rate is generally attributed to there being a mass diffusion layer between the bulk vapour and the surface of the condensate film. This vapour film creates an additional resistance to the condensation process. Although this effect can be ameliorate by high thermal gradients, vapour velocities and finned tubes [1], the reduction was, until recently, largely accepted as unavoidable.

International Journal of HEAT and MASS TRANSFER

It is notable, however, that this conclusion was reinforced by numerical studies where the condensate film was assumed to be smooth and laminar. While such a condition readily facilitates modelling of the binary condensation problem, it ignores the potential of binary vapours to exhibit different condensation behaviours not possible with pure vapours. In particular, condensation of binary vapours may be influenced significantly by the Marangoni effect. This effect describes the influence of surface tension gradient, which may occur in liquid mixtures where there are local perturbations in concentration and temperature and where the 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 [2–5]. However, it was Ford and Missen [6] who 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

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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

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

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

For condensation, the derivative $\delta T/\partial \delta$ 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.

Recent research has identified the Marangoni effect manifested in non-smooth condensation behaviour from 'pseudo droplet' [5, 7] to 'ring-wise' [8] condensation. Also the disturbance of the condensate film has been shown to measurably reduce the condensate film heat transfer resistance, although this effect has been outweighed by the increased resistance of the diffusion layer. It was in this context that Morrison and Deans [10] published research showing that at very low concentrations of ammonia, steam condensation heat transfer was actually enhanced by up to 13% as the Marangoni effect caused rippling of the condensate film while the diffusion layer resistance remained low. In this note, the authors report the results of similar work concerning water-methylamine mixtures and compare the findings with those for ammonia-water mixtures.

2. Experimental method

The research presented here concerns the external condensation of down-flowing methylamine-water vapours on a 145 mm long cooled horizontal tube of 25 mm external diameter (Fig. 1). 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 vapour was generated with an in-tube vaporiser consisting of 6 parallel 6 m stainless steel tubes immersed in hot oil baths. This made it possible to generate vapours at near atmospheric conditions with very low concentrations of the more volatile component. The concentration of the vapour was implied from that of liquid sampled at the inlet of the in-tube vaporiser. This liquid was titrated with standardised hydrochloric acid. Further details of the experimental apparatus and procedures may be obtained from the earlier paper by Morrison and Deans [10], and the Ph.D. thesis, 'The condensation of ammonia-water vapours on a horizontal tube', by Morrison [11].

The tube surface temperature was determined by rotating the tube through 360° and measuring the embedded thermocouple temperature at intervals of 30°. Each recorded experiment was therefore an amalgamation of 12–18 point measurements. Additional parameters such as vapour temperature were recorded repeatedly



Fig. 1. Test section showing condensing tube and spiral insert with thermopile.

throughout the experiment. By fitting a continuous function to the measured points, an average embedded thermocouple temperature could be calculated. The tube surface temperature was then calculated by using the overall heat transfer and the thermal resistance between the thermocouple and the tube surface [equation (3)]. 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 Nusselt's theory [9]. The average surface temperature was then used to calculate the condensing heat transfer coefficient as shown in equation (4). The difference between the bulk vapour temperature and the surface temperature in this equation represents the average thermal gradient in the process.

$$\bar{T}_{\rm w,o} = \bar{T}_{\rm tc} + \frac{Q}{R} \tag{3}$$

$$h_{\rm w,o} = \frac{Q}{A_{\rm w,o}(T_{\rm v,\infty} - \bar{T}_{\rm w,o})}.$$
 (4)

To provide a comparison with the experiments a theoretical condensation heat transfer coefficient was calculated from Nusselt's theory of condensation [equation (5)].

$$h_{Nu} = 0.728 \left(\frac{k_1^3 \cdot g \cdot \rho_1 \cdot (\rho_1 - \rho_v) \cdot h'_{1v}}{\mu_1 \cdot (T_v - \bar{T}_{w,o}) \cdot D_o} \right)^{0.25}.$$
 (5)

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 the average wall temperature measured in the experiments.

3. Results

Table 1 contains the results from 25 condensation tests. To provide background to the current research, seven tests conducted with pure steam and eight with binary

Test conditions and results for steam, ammonia-water and methylamine-water condensation

Test	x _v [wt%]	<i>Re</i> _v	P _v [kPa]	T_{v} [°C]	$T_{\rm w,o}$ [°C]	$\Delta T_{\rm v}$ [K]	Film type	q [W m ⁻²]	$h_{ m w,o}$ [W m ⁻² K	h/h_{Nu}	Error [%]
1 S	0.00	588	100.2	99.7	82.3	17.4	S	184 839	10 629	0.98	5
2S	0.00	577	100.6	99.8	79.6	20.2	S	205 562	10161	0.97	5
3S	0.00	588	101.3	100.0	86.3	13.7	S	154282	11 270	0.97	5
4S	0.00	471	100.6	99.8	91.1	8.7	S	110025	12 690	0.97	6
5S	0.00	455	146.5	110.7	97.1	13.6	S	162 009	11930	1.00	5
6S	0.00	455	146.7	110.7	93.8	16.9	S	186 069	10 991	0.97	5
7 S	0.00	408	69.1	89.6	73.6	16.1	S	172 634	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	171 317	11 289	1.04	5
3A	0.39	537	63.9	87.6	73.0	14.6	RB	173 252	11881	1.09	5
4A	0.52	535	67.6	89.0	74.0	15.0	RB	175 228	11 692	1.07	5
5A	0.71	536	66.6	88.6	73.7	14.9	R	184 191	12 365	1.13	5
6A	0.88	535	66.9	88.7	73.9	14.8	R	178 608	12 053	1.10	5
7A	2.05	535	67.2	88.7	70.4	18.3	R	168 645	9197	0.89	5
8A	2.20	181	109.0	101.9	86.9	15.0	В	127617	8519	0.75	6
1 M	0.00	498	69.1	89.6	73.6	16.1	S	172634	10736	1.006	5
2M	0.03	502	68.2	89.3	81.4	7.9	SR	126 622	15989	1.243	5
3M	0.03	490	68.0	89.2	79.1	10.1	BR	192215	19014	1.575	5
4M	0.20	497	61.7	86.7	83.8	6.4	PD	198713	31 172	2.310	6
5M	0.22	494	68.3	89.3	80.3	5.6	RB/PD	136 193	24 4 34	1.734	5
6M	0.22	496	68.0	89.2	81.5	7.8	PD/RB	203 104	26216	2.018	5
7M	1.04	482	68.5	89.4	83.2	6.2	PD	133 822	21 631	1.582	5
8M	1.04	472	72.0	81.5	81.5	9.2	PD	201 962	21 986	1.776	5
9M	2.31	500	66.6	88.7	77.7	11.0	PD	190 020	17 273	1.474	6
10M	4.29	502	66.7	88.7	73.0	15.7	PD	173775	11 051	1.036	5

Test: S = steam, A = ammonia, M = methylamine.

Film types : S =smooth, B = banded, R = rippled, PD = pseudo-droplet.

ammonia–water vapours, are presented from previous research [10]. A further ten tests with binary methylamine–water mixtures having low concentrations of methylamine are reported. The table also lists the ratio of the measured heat transfer coefficient to the value for pure steam calculated using equation (5). Figure 2 demonstrates the ammonia–water and methylamine– water test results graphically. Furthermore, the nature of the condensate film is listed and this is discussed in detail later.

The values for the pure steam tests are in good agreement (error < 3%) with the theoretical values calculated using equation (5). 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.

As discussed by Morrison and Deans [10] 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 at the same conditions. This value was of the order expected from the findings of earlier studies of binary vapour condensation.

In contrast the methylamine–water condensation results show that with increasing concentration of methylamine, the condensate film behaviour tended to be more vigorous and became non-smooth far more rapidly. Test 1M exhibited smooth film condensation as would be expected for pure steam. For test 2M at 0.03 wt% and $\Delta T_v = 7.9^{\circ}$ C, the film was characterised by unstable bands, and occasional ripples. At the same concentration, but with a higher thermal gradient (Test 3M, $\Delta T_v = 10.1^{\circ}$ C), the film exhibited more vigorous rippled behaviour. The heat transfer was enhanced correspondingly: test 2M had a heat transfer enhancement of 20.4% while test 3M showed a 58.0% enhancement.

At slightly higher concentrations the film behaviour tended towards vigorous pseudo-droplet condensation. Heat transfer enhancement was observed to increase with the degree of pseudo-droplet condensation behaviour. At a concentration of approximately 0.2 wt% methylamine, heat transfer was enhanced by 73% for $\Delta T_v = 5.6^{\circ}$ C (test 5M) with the film bordering on pseudo-droplet behaviour. At a thermal gradient of 6.4°C the film behaviour was fully pseudo-droplet, producing an even greater heat transfer rate that exceeded the Nusselt prediction by 131%.

However, further increases in the concentration of methylamine did not result in corresponding increases in the heat transfer enhancement. In fact, with 1.04 wt% methylamine, the condensation heat transfer enhancement was 58% for $\Delta T_v = 6.2^{\circ}$ C and 78% for $\Delta T_v = 9.2^{\circ}$ C. Also for 2.31 wt% methylamine, the enhancement was only 47% at $\Delta T_v = 11^{\circ}$ C. For these three tests, the film was characterised by vigorous pseudodroplet behaviour. It is reasonable to assume that the vapour diffusion layer was becoming more significant at this concentration, and that this was affecting the rate of heat transfer.

Finally, no heat transfer enhancement was discerned



Fig. 2. Enhancement of condensation heat transfer. Film types: S = smooth, B = banded, R = rippled, PD = pseudo-droplet. It should be noted that test 1 is a pure steam test, but is included at a concentration of 0.01 wt% to facilitate a sensible presentation of the results.

at a concentration of 4.29 wt% methylamine and $\Delta T_v = 15.7^{\circ}$ C. At this concentration, it can be assumed that the magnitude of the vapour diffusion film was such that it negated the effect of increased heat transfer through the condensate film.

4. Discussion

The results presented in this paper demonstrate that the addition of methylamine produces an even greater enhancement of condensation heat transfer than ammonia. This is important because it raises several points for ongoing investigation.

The first point is that methylamine cause far more vigorous film disturbances (i.e. pseudo-dropwise) than ammonia. This behaviour began to occur at lower concentrations than for ammonia, and rapidly established pseudo-dropwise condensation. In addition, pseudo-dropwise condensation was identified as the culmination of a series of progressively more vigorous modes of condensation. It must be concluded that the Marangoni effect (i.e. influence of surface tension gradients) is greater for methylamine–water mixtures than for ammonia–water mixtures. This is probably due to methylamine having a lower surface tension than ammonia, the effect of which must be greater than that due to it being less volatile.

The results also suggest pseudo-droplet condensation causes greater heat transfer enhancement than other modes of film behaviour. This result is not unexpected as it has been noted by previous researchers that pseudodropwise condensation reduces the condensate film resistance by 50% [5]. However, the fact that the overall effect for the tests conducted in this experimented exceeded that finding, and persisted up to a concentration of 4.3 wt%, suggest that the condensate film behaviour also influenced the vapour film heat transfer resistance. It is postulated that the vigorous pseudo-droplet condensation behaviour observed for the methylamine-water tests actually increased heat transfer through the vapour diffusion layer both because the droplets penetrated the vapour layer and also because the passage of the droplets disturbed the vapour film.

The final point of interest is that the effect of the thermal driving force on the process was significant. At low thermal driving forces, the film behaviour tended to be less vigorous and the heat transfer enhancement was accordingly less than for tests with a high thermal driving force. This result has implications for commercial applications where both the concentration and the thermal driving force could be treated as variable design parameters and optimised accordingly.

5. Conclusions

The results presented in this paper show that for the condensation of binary methylamine-water vapours at low concentrations, surface tension effects generate significant disturbances in the condensate film. These disturbances, similar to those observed for ammonia-water mixtures, causes the heat transfer coefficient of the condensate film to increase over the range 0.03-4.3 wt% methylamine by as much as 130%. The heat transfer enhancement is inherent in the process itself and occurs over the entire condensation surface. High thermal gradients were identified as a factor leading to more vigorous behaviour. The results also show that the condensate film behaviour tends to become more vigorous with further increase of the methylamine concentration in the vapour. However, above concentrations of 4.3 wt% the vapour film resistance to condensation becomes more dominant and hence the overall heat transfer is reduced.

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