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Brief communication

An analytical model for nucleate pool boiling with surfactant additives

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1. Introduction

Surfactants are known to enhance nucleate pool boiling heat transfer. A number of investigators have published experimental studies regarding boiling enhancement by means of anionic, cationic and non-ionic surfactant additives to the boiling liquid. Several hypotheses about the surfactant boiling enhancement mechanism were published, but no qualitative model has been developed. Jontz and Myers (1960) have studied the effect of dynamic surface tension on nucleate boiling. They measured deviation from equilibrium of the liquid–vapor surface tension of a growing bubble in an aqueous surfactant solution. They found considerable deviation in presence of the surfactant Tergitol, and almost no deviation in presence of the surfactant Aerosol. In the heat transfer measurements they found that Aerosol was a much better boiling enhancer. Therefore they concluded that enhanced boiling heat transfer coefficient could not be correlated with liquid–vapor dynamic surface tension alone. Wu et al. (1995) conducted nucleate boiling experiments with nine surfactant additives. They concluded that there is no correlation between the enhancement of the heat transfer coefficient and equilibrium liquid–vapor decrease in surface tension by the surfactant additives. Instead, they suggested that future explanation should rely on the Marangoni effect, as suggested earlier by Yang (1990). Wu et al. (1998) have studied experimentally nucleate pool-boiling enhancement with SDS and Triton X-100 surfactant additives. Their conclusion was that nucleate boiling heat transfer coefficients could not be correlated with equilibrium and dynamic liquid–vapor surface tensions. They correlated boiling heat transfer coefficient enhancement with the vapor bubble occupied area increase. Tzan and Yang (1990) showed in their experimental study of nucleate pool boiling with SLS surfactant additive, that there is an optimum additive concentration to increase the heat fluxes. Hetsroni et al. (2001)

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studied experimentally nucleate pool boiling with Habon G surfactant additive. They obtained the boiling curves for various surfactant concentrations. Some of those boiling curves exhibit non-monotonous (“S-shaped”) behavior with respect to wall superheat. They also found an optimum additive concentration to increase the heat fluxes, which was associated with the critical micelle concentration (c.m.c.). In the present study, liquid–vapor and solid–liquid surface tensions are postulated to be controlled by a surfactant diffusion mechanism. Hence, expressions for them are obtained from basic equations. Substituting these expressions in the Rohsenow (1962) nucleate pool boiling correlation, yields an explicit expression for the boiling curve as a function of surfactant bulk concentration. If the surfactant affects the two surface tensions in an opposite manner, e.g., decreases liquid–vapor surface tension and increases solid–liquid surface tension, a non-monotonous boiling curve could be expected, in some circumstances, to be obtained from this model.

2. Formulation

The contact angle between a solid and a liquid–vapor interface is given by Young’s equation:

$$\cos \theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}} \quad (1)$$

where σ_{SG} , σ_{SL} , and σ_{LG} are solid–vapor, solid–liquid, and liquid–vapor surface tensions, respectively.

The surface tension at the liquid–vapor interface in the presence of an adsorbate (surfactant) is given by the Gibbs equation:

$$d\sigma_{LG} = -\bar{R}T\Gamma_{LG}d(\ln x) \quad (2)$$

where \bar{R} is the molar universal gas constant, T is the temperature, Γ_{LG} is the surfactant excess molar amount at the liquid–vapor interface, and x is the dimensionless surfactant concentration in the bulk liquid.

Surfactant can be adsorbed to the solid at the solid–liquid interface by a variety of mechanisms, with either its hydrophilic or hydrophobic group attached to the solid, depending on the system’s physical and chemical properties (Rosen, 1989). Therefore, the unattached group is in contact with the liquid instead of the attached solid below it, and the overall surface tension at that interface is changed. For a portion of surface coated with homogeneously distributed surfactant, the overall surface tension can be calculated as a spatial average:

$$\sigma_{SL} = (1 - \bar{A}\Gamma_{SL})\sigma_{SL}^0 + \bar{A}\Gamma_{SL}\sigma_{\text{Surf-L}} \quad (3)$$

where \bar{A} is net area occupied by a mole of surfactant adsorbed to the surface, Γ_{SL} is the surfactant excess molar amount at the solid–liquid interface, σ_{SL}^0 is solid–liquid surface tension of an interface with no adsorbate excess mass, and $\sigma_{\text{Surf-L}}$ is the surface tension between the liquid and the unattached group of the surfactant. Introducing a molar free energy difference coefficient: $\bar{\alpha} = \bar{A}(\sigma_{\text{Surf-L}} - \sigma_{SL}^0)$, yields:

$$\sigma_{SL} = \sigma_{SL}^0 + \bar{\alpha}\Gamma_{SL} \quad (4)$$

Assuming no surfactant is present in the vapor phase, the solid–vapor interface can be considered to contain no adsorbed surfactant. Therefore, solid–vapor surface tension is approximately independent of bulk liquid surfactant concentration:

$$\sigma_{SG} \approx \sigma_{SG}^0 \quad (5)$$

Due to the transient nature of the ebullition mechanism, the amount of adsorbate at the interfaces is not the equilibrium amount. This deviation from equilibrium may be assumed to be diffusion controlled and may be correlated with the ebullition associated velocity in the vicinity of the solid–liquid and liquid–vapor interfaces. Assuming quasi-equilibrium and one component velocity (parallel to the interface), neglecting the parallel conduction term in comparison to the parallel convection term, due to the high velocity along the interface, and approximating the adsorption rate to be linear, the surfactant surface transport equation for an interface is:

$$U \frac{d\Gamma}{d\xi} - k(\Gamma^{\text{Eq.}} - \Gamma) = 0 \quad (6)$$

where Γ and $\Gamma^{\text{Eq.}}$ are local and equilibrium surfactant excess molar amounts at the interface, respectively, ξ is a coordinate parallel to the interface, beginning from the interface leading edge, U is the parallel velocity, and k is the adsorption rate coefficient. Bulk diffusion of the surfactant has been neglected due to the high stirring velocity that exists in the vicinity of the heater during boiling. Therefore, the adsorption rate coefficient, k , accounts for the whole process of surfactant migration to the interface from the near bulk. Since the leading edge is the location of the onset of adsorption to a moving element of the interface, the boundary condition for this equation is:

$$\Gamma(\xi = 0) = 0 \quad (7)$$

The solution of the surfactant surface transport equation (Eq. (6)) with the boundary condition of Eq. (7) is:

$$\Gamma = \Gamma^{\text{Eq.}}(1 - e^{-k\xi/U}) \quad (8)$$

In order to obtain an effective Γ for the bubble departure process, a characteristic distance between the leading edge and the location of relevance to Young's equation at bubble departure should be determined: $\xi = l$. The leading edge is considered to be the location of the triple contact line at its onset, where Eq. (7) is assumed to hold, and the location of relevance to Young's equation at bubble departure is the location of the triple contact line at bubble departure. Then, a surfactant velocity coefficient for adsorption could be set: $D = kl$. This coefficient depends on physical and surface properties through k and l . Therefore, with these postulated parameters, the solutions for the liquid–vapor and solid–liquid interfaces are, respectively:

$$\Gamma_{LG} = \Gamma_{LG}^{\text{Eq.}}(1 - e^{-D_{LG}/U}) \quad (9)$$

$$\Gamma_{SL} = \Gamma_{SL}^{\text{Eq.}}(1 - e^{-D_{SL}/U}) \quad (10)$$

where D_{LG} and D_{SL} are liquid–vapor and solid–liquid surfactant velocity coefficients for adsorption, respectively.

U can be taken as a velocity scale of the process (as in Rohsenow, 1962):

$$U = \frac{q''}{\rho_G h_{LG}} \quad (11)$$

where q'' is heater heat flux, ρ_G is vapor density, and h_{LG} is the latent heat of vaporization. This velocity scale can be considered to be a characteristic vapor velocity. As such, it is assumed to scale the triple contact line velocity during the ebullition cycle, which is relevant to Eqs. (9) and (10).

The equilibrium amount of adsorbate at every interface may be assumed to obey a Freundlich isotherm:

$$\Gamma_{LG}^{Eq.} = m_{LG} x^{1/n_{LG}} \quad (12)$$

$$\Gamma_{SL}^{Eq.} = m_{SL} x^{1/n_{SL}} \quad (13)$$

where m_{LG} , n_{LG} , m_{SL} , and n_{SL} are constants of the system.

Substituting Eq. (12) in Eq. (9) and the result in Eq. (2), and integrating Eq. (2) from 0 to x , at the saturation temperature, $T \approx T_{Sat.}$, yields the liquid–vapor surface tension as a function of surfactant bulk concentration and the heat flux:

$$\sigma_{LG} = \sigma_{LG}^0 - \bar{R}T_{Sat.} n_{LG} m_{LG} x^{1/n_{LG}} (1 - e^{-\rho_G h_{LG} D_{LG}/q''}) \quad (14)$$

where σ_{LG}^0 is liquid–vapor surface tension of an interface with no adsorbate excess mass. Substituting Eq. (13) in Eq. (10), and then in Eq. (4), gives an expression for σ_{SL} . Substituting this expression along with Eq. (14) in Eq. (1), and solving for θ , yields the contact angle as a function of surfactant bulk concentration and heat flux:

$$\theta = \cos^{-1} \left[\frac{\sigma_{SG}^0 - \sigma_{SL}^0 - \bar{\alpha} m_{SL} x^{1/n_{SL}} (1 - e^{-\rho_G h_{LG} D_{SL}/q''})}{\sigma_{LG}^0 - \bar{R}T_{Sat.} n_{LG} m_{LG} x^{1/n_{LG}} (1 - e^{-\rho_G h_{LG} D_{LG}/q''})} \right] \quad (15)$$

Taking, for example, the Rohsenow (1962) forced convection analogy as the nucleate boiling model, namely:

$$C^{1/r} \frac{q''}{\mu_L h_{LG}} \left[\frac{\sigma_{LG}}{g(\rho_L - \rho_G)} \right]^{1/2} \theta^{1/r} = Pr_L^{-s/r} \left[\frac{c_{pL}(T_{Wall} - T_{Sat.})}{h_{LG}} \right]^{1/r} \quad (16)$$

where μ_L is liquid dynamic viscosity, c_{pL} is liquid specific heat capacitance at constant pressure, Pr_L is liquid Prandtl number, g is the acceleration due to gravity, T_{Wall} is the wall (heater) temperature, and r , s and C are empirical constants.

Solving Eq. (16) for wall temperature yields:

$$T_{Wall} - T_{Sat.} = C \frac{Pr_L^s h_{LG}}{c_{pL} \left\{ \mu_L h_{LG} [g(\rho_L - \rho_G)]^{1/2} \right\}^r} q''^r \sigma_{LG}^{r/2} \theta \quad (17)$$

By substituting the obtained expressions for σ_{LG} and θ from Eqs. (14) and (15), respectively, an equation of the boiling curve (wall temperature vs. heat flux, solved explicitly for wall temperature) as a function of surfactant bulk concentration is obtained. In dimensionless form:

$$\frac{c_{pL}(T_{\text{Wall}} - T_{\text{Sat.}})}{h_{\text{LG}}} = CPr_L^s \left[\frac{q'' \sqrt{\sigma_{\text{LG}}^0 - \bar{R}T_{\text{Sat.}}n_{\text{LG}}m_{\text{LG}}x^{1/n_{\text{LG}}}(1 - e^{-\rho_G h_{\text{LG}} D_{\text{LG}}/q''})}}{\mu_L h_{\text{LG}} \sqrt{g(\rho_L - \rho_G)}} \right]^r \times \cos^{-1} \left[\frac{\sigma_{\text{SG}}^0 - \sigma_{\text{SL}}^0 - \bar{\alpha}m_{\text{SL}}x^{1/n_{\text{SL}}}(1 - e^{-\rho_G h_{\text{LG}} D_{\text{SL}}/q''})}}{\sigma_{\text{LG}}^0 - \bar{R}T_{\text{Sat.}}n_{\text{LG}}m_{\text{LG}}x^{1/n_{\text{LG}}}(1 - e^{-\rho_G h_{\text{LG}} D_{\text{LG}}/q''})}} \right] \quad (18)$$

3. Results and discussion

In order to verify model's validity, we fit it to experimental data from Hetsroni et al. (2001), considering water solutions of the surfactant Habon G. According to these experimental data, certain available physical properties of the bulk liquid were taken as of pure water at saturation: $T_{\text{Sat.}} = 373 \text{ K}$, $\rho_L = 958.3 \text{ kg/m}^3$, $\rho_G = 0.597 \text{ kg/m}^3$, $h_{\text{LG}} = 2256.7 \text{ kJ/kg}$, $c_{pL} = 4.22 \text{ kJ/kg K}$, $\mu_L = 277.53 \text{ } \mu\text{Ns/m}^2$, $Pr_L = 1.72$, $\sigma_{\text{LG}}^0 = 0.059 \text{ N/m}$. The constants s and r were given generally recommended values (Carey, 1992): $s = 1$, $r = 0.33$, and the constant C is to be set for best fit. Unavailable physical and system properties were given plausible values that fit experimental results of liquid–vapor surface tension and of the boiling curve: $\sigma_{\text{SG}}^0 - \sigma_{\text{SL}}^0 = 0.035 \text{ N/m}$, $\bar{\alpha}m_{\text{SL}} = 0.093 \text{ N/m}$, $m_{\text{LG}} = 1.229 \times 10^{-5} \text{ mole/m}^2$, $n_{\text{SL}} = 7.245$, $n_{\text{LG}} = 5.050$, $D_{\text{SL}} = 0.334 \text{ m/s}$, $D_{\text{LG}} = 0.854 \text{ m/s}$. The constant C was set to a value of: $C = 0.0202$. These values are believed to be in an accepted range for the properties they represent. Being determined for model's possible validity evaluation only, those values were also not formally optimized for best fit. Using the values set above, a plot of σ_{LG} (Eq. (14)) and $\sigma_{\text{SG}} - \sigma_{\text{SL}}$ as a function of heat flux, for various surfactant bulk concentrations, is presented in Fig. 1. Fig. 2 presents a plot of θ (Eq. (15)) as a function of heat flux for various surfactant bulk concentrations. Boiling curves for various surfactant bulk concentrations (Eq. (18)) are plotted in Fig. 3, with experimental results from Hetsroni et al. (2001). The dashed line in the boiling curve is calculated for surfactant concentration which is above the c.m.c. At these conditions the diffusion mechanism is known to be slow compared with below-c.m.c. conditions (Cussler, 1997), so the surfactant velocity coefficient for adsorption is expected to decrease. However, for Habon G there are not enough post-c.m.c. experimental results, to determine quantitatively those changes, so the dashed line was plotted using best fitted reduced values of D : $D_{\text{SL}} = 0.297 \text{ m/s}$, $D_{\text{LG}} = 0.557 \text{ m/s}$. Other properties were not changed. It is also worth noting that x in the Freundlich isotherm refers to monomer surfactant, so at post-c.m.c. conditions, where monomer surfactant concentration is practically constant with respect to total surfactant concentration, x has the value of the c.m.c. The boiling curves for below-c.m.c. conditions generally fit the experimental results using the set values. However, it is important to notice that the model idealizes the heater as a homogeneous surface. Real surface inhomogeneity can result in local deviation of physical properties from those calculated. It is presumed that should this model be considered acceptable for below-c.m.c. conditions, other properties, besides surfactant velocity coefficients for adsorption, are probably altered at post-c.m.c. conditions. Moreover, the postulated diffusion and adsorption mechanisms might be altered at these conditions, undermining post-c.m.c. validity of their here-used formulation. It should be noted that the experimental results of Hetsroni et al. (2001) were obtained with a

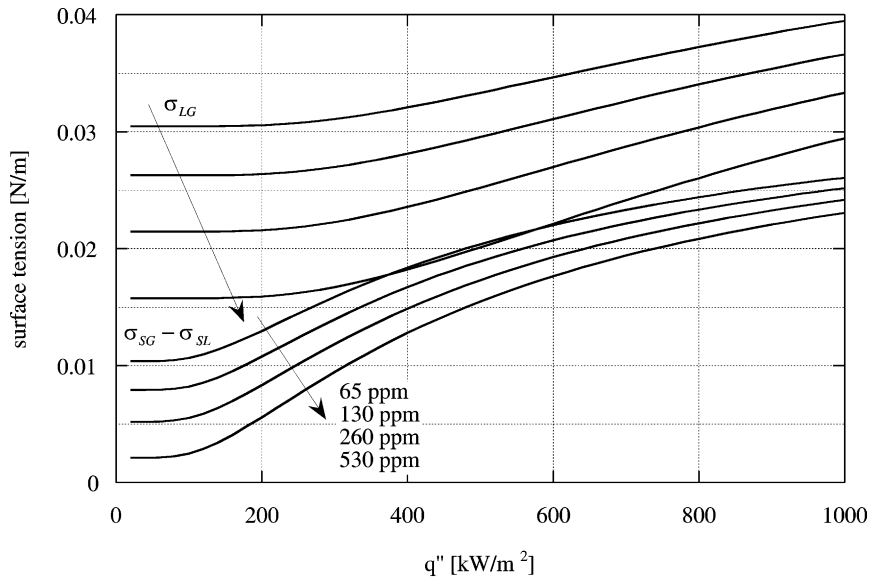


Fig. 1. Theoretical surface tensions of liquid–vapor and solid–vapor minus solid–liquid interfaces as a function of heat flux for various Habon G concentrations.

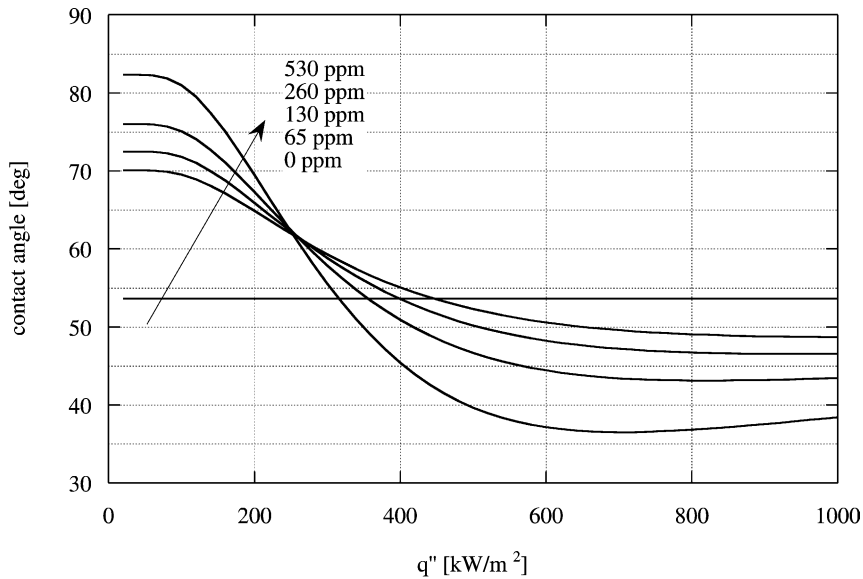


Fig. 2. Theoretical contact angle as a function of heat flux for various Habon G concentrations.

metallic heater and a cationic surfactant. Being a heated metal, the heater was probably a slightly negatively charged, hydrophilic surface. Therefore it is reasonable to assume that the adsorbed cationic surfactant at the solid–liquid interface was attached to the solid metal with its hydrophilic group. As a consequence hydrophobic groups of surfactant were in contact with the liquid at the

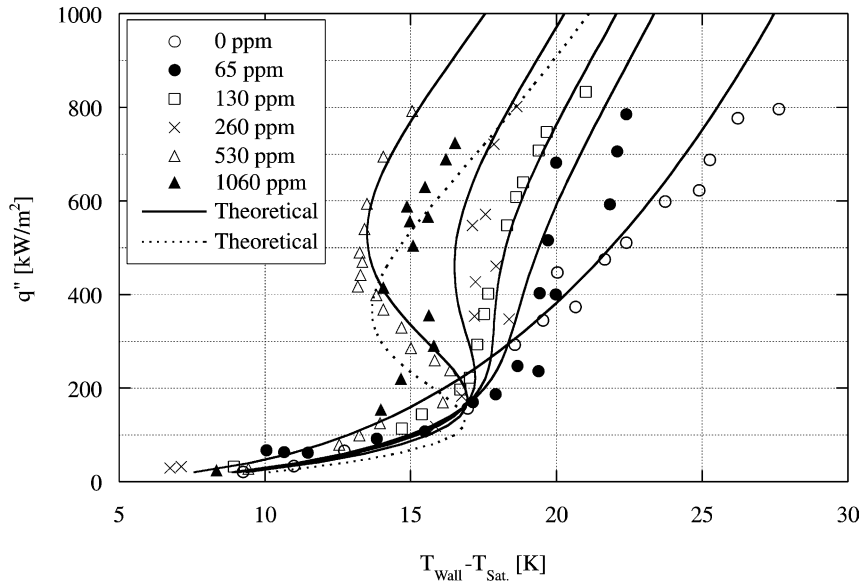


Fig. 3. Boiling curve: comparison between theoretical and experimental results for various Habon G concentrations.

solid–liquid interface, instead of the hydrophilic metal below them. In that case $\bar{\alpha}$ is a positive value, and hence, the overall solid–liquid surface tension is increased. Mathematical analysis of Eq. (18) shows that only positive values of $\bar{\alpha}$ can, in some circumstances, generate a non-monotonous, “S-shaped” boiling curve, as in the experimental results. This fact is consistent with the physical reasoning.

4. Conclusions

A first general model of nucleate pool boiling with surfactant additives was developed. Liquid–vapor and solid–liquid surface tensions were postulated to be surfactant diffusion controlled, and expressions for them were derived from basic equations. Using those expressions in the Rohsenow (1962) nucleate pool boiling correlation, yielded an explicit expression for the boiling curve as a function of surfactant bulk concentration. When the surfactant has an opposite effect on the two surface tensions, a non-monotonous (“S-shaped”) boiling curve could be generated, in agreement with experimental data of Hetsroni et al. (2001). The model was successfully fitted to these data.

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