

# THE EFFECT OF SURFACTANT ON EVAPORATIVE HEAT TRANSFER IN VERTICAL FILM FLOW

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**Abstract**—Evaporative heat transfer coefficients for water with various concentrations of a surfactant were measured in vertical downward film flow over a flat plate, over a range of flow rates and temperature differences typical of those employed in desalination evaporators. The coefficients were found to be insensitive to flow rate, but strongly dependent upon temperature difference and surfactant concentration. The temperature dependence varied with the presence or absence of significant nucleate boiling. The dependence on surfactant concentration could not be correlated with surface tension, but was apparently due to foaming and could be explained in light of a theory of foam stability.

## NOMENCLATURE

Where two sets of units are given the first are English and the second are SI.

$A$ ,	area of the heating surface [ft <sup>2</sup> ], [m <sup>2</sup> ];
$a$ ,	constant in equation (6) [molecules/ft <sup>3</sup> ], [molecules/m <sup>3</sup> ];
$B$ ,	constant defined by equation (5) [molecules/ft <sup>3</sup> ], [molecules/m <sup>3</sup> ];
$b$ ,	constant in equation (6) [dynes/cm];
$C$ ,	bulk surfactant concentration [ppm];
$c$ ,	concentration of surfactant in the film liquid [molecules/ft <sup>3</sup> ], [molecules/m <sup>3</sup> ];
$c_0$ ,	optimum value of $c$ for maximum elasticity of foam film [molecules/ft <sup>3</sup> ], [molecules/m <sup>3</sup> ];
$E$ ,	elasticity of foam film [dynes/cm];
$h_b$ ,	boiling side heat transfer coefficient [Btu/hft <sup>2</sup> °F], [W/(m <sup>2</sup> °K)];
$k_b$ ,	Boltzmann's constant [ergs/molecule-°K];
$M_v$ ,	volumetric flow rate of liquid in equation (11) [ft <sup>3</sup> /h], [m <sup>3</sup> /s];
$m$ ,	exponent of surface tension in equation (1) [dimensionless];

ppm,	parts per million by weight [dimensionless];
$Q$ ,	rate of heat flow [Btu/h], [W];
$R$ ,	gas constant [ergs/mole°K];
$S_F$ ,	surface area of foam film [ft <sup>2</sup> ], [m <sup>2</sup> ];
$S_L$ ,	surface area of liquid phase [ft <sup>2</sup> ], [m <sup>2</sup> ];
$\Delta T$ ,	overall temperature difference [°F], [°K];
$\Delta T_b$ ,	temperature drop over the liquid film used in equation (10) [°F], [°K];
$V_F$ ,	volume of liquid in foam phase [ft <sup>3</sup> ], [m <sup>3</sup> ];
$V_L$ ,	volume of liquid phase [ft <sup>3</sup> ], [m <sup>3</sup> ];
$w$ ,	width of heating surface [ft], [m];
$X$ ,	foam film thickness [ft], [m].

## Dimensionless groups

$N_{Re}$ ,	Reynolds number for the liquid film $4M_v/wv$ .
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## Greek letters

$\Gamma$ ,	concentration of surfactant at the interface [molecules/area];
$\Gamma_L$ ,	value of $\Gamma$ for liquid surface;
$\Gamma_0$ ,	value of $\Gamma$ for foam surface;
$\Gamma_\infty$ ,	value of $\Gamma$ corresponding to complete

- monomolecular layer at the interface [molecules/area];
- $\Delta$ ,  $\sigma_0 - \sigma$ : surface tension depression of solution relative to pure solvent [dynes/cm];
- $\Delta_0$ , surface tension depression for solution of concentration  $c_0$  [dynes/cm];
- $\nu$ , kinematic viscosity [ $\text{ft}^2/\text{h}$ ], [ $\text{m}^2/\text{s}$ ];
- $\sigma$ , surface tension of solution [dynes/cm];
- $\sigma_0$ , surface tension of pure water [dynes/cm].

### INTRODUCTION

RELATIVELY small amounts of certain substances in solution have been known to significantly alter the rate of boiling heat transfer relative to that predicted by existing correlations [1-6]. These additives were mostly surface-active with respect to water, and caused a depression in surface tension of the boiling solution. Since surface tension is an important theoretical parameter affecting nucleation in a boiling liquid [7], a study was initiated to investigate the influence of surfactant additives on evaporative heat transfer in convected boiling in a vertical liquid film.

A number of studies have been made in the past to establish a quantitative relationship between the depression in surface tension of a solution and the increase in the heat transfer coefficient in the nucleate boiling region. These attempts, which were mostly limited to pool boiling studies, resulted in widely varying results. If the heat transfer coefficient in the nucleate boiling region is related to its surface tension by an equation of the form

$$h_b = (\text{constant}) \sigma^m \quad (1)$$

the value of  $m$  has been found to vary from -2.5 to 1.275, as illustrated in Table 1. With organic liquids, however, Lowery and Westwater [13] and Dunskus and Westwater [14] found no change in surface tension but an increase in heat flux upon the addition of water-active surfactants. It is evident that the influence

Table 1. Exponent of surface tension in boiling correlations

Reference	$m$
Jakob and Linke [7]	-2.50
Stroebe <i>et al.</i> [3]	-2.00
Cryder and Gilliland [7]	-1.65
Insinger and Bliss [7]	-1.60
Levy [8], Chang and Snyder [9]	-1.00
Rohsenow [10], Forster and Zuber [7]	-0.50
Averin and Kruzhillin [11]	-0.33
Nishikawa and Yamagata [12]	-0.33
Kutateladze [7]	+0.25
Nakagawa and Yoshida [7]	+1.275

of surfactant additives on boiling heat transfer is neither simple nor direct. While these additives generally depress surface tension, the primary effect may well be due to other factors which may be independent of, or at best only indirectly related to, changes in surface tension. Such factors may include changes in contact angle [14] or the rate of nucleation [13].

In recent studies made by the Office of Saline Water [15, 16], an increase in the heat transfer coefficient due to addition of traces of surfactant in water has been attributed to foaming produced in the liquid film by the surfactant, and not to a decrease in surface tension as previously thought [1, 5]. The addition of an antifoaming agent to the boiling feed resulted in a reduction in the evaporative coefficient [16]. However no mechanism was postulated which would explain the observed effects and how they relate to surfactant concentration, foam stability, and surface tension. A consideration of these effects is presented below.

### FOAM STABILITY THEORY

It is logical to expect enhanced evaporative heat transfer performance when foaming occurs, because of the tremendous increase in liquid surface area generated by the foam phase. In such cases, a direct correlation of the heat transfer coefficient with surface tension of the base liquid would not be expected since foaming is only indirectly related to surface tension, although they are both a function of surfactant concentration.

According to Freundlich [17], for a large development of vapor-liquid interface (as during foaming) the surface tension must be small. Now pure liquids with low surface tension and high vapor pressure are never far removed from their boiling points. The lamellae of liquid in foam films, therefore, evaporate very quickly when formed. However, pure liquids with a sufficiently small vapor pressure generally have too large a surface tension to produce a stable foam. Thus only capillary-active solutions unite both properties, and as matter of fact all solutions of capillary-active organic substances in water foam more or less strongly. However, all surface-active agents do not promote foam formation to the same extent and their effectiveness may be assessed by means of a so-called 'foam stability' criterion, as discussed below.

The subject of foam stability has been reviewed by Ewers and Sutherland [18], Bikerman [19] and later by Sheludko [20]. According to Gibbs [18, 20] stability of foam films is due to the 'elasticity' of such films. If a certain section of the film is stretched so that its surface  $S_F$  increases at constant volume its thickness  $X$  is decreased then, since the total content of the surface-active component per unit volume remains constant, the concentration per unit area or surface will decrease and the surface tension will be increased. The increased tension of the stretched section as compared with the adjacent unstretched films will then give rise to a force along the film, which will tend to compress the stretched section and restore uniform thickness throughout the entire film. This force, related to a unit increase of the film surface, was called the 'film elasticity' by Gibbs and is represented as:

$$E = 2 \frac{d\sigma}{dS} S_F. \quad (2)$$

For the region of medium rate deformations, the function  $E$  can be calculated by making use of the conditions that the deformed section preserves a constant volume. Thus it can be shown [20] that

$$E = \frac{4RT\Gamma_\infty^2 c}{2B\Gamma_\infty + X(c + B)^2}. \quad (3)$$

Equation (3) shows that  $E$  increases with decreasing  $X$ . The variation of  $E$  with surfactant concentration in the film  $c$  passes through a maximum at

$$c_0 = B \sqrt{\left(1 + \frac{2\Gamma_\infty}{BX}\right)} \quad (4)$$

which can be obtained by differentiating equation (3) and setting the result equal to zero. For  $X > 10^{-6}$  cm, the second term under the root sign in equation (4) can be neglected, so that

$$c_0 \cong B \quad (5)$$

where  $c_0$  is the surfactant concentration in the film liquid corresponding to the maximum value of  $E$ , for maximum stability of the foam film.

An empirical equation relating the decrease in surface tension of solutions of lower fatty acids ( $C_3$  to  $C_6$ ) in water to the bulk concentration of the surface-active component within the solution has been given by Szyszkowski [21]

$$\Delta = b \ln\left(\frac{C}{a} + 1\right). \quad (6)$$

Although Szyszkowski's equation is accurately obeyed by relatively few systems it has been theoretically interpreted, and it can be shown [20] that

$$a = B, \quad \text{and} \quad b = \Gamma_\infty k_b T$$

where  $1/\Gamma_\infty$ , the area per molecule of the adsorbed substance, usually lies in the range 20-40 Å<sup>2</sup> [21]. Equation (6) can thus be written as

$$\Delta = \Gamma_\infty k_b T \ln\left[\frac{C}{B} + 1\right]. \quad (7)$$

Eliminating  $B$  from equations (5) and (7) gives

$$\Delta = (\Gamma_\infty k_b T) \ln\left[\frac{C}{c_0} + 1\right]. \quad (8)$$

If the bulk concentration of the surfactant is equal to  $c_0$ , then equation (8) reduces to

$$\Delta_0 = 0.692(\Gamma_\infty k_b T) \quad (9)$$

where  $\Delta_0$  is the surface tension depression for a solution of bulk concentration  $c_0$ , i.e. the concentration in the film at which foam stability is maximum. Using a typical value of  $30 \text{ \AA}^2$  for  $1/\Gamma_\infty$  (the area occupied by an adsorbed molecule at the interface) equation (9) predicts  $\Delta_0 = 13.6$  dyne/cm at  $73^\circ\text{F}$  ( $296^\circ\text{K}$ ). That is, a bulk surfactant concentration which produces a surface tension depression of about 13.6 dyne/cm should be the concentration which produces the most stable foam.

The objective of this investigation was to determine the influence of the addition of small amounts of surfactant upon the heat transfer coefficient for water in forced convection film evaporation under conditions approximating those encountered in desalination evaporators,

and to test the compatibility of the results with the above concepts relating surface tension to foam stability.

## EXPERIMENTAL

### Apparatus

The experimental apparatus was designed to measure the evaporating heat transfer coefficient along a  $12 \text{ in} \times 6 \text{ in.} \times \frac{1}{8} \text{ in.}$  ( $30.5 \text{ cm} \times 15.2 \text{ cm} \times 0.3 \text{ cm}$ ) smooth-vertical copper plate with a falling film of boiling liquid on one side and condensing steam on the other. Copper-constantan thermocouples were used to measure the temperatures inside the boiling and condensing chambers as well as at several points along the boiling and condensing surfaces. A schematic diagram of the experimental set-up is given in Fig. 1. Details of the equipment construction and operating procedures are given in [22].

The boiling surface was smoothed and polished

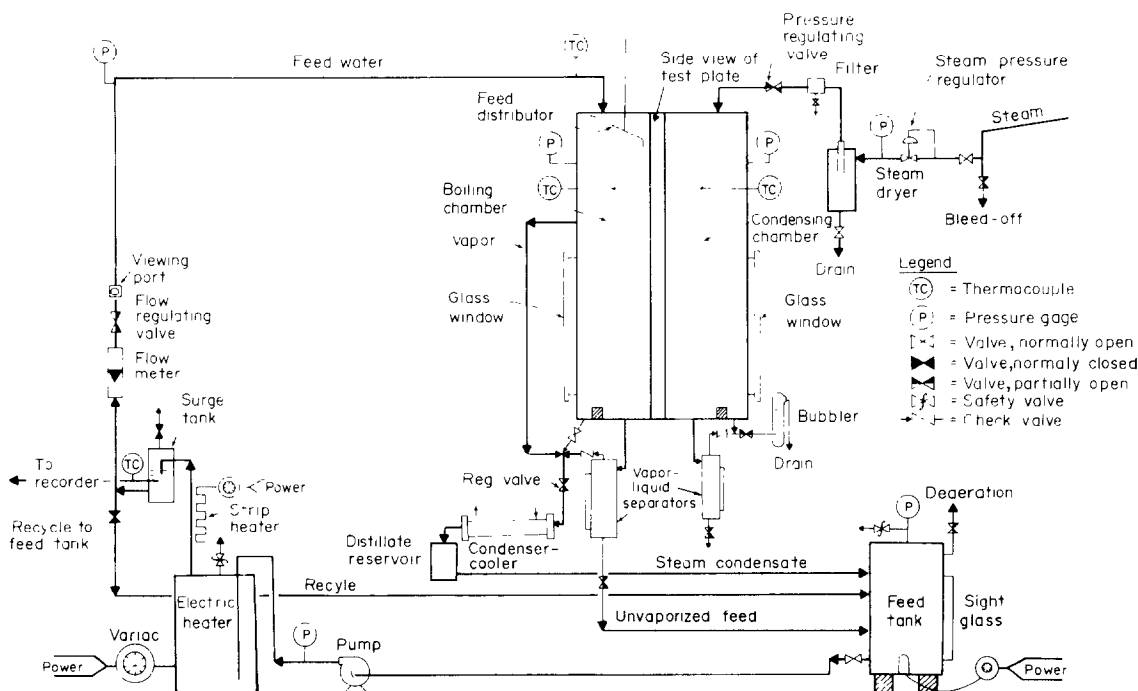
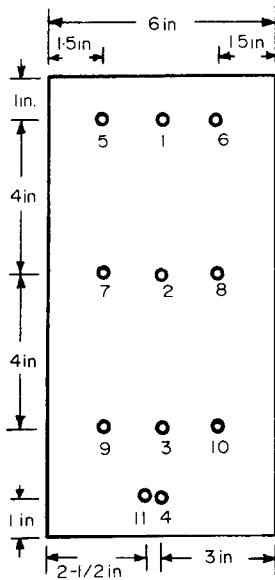


FIG. 1. Schematic diagram of the flow loop.

and, after imbedding of thermocouples, was stabilized by oxidation [15]. Arrangement of the imbedded thermocouples in the plate is shown in Figs. 2 and 3.



Thermocouples number 1–4 measure the condensing surface temperature and those from 5 to 11 measure the boiling surface temperature.

FIG. 2. Position of the imbedded thermocouples along the test plate surfaces.

The test plate was vertically secured through neoprene gaskets between two halves of a predesigned mild steel box which comprised the boiling and condensing chambers. The box had two pyrex glass windows, one on each side, to provide an internal view of the boiling/condensing chambers. The bulk temperatures in the boiling and condensing chambers were measured by two additional copper–constantan thermocouples, one in each chamber. All thermocouples were calibrated using saturated steam and recording the pressure (and hence its temperature) with a mercury manometer.

#### Procedure

Fifty gallons of distilled water (equilibrium

surface tension 69.7 dyne/cm at 73°F (296°K)) in the reservoir tank was recycled through the water heater until its temperature rose to 215°F (375°K). This hot water (at its boiling point corresponding to the pressure in the system) was then circulated through the entire loop to ensure that the surface tension had

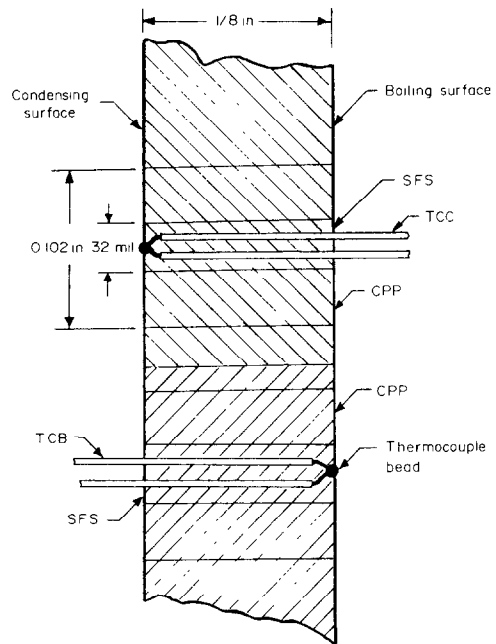


FIG. 3. Sectional view of the test plate showing two imbedded thermocouples.

CPP—copper plug press fitted into test plate

SFS—space filled with soft solder

TCB—thermocouple for boiling surface temperature

TCC—thermocouple for condensing surface temperature

stabilized after picking up any contamination in the loop. After sufficient recirculation, the equilibrium surface tension was measured at 73°F (296°K) using a precalibrated du Noüy tensiometer. The surface tension had dropped from 69.7 dynes/cm to 63.5 dynes/cm and remained essentially constant at this value throughout the work with pure water.

The water at  $215 \pm 0.1^\circ\text{F}$  ( $375 \pm 0.06^\circ\text{K}$ ) was then passed through a calibrated rotameter onto the top of the boiling chamber, where it

was evenly distributed along the top edge of the boiling surface. Saturated steam at a controlled pressure was introduced into the condensing chamber, and the steam condensate was allowed to flow under pressure into a calibrated condensate collector. The uncondensed steam was

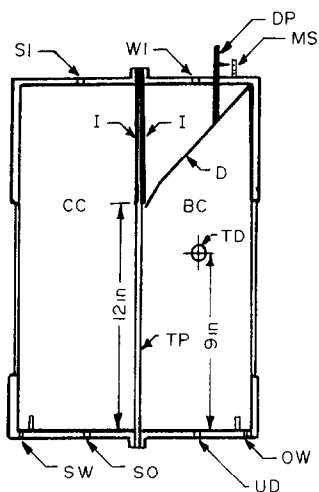


FIG. 4. Sectional view of the boiling-condensing chamber showing test plate assembly.

- BC—boiling chamber
- CC—condensing chamber
- D—water distributor
- DP—water distributor pin
- I—neoprene insulation
- MS—measuring scale
- OW—outlet for vapor condensed along walls
- SI—steam inlet
- SO—outlet for steam condensed along condensing surface of the test plate
- SW—outlet for steam condensate formed along walls
- TD—outlet for vapor formed in the boiling chamber
- TP—test plate
- UD—outlet for unboiled water
- WI—water inlet

throttled through a needle valve and vented to the drain. Any steam condensing on the inner walls of the chamber was collected separately in a trough in the bottom and routed to the drain. The water vapor from the boiling chamber was passed through a water-cooled condenser and collected for measurement. The unboiled water collected at the base of the

boiling surface was allowed to flow into an insulated collector from where it was continuously recycled to the main reservoir.

The flow rate of water to the boiling surface was initially fixed at 1.025 gpm ( $6.47 \times 10^{-5}$  m<sup>3</sup>/s) and the steam pressure in the condensing chamber was adjusted to give an overall temperature driving force of 10°F (5.6°K). Under steady state conditions, the rate of water boiled off and the corresponding steam condensate rate were measured. The heat flux calculated from each of these values provided a check on the heat balance. At the same time all the thermocouple readings were recorded. A duplicate run was then made under identical conditions, and only those runs for which the heat balance was close to unity were recorded. The procedure was repeated for temperature driving forces of 15° and 20°F (8.3 and 11°K).

Keeping the water temperature fixed at 215°F (375°K), similar procedures were followed for water flow rates of 1.275 and 1.55 gpm ( $8.05 \times 10^{-5}$  and  $9.78 \times 10^{-5}$  m<sup>3</sup>/s). During these runs the surface tension of the water was checked periodically, and no significant change was noticed.

To study the effect of surfactant concentration on the boiling coefficients, a measured amount of a commercial surfactant (Procter and Gamble 'Joy,' which contains 3:1 ammonium lauryl sulphate and C<sub>12</sub> - C<sub>14</sub> diethanolamine) was injected into 50 gallons ( $18.9 \times 10^{-2}$  m<sup>3</sup>) of water in the reservoir tank to produce solutions corresponding to 15, 30 and 50 ppm of surfactant. Data for these solutions were obtained for the same temperature differences and flow rates as above. The evaporated water, after condensing and weighing, was immediately recycled through a peristaltic tubing pump (to avoid contamination) to the main reservoir to maintain the solution at constant concentration. The evaporated water was continuously recycled when no measurements were being made. During these runs, small amounts of the solution were taken out at random times and equilibrium surface tensions were measured at 73°F (296°K).

### Heat balance

A heat balance was obtained by comparing the rate of heat output in the evaporated water to heat input from condensation of steam. The mean heat balance, expressed as a ratio of these two values, for a total of 68 consecutive experiments in this work was 0.984 with a standard deviation of  $\pm 0.12$ .

### Temperature measurements

The liquid was introduced along the top edge of the boiling surface at a temperature of  $215 \pm 0.1^\circ\text{F}$  ( $275 \pm 0.06^\circ\text{K}$ ). The average bulk temperature in the boiling chamber was controlled at  $215 \pm 0.3^\circ\text{F}$  ( $375 \pm 0.2^\circ\text{K}$ ) and that in the condensing chamber was controlled to within  $\pm 0.2^\circ\text{F}$  ( $\pm 0.1^\circ\text{K}$ ). The average temperature of the boiling surface as indicated by the imbedded thermocouples was found to be higher than the average temperature of the condensing surface. The mean excess in the boiling surface temperature over that for the condensing surface was  $0.6^\circ\text{F}$  ( $0.3^\circ\text{K}$ ) with a standard deviation of  $\pm 0.38^\circ\text{F}$  ( $\pm 0.21^\circ\text{K}$ ). This discrepancy in the thermocouple readings was found to be due to the thermocouple arrangement (Fig. 3) and the accompanying fin effect [23]. The beads of the thermocouples which measure the condensing surface temperature lie in the condensing surface while the thermocouple wires are mainly in the boiling chamber which is at a temperature of  $8^\circ\text{F}$  ( $4.4^\circ\text{K}$ )– $18^\circ\text{F}$  ( $10^\circ\text{K}$ ) lower than that of the condensing surface. Some heat is conducted away (from the thermocouple beads) along the thermocouple wires due to this temperature gradient. Thus the indicated condensing temperature is lower than the true temperature of the surface. For the boiling surface, the thermocouple beads lie in the boiling surface while the thermocouple wires lie in the condensing chamber where the temperature is from  $4^\circ\text{F}$  ( $2.2^\circ\text{K}$ ) to  $15^\circ\text{F}$  ( $8.3^\circ\text{K}$ ) higher than that at the boiling surface. Thus the fin effect results in a higher indicated temperature. Thermocouple corrections for this fin effect were calculated

and true surface temperatures were obtained by a method outlined in [22]. This correction ranged from  $0.40$  to  $1.5^\circ\text{F}$  ( $0.2$ – $0.8^\circ\text{K}$ ).

The temperature was also found to vary from point to point along the boiling and condensing surfaces, with a typical maximum variation being from  $3^\circ$  to  $4^\circ\text{F}$  ( $1.7$ – $2.2^\circ\text{K}$ ). At any particular location along the test plate, the temperature was found to fluctuate rapidly with time. However, the fluctuations were usually limited to within  $\pm 0.1^\circ\text{F}$  ( $\pm 0.06^\circ\text{K}$ ). Arithmetic averages of the mean readings for the thermocouples in each surface were taken as the temperature of that surface.

### Estimate of error

A consideration of the cumulative effects of all sources of error from the measurement of temperatures, flow rates, time, condensate volumes, etc. showed that the overriding source of error was that due to measurement of the boiling side surface temperature. For the most extreme case ( $\Delta T_b$  of  $5^\circ$  or  $2.8^\circ\text{K}$ ) the cumulative error in the resulting evaporative coefficient was estimated to be  $\pm 16$  per cent, so that all calculated values should be accurate to within this limit.

### Appearance of the boiling surface

For pure water, the liquid film fell uniformly along the heating surface. At a  $\Delta T$  of  $10^\circ\text{F}$  ( $5.6^\circ\text{K}$ ), very few nucleation sites were visible on the surface. However, at a  $\Delta T$  of  $15^\circ\text{F}$  ( $8.3^\circ\text{K}$ ), the number of nucleation sites was significantly increased, and vigorous nucleate boiling was observed at a  $\Delta T$  of  $20^\circ\text{F}$  ( $11^\circ\text{K}$ ). Streaks of bubbles issuing from the nucleation sites were visible, which were swept away by the flowing liquid. However for the surfactant solutions, the falling liquid films were swollen into bubbly two phase layers. Except for a small section extending about two inches below the top edge of the boiling surface, the rest of the surface was entirely hidden by the foamy layer. Along the top section of the surface, nucleation sites were observed to increase

with an increase in the overall temperature difference, as was observed in the case of pure water.

The mode of condensation along the condensing surface was observed to be dropwise throughout this work.

## RESULTS

### Heat transfer coefficients

Evaporative heat transfer coefficients were calculated from the measured heat flux and temperature difference:

$$h_b = \frac{Q/A}{\Delta T_b} \quad (10)$$

Where  $Q/A$  is the heat flux based on the steam condensate rate and  $\Delta T_b$  is the mean temperature drop across the liquid layer based on the average corrected plate temperature and the bulk vapor temperature in the boiling chamber.

### Effect of liquid flow rate

The Reynolds number in the liquid film was calculated as follows:

$$N_{Re} = \frac{4M_v}{wv} \quad (11)$$

The values of the Reynolds number at 215°F (374°K) for 1.025, 1.275 and 1.55 gpm ( $6.47 \times 10^{-5}$ ,  $8.05 \times 10^{-5}$  and  $9.78 \times 10^{-5}$ ) flow rates are 5825, 7246, 8809, respectively. Thus the flow in the liquid film was in the turbulent region for all flow rates. Figure 5 shows that, within experimental scatter, the evaporative coefficients are independent of the liquid flow rate over the range indicated.

### Effect of liquid film $\Delta T$

In Figs. 6–8 the evaporative coefficients are plotted as functions of  $\Delta T_b$  with concentration as the parameter, for each of the three flow rates. For any concentration of surfactant and flow rate, the heat transfer coefficients are observed to increase as the temperature difference across the liquid film is increased. For surfactant solutions, an increase in  $\Delta T_b$  appeared

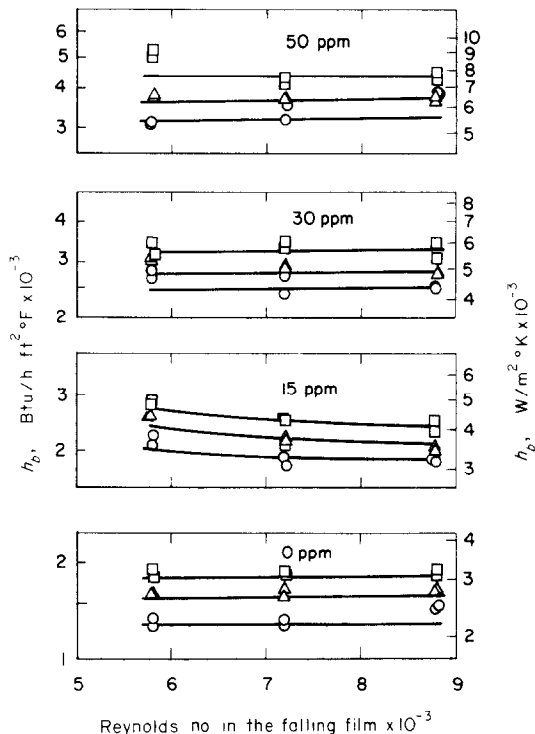


FIG. 5. Dependence of evaporative coefficient on Reynolds number.

□ —  $\Delta T = 20^\circ\text{F}$  (11.1°C),  $\Delta$  —  $\Delta T = 15^\circ\text{F}$  (8.3°C),  $\circ$  —  $\Delta T = 10^\circ\text{F}$  (5.6°C)

to induce more foaming in the liquid film due to the increase in the rate of vapor bubbles issuing from the heating surface and agitation of the liquid film. The resultant heat transfer coefficients thus obtained reflect the combined effects of nucleate boiling and foaming. The top point on the 50 ppm curve of Fig. 6 is probably in error, since for this run the liquid film was not continuous over the entire plate, dry spots being observed on the bottom portion of the plate due to the rapid evaporation rate.

Visually, it was observed that a significant rate of vapor bubble generation due to nucleate boiling occurred only for an overall  $\Delta T$  of 15°F (8.3°K) or greater. Therefore, the convective mechanism in this range was assumed to be due to a combination of stirring from the bubbles and forced flow, whereas for lower  $\Delta T$ 's the nucleation effects were not significant. The



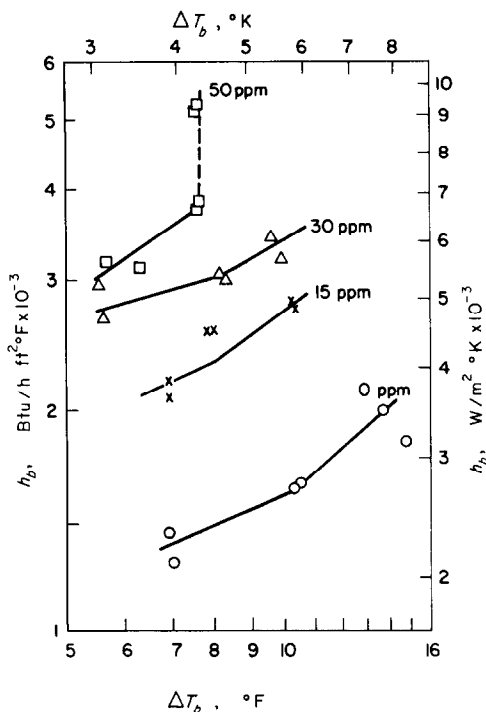


FIG. 6. Evaporative coefficient as a function of temperature drop over the liquid film (liquid flow rate of 1.025 gpm or  $6.47 \times 10^{-5} \text{ m}^3/\text{s}$ ).

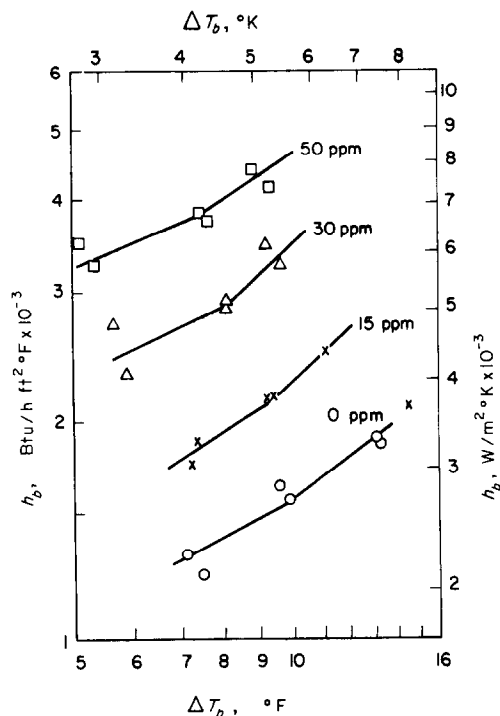


FIG. 7. Evaporative coefficient as a function of temperature drop over the liquid film (liquid flow rate of 1.275 gpm or  $8.05 \times 10^{-5} \text{ m}^3/\text{s}$ ).

degree of foaming in the surfactant solutions also increased markedly at the higher  $\Delta T$ 's. For this reason, the data in Figs. 6–8 are separated into two distinct regions represented by the two straight line segments, rather than drawing a smooth curve through all of the data points. At low  $\Delta T$ 's foaming was due to mechanical agitation, while at the higher  $\Delta T$ 's the additional agitation due to vapor bubble nucleation considerably increased the degree of foaming. The existence of nucleation was determined by visual observation of the flow over the top 2 in. (5.1 cm) of the plate, the remainder of the plate being obscured by the foam except for pure water for which no nucleation was observed at 10°F (5.6°K)  $\Delta T$ .

*Effect of heat flux*

In Figs. 9–11 the evaporative coefficients are plotted as a function of heat flux for different

concentrations of surfactant as the parameter, for each of the three flow rates. At a given heat flux the evaporative coefficient increases as surfactant concentration is increased. Figure 11 includes a comparison with the results reported by OSW [16]. The OSW data are for water at 210°F (372°K) in a vertical 2 in. (5.1 cm) o.d. 8 ft (2.4 m) long aluminum brass tube at a flow rate of 1.5 gpm ( $9.5 \times 10^{-5} \text{ m}^3/\text{s}$ ) with various concentrations of P & G No. 128 surfactant, and condensing steam outside the tube. Besides the apparent differences in geometry and surfactant (no surface tension data were reported by OSW for comparison), the OSW coefficients were based on measurements of overall  $\Delta T$  and an estimated value of condensing coefficient using the modified Nusselt theory.

*Effect of surfactant concentration*

Figures 12–14 show the variation of evapora-

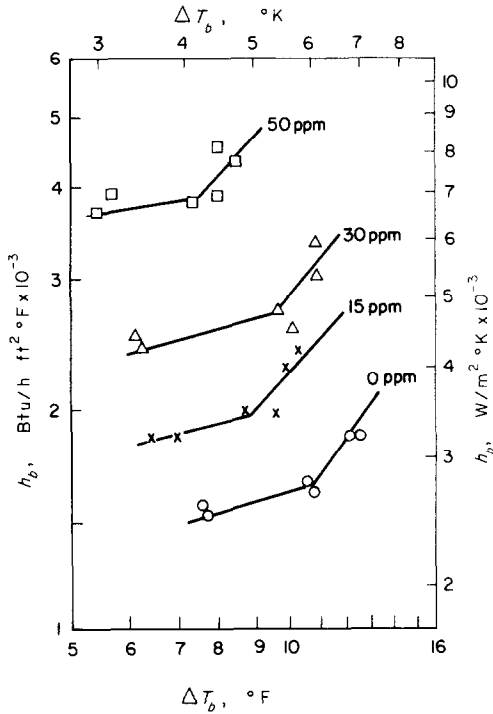


FIG. 8. Evaporative coefficient as a function of temperature drop over the liquid film (liquid flow rate of 1.55 gpm or  $9.78 \times 10^{-5} \text{ m}^3/\text{s}$ ).

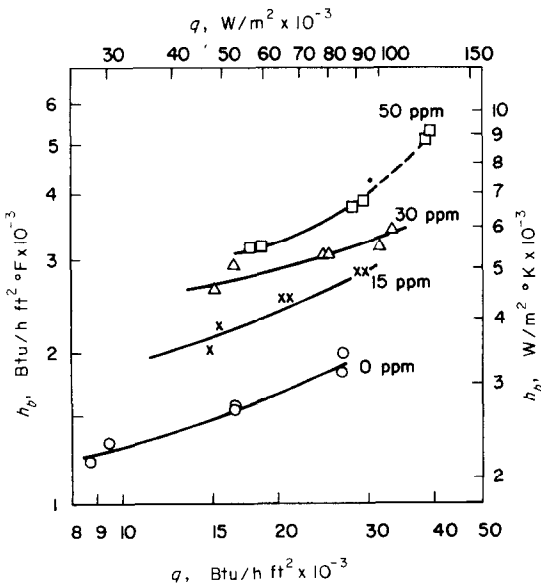


FIG. 9. Evaporative coefficient as function of heat flux (liquid flow rate of 1.025 gpm or  $6.47 \times 10^{-5} \text{ m}^3/\text{s}$ ).

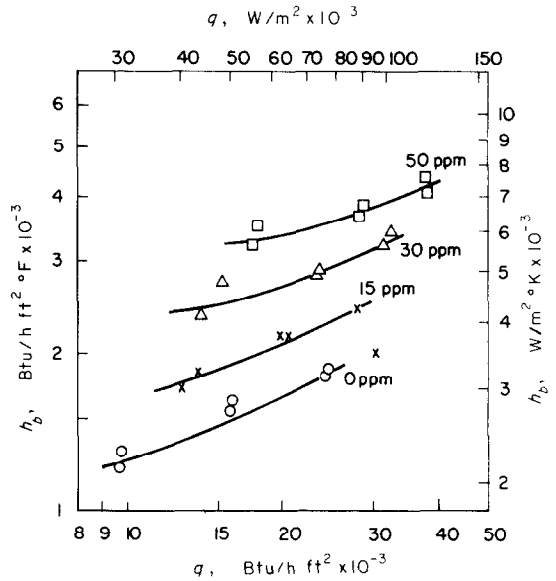


FIG. 10. Evaporative coefficient as function of heat flux (liquid flow rate of 1.275 or  $8.05 \times 10^{-5} \text{ m}^3/\text{s}$ ).

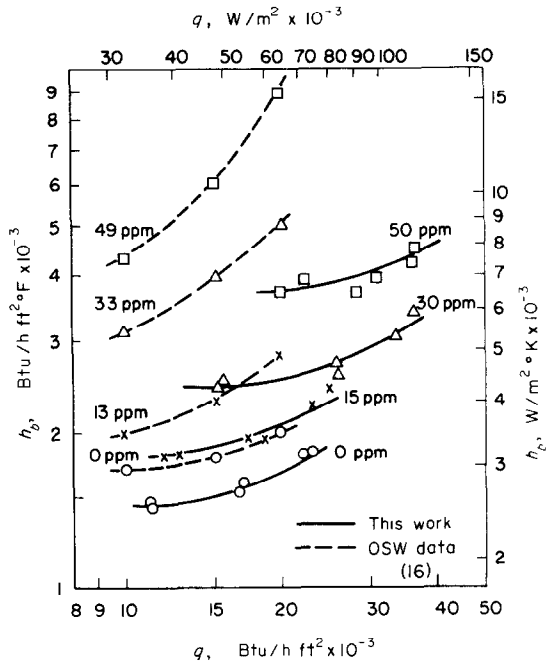


FIG. 11. Evaporative coefficient as function of heat flux (liquid flow rate of 1.55 gpm or  $9.78 \times 10^{-5} \text{ m}^3/\text{s}$ ).

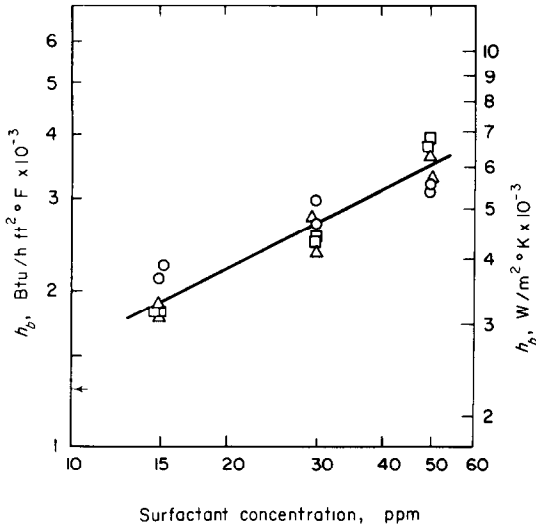


FIG. 12. Evaporative coefficient as function of surfactant concentration (overall temperature difference of 10°F or 5.6°K).

○ = 1.025 gpm ( $6.47 \times 10^{-5}$  m<sup>3</sup>/s), Δ = 1.275 gpm ( $8.05 \times 10^{-5}$  m<sup>3</sup>/s), □ = 1.55 gpm ( $9.78 \times 10^{-5}$  m<sup>3</sup>/s)

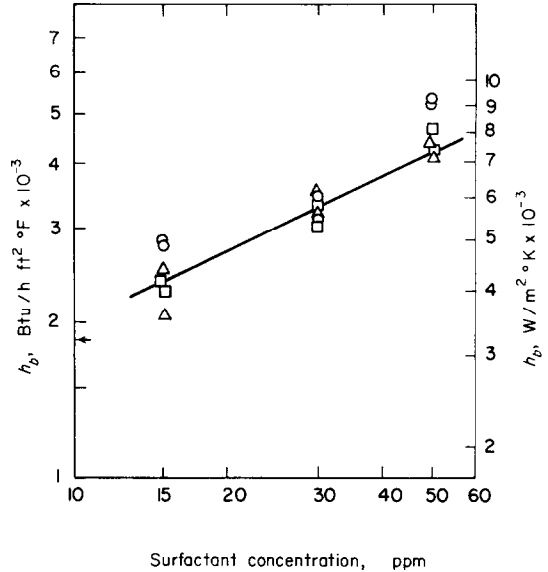


FIG. 14. Evaporative coefficient as function of surfactant concentration (overall temperature difference of 20°F or 11.1°K).

○ = 1.025 gpm ( $6.47 \times 10^{-5}$  m<sup>3</sup>/s), Δ = 1.275 gpm ( $8.05 \times 10^{-5}$  m<sup>3</sup>/s), □ = 1.55 gpm ( $9.78 \times 10^{-5}$  m<sup>3</sup>/s)

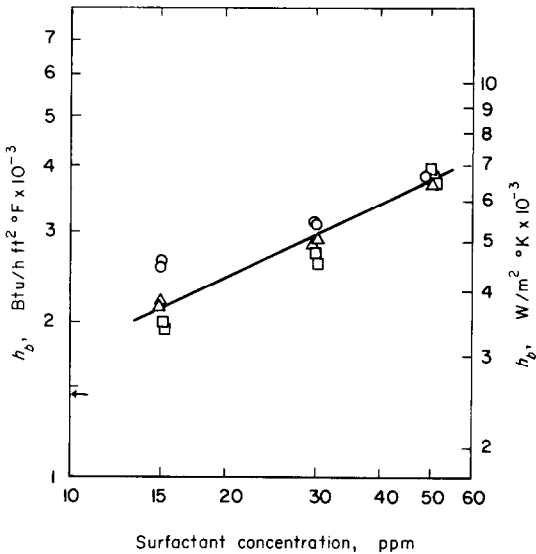


FIG. 13. Evaporative coefficient as function of surfactant concentration (overall temperature difference 15°F or 8.3°K).

○ = 1.025 gpm ( $6.47 \times 10^{-5}$  m<sup>3</sup>/s), Δ = 1.275 gpm ( $8.05 \times 10^{-5}$  m<sup>3</sup>/s), □ = 1.55 gpm ( $9.78 \times 10^{-5}$  m<sup>3</sup>/s)

evaporative coefficients with surfactant concentration for each of the overall  $\Delta T$ 's. It is apparent from these plots that for a fixed overall  $\Delta T$  the average evaporative coefficients increase as the surfactant concentration is increased, with no significant dependence on flow rate. As these plots are all on a log-log scale, the average coefficient for pure water (no surfactant) is indicated by the arrow on the vertical axis.

**Correlation**

It was found that all of the data could be correlated by an empirical equation of the form

$$h_b = (a_0 + a_1 C^{a_2}) \Delta T_b^{a_3} \quad (12)$$

if two sets of constants were used, one for the range of  $\Delta T \leq 15^\circ\text{F}$  ( $8.3^\circ\text{K}$ ) and another for  $\Delta T \geq 15^\circ\text{F}$  ( $8.3^\circ\text{K}$ ). The division at  $\Delta T = 15^\circ\text{F}$  ( $8.3^\circ\text{K}$ ) corresponds to the point at which nucleate boiling was visually observed to be definitely significant. The resulting values of the empirical constants are given in Table 2.

Although values of the constants were determined statistically from the data, with a resulting correlation coefficient of 0.999 indicating an excellent fit, the limited amount and the relatively small range of the data would not justify

Table 2. Empirical constants for equation (12)

	$\Delta T \leq 15^\circ\text{F} (8.3^\circ\text{K})$	$(8.3^\circ\text{K}) 15^\circ\text{F} \leq \Delta T$
$a_0$ (English units)	900	372
$a_0$ (SI units)	1773	938
$a_1$ (English units)	18	4.8
$a_1$ (SI units)	36	12
$a_2$	1.12	1.25
$a_3$	0.20	0.62

confidence in the use of the correlation for extrapolation significantly beyond this range.

### Surface tension

Curve A of Fig. 15 shows the surface tension of freshly-made solutions of the surfactant (Joy) as a function of concentration. These solutions were made using fresh water which had been circulated in the test loop until its surface tension had stabilized (to a value of 63.5 dynes/cm at 73°F or 296°K). Curve B

shows the surface tension of the test liquids used in the study as a function of the bulk concentration. The latter are measured values from samples which had been withdrawn from the system after recirculation for a time sufficiently long for the surface tension to stabilize. All values were determined on samples cooled to 73°F (296°K). While the surface tension of the fresh solutions decreased uniformly with increasing surfactant concentration, that of the recirculated solutions leveled off in the vicinity of 30 ppm surfactant, and actually increased slightly at 50 ppm. Although  $h_b$  could be correlated reasonably well with surfactant concentration, there was no apparent correlation with solution surface tension. It therefore appears that the effect of surfactant on heat transfer is more complex than a simple modification of surface tension.

### DISCUSSION

Although the heat transfer coefficient could not be simply related to solution surface tension, a simple correlation indicated an almost linear dependence on surfactant concentration. Also, it was visually observed that the degree of foaming increased in proportion to the amount of surfactant added. It is reasonable that the evaporative heat transfer rate should increase with foaming intensity because of the tremendous surface area in the foam available for evaporation.

Now surface tension, surfactant concentration, and foam stability are all interrelated, as previously discussed. That this theory is consistent with present observations, in particular the surface tension curves of Fig. 15, may be seen as follows. Equation (9) gives the predicted surface tension depression for a solution in which the bulk surfactant concentration  $c_0$  is the same as that in a foam of maximum stability. This, of course, does not imply that foaming could not occur in a solution of lower concentration. Since the surfactant, by nature, adsorbs at the gas-liquid interface, its concentration there will be greater than the bulk

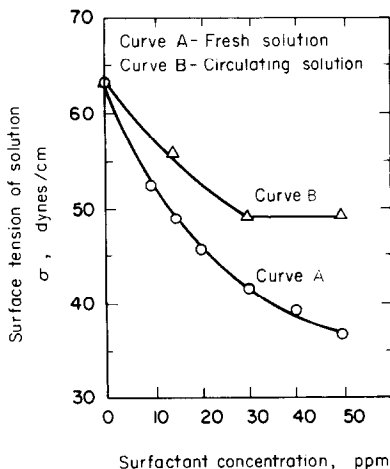


FIG. 15. Variation of surface tension with surfactant concentration.

Curve A—fresh solution  
Curve B—circulated solution

concentration. Thus even for solutions less concentrated than  $c_0$ , the surface concentration may well be large enough to produce a stable foam if agitated. The only criterion is that the surfactant concentration in the foam phase should be  $c_0$ .

Thus, if a solution of bulk concentration  $C_b$  is agitated to produce a foam, the resulting distribution of surfactant between the liquid phase, concentration  $C_L$ , and the foam phase, concentration  $c_0$ , follows from a surfactant balance. Accounting for both volumetric and surface concentrations in both phases, the balance is:

$$C_b V_L = C_L (V_L - V_F) + \Gamma_L S_L + c_0 V_F + \Gamma_0 S_F. \quad (13)$$

Since the liquid volume in the foam is much less than that in the bulk liquid and the surface area of the foam is much greater, equation (13) reduces to

$$C_b V_L \doteq C_L V_L + \Gamma_0 S_F. \quad (14)$$

Now the surface concentration in the foam film is given by the Langmuir isotherm:

$$\Gamma_0 = \frac{\Gamma_\infty c_0}{c_0 + B} = \frac{1}{2} \Gamma_\infty \quad (15)$$

since  $B = c_0$ , a consequence of the foam stability criterion. Thus equation (14) becomes

$$C_L \doteq C_b - \frac{\Gamma_\infty S_F}{2V_L}. \quad (16)$$

The concentration of the liquid phase of an agitated (foamy) solution,  $C_L$ , is therefore always less than the overall bulk concentration,  $C_b$ , which would be the actual liquid concentration of the same solution if it were not agitated to produce foam. The difference is proportional to the ratio of foam surface to liquid volume.

It is proposed that these conditions correspond to Curves A and B of Fig. 15. The data of Curve A were obtained from non-agitated surfactant solutions, for which  $C_L = C_b$ . Curve B represents solutions of the same overall bulk

concentration which had been agitated by circulation through the system, for which the actual liquid phase concentration  $C_L$  is now less than  $C_b$  by equation (16). Thus Curves A and B are both equivalent, Curve B being actually  $\sigma$  vs  $C_L$  and Curve A being  $\sigma$  vs  $C_b$  for the same solution after agitation. Thus at a given value of  $\sigma$ , the difference between the two curves represents  $C_b - C_L$ , which, by equation (16), is proportional to the amount of foam generated.

It is seen that Curve B levels off at a value of  $\sigma$  slightly less than 50 dynes/cm. It should be noted that possible effects due to contamination were accounted for by using fresh water which had stabilized after circulation in the system to make up the surfactant solutions. Thus any contamination should have an equal effect on both Curves A and B. Now the result of the foam stability criterion, equation (9), predicted that a surface tension depression of 13.6 dynes/cm would occur for a solution of concentration equal to that in a foam of maximum stability. This corresponds to just under 50 dynes/cm, which in turn corresponds to a liquid concentration of about 15 ppm. It thus follows that  $c_0$  is approximately 15 ppm, the surfactant concentration in a stable foam film. The significance of Curve B leveling off at this point is simply that essentially all of the surfactant added to solution in excess of that corresponding to  $C_L = 15$  ppm goes into the foam phase, producing foam in direct proportion to the amount of surfactant added. This, therefore, supports the contention that the enhanced heat transfer coefficient is primarily a consequence of foaming, since both are essentially proportional to surfactant concentration in excess of 15 ppm.

#### CONCLUSIONS

The evaporating heat transfer coefficient for vertical film flow over a flat plate was found to be essentially independent of flow rate but markedly dependent upon temperature drop and surfactant concentration, over a range of temperatures and flow rates typical of those

employed in desalination evaporators. The temperature dependence was significantly greater at higher temperature differences where nucleate boiling prevailed than at lower temperature differences. The dependence upon surfactant concentration was essentially linear, but could not be correlated with corresponding changes in surface tension. The effect of surfactant addition was attributed to foaming, and could be explained in terms of a foam stability criterion relating surface tension depression to surfactant concentration at which foam stability is a maximum. Surface tension versus concentration data for agitated and non-agitated solutions were consistent with the derived criterion, and indicated that the degree of foaming should be proportional to the amount of surfactant added, in agreement with the observed dependence of the heat transfer coefficient upon surfactant concentration.

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#### EFFET D'UN AGENT TENSIO-ACTIF SUR LE TRANSFERT THERMIQUE PAR EVAPORATION DANS UN FILM TOMBANT

**Résumé**—Des coefficients de transfert thermique par évaporation pour de l'eau avec diverses concentrations d'un agent tensio-actif ont été mesurés dans l'écoulement d'un film tombant sur une plaque plane verticale pour un domaine de débit et de différence de température correspondant au cas des évaporateurs de désalination. On a trouvé que les coefficients étaient insensibles au débit mais fortement dépendants de la différence de température et de la concentration de tensio-actif. La dépendance vis-à-vis de la tem-

pérature varie selon la présence ou l'absence d'ébullition nucléée significative. La dépendance vis-à-vis de la concentration de tensio-actif ne pouvait être reliée à la tension superficielle mais était apparemment due à la production de mousse et pouvait être expliquée à la lumière d'une théorie de stabilité.

#### DER EFFEKT EINES SCHAUMBILDNERS AUF DEN WÄRMEÜBERGANG BEI VERDAMPFUNG IN EINEM SENKRECHT ABSTRÖMENDEN FILM

**Zusammenfassung**—Es wurden die Wärmeübergangszahlen für Wasser bei Verdampfung in einem senkrecht über eine Platte abströmenden Film für verschiedene Konzentrationen eines Schaumbildners gemessen, mit unterschiedlichen Massenströmen und Temperaturdifferenzen in einem für Entsalzungsanlagen typischen Bereich. Die Koeffizienten zeigten sich unempfindlich gegen Änderungen des Massenstromes, jedoch stark abhängig von der Temperaturdifferenz und der Konzentration des Schaumbildners. Die Temperaturabhängigkeit variiert mit dem Vorhandensein oder Nicht-Vorhandensein von deutlichem Blasensieden. Die Abhängigkeit von der Schaumbildner-Konzentration konnte mit der Oberflächenspannung nicht korreliert werden, stand jedoch offensichtlich in Zusammenhang mit der Schaumbildung und liess sich auf Grund einer Schumstabilitätstheorie erklären.

#### ВЛИЯНИЕ ПОВЕРХНОСТНО-АКТИВНОГО ВЕЩЕСТВА НА ПРОЦЕСС ТЕПЛООБМЕНА ПРИ ВЕРТИКАЛЬНОМ ТЕЧЕНИИ ПЛЕНКИ

**Аннотация**—Измерялись коэффициенты теплообмена при испарении стекающей по вертикальной плоской пластине пленки воды в зависимости от концентрации в ней добавки поверхностно-активного вещества. Измерения проводились в широком диапазоне изменения плотностей орошения и разностей температур, характерных для опреснителей. Найдено, что скорость течения не влияет на величины коэффициентов теплообмена; последние сильно зависят от разности температур и концентрации поверхностно-активного вещества. Влияние температуры зависит от наличия или отсутствия пузырькового кипения и его интенсивности. Влияние концентрации поверхностно-активного вещества нельзя связать с поверхностным натяжением. Скорее всего оно связано с пенообразованием и может быть объяснено с помощью теории устойчивости пены.