Boiling enhancement with environmentally acceptable surfactants

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Abstract
Saturated and subcooled pool boiling of environmentally acceptable surfactant solutions, on a horizontal tube, was investigated experimentally. The kinetics of boiling (bubble nucleation, growth and departure) was investigated by high-speed video recording. Boiling curves for various concentrations were obtained and compared. The results show that the bubble behavior and the heat transfer mechanism for the surfactant solution are quite different from those of pure water. Specific features of boiling of nonionic surfactant solutions were revealed.

Keywords: Pool boiling; Heat transfer enhancement; Nonionic surfactant; Environmentally acceptable; Boiling curve

1. Introduction
Boiling is a very effective and efficient mode of heat transfer, and it is encountered in numerous engineering applications. One important field of application of boiling and evaporation is in desalination of seawater, which is becoming essential in some arid regions. Boiling with surfactant additives, is generally an exceedingly complex process, and it is influenced by a larger set of variables than the phase-change process of pure water. Besides the wall heat flux (or wall excess temperature), heating surface geometry, and bulk concentration of additives, the boiling behavior is also dependent upon interfacial properties, the nature of the additive, its chemistry, foaming etc.

The study of the saturated pool boiling of a surfactant solution shows a significant enhancement of heat transfer (Wasekar and Manglik, 2000; Hetsroni et al., 2001). It was shown by Sephton (1974) that addition of small amounts of surfactants to seawater could substantially enhance the boiling desalination process. Yang and Maa (1983) showed that the surface tension of the surfactant solution had significant influence on the heat transfer coefficient at boiling of a dilute sodium lauryl benzene sulfonate and sodium lauryl sulfate solution. Pool boiling experiments were carried out by Tzan and Yang (1990) for a wide range of surfactant concentrations and heat fluxes. The results verify again that a small amount of surface-active additive makes the nucleate boiling heat transfer coefficient considerably higher. It was also found, that for some additives, the heat transfer increases at low concentration of surfactant, reaches a maximum and decreases with further increase in the concentration. Wu et al. (1995) reported experimental data on the effect of surfactants on nucleate boiling heat transfer in water with nine different additives. Anionic, cationic, and nonionic surfactants were studied at concentration up to 400 ppm. The enhancement of heat transfer was related to the depression of the static surface tension. Boiling heat transfer coefficients were measured by Ammerman and You (1996) for an electrically heated platinum wire immersed in saturated water, and in water mixed with three different concentrations of sodium dodecyl sulfate (an anionic surfactant). Their results showed that addition of an anionic surfactant to water caused an increase in the convection component and a corresponding reduction in the latent heat component of the heat flux in the fully developed boiling region. The comprehensive reviews on the heat transfer in nucleate pool boiling of aqueous surfactants and polymeric solutions have been

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published by Kandlikar and Alves (1999) and by Wasekar and Manglik (1999). It was shown that surfactant additives at low concentrations could enhance the nucleate boiling heat transfer significantly. The subcooled pool boiling of cationic surfactant solution at various concentrations was studied by Hetsroni et al. (2002). It was found that the subcooled nucleate boiling of surfactants could not be described by a single curve, in contrast to water. They also noted a significant enhancement of the heat transfer and showed drastic change in the bubble structure next to the heated tube wall.

Unfortunately, most of surfactants are not suited for industrial systems because of degradation and because of their environmental impact. That is why we have begun to study an enhancement of boiling by alkyl polyglycosides. They are nonionic surfactants with negligible environmental impact (von Rybinski and Hill, 1998). Their production from the renewable resources glucose and fatty alcohol and their ultimate biodegradation is an example for a closed cycle. We used Alkyl (8–16) Glucoside (Plantacare 818 UP) with molecular weight of 390 g/mol for our experiments.

We have used some other kind of surfactant in our previous study (Hetsroni et al., 2001) for the boiling enhancement. It was the cationic surfactant Habon G of molecular weight 500 g/mol. The cation of this surfactant is hexadecyldimethyl hydroxyethyl ammonium and the counter-ion is 3-hydroxy-2-naphthoate. The kinetics of surfactant adsorption and desorption, associated with its diffusion in the bulk fluid and the vapor–liquid interface, might be altered by the different electrostatic interactions induced by its ionic nature. These interactions also tend to govern the development of the interfacial concentration sublayer, thereby influencing the boiling behavior.

The main objective of the present investigation is to study the boiling heat transfer and bubble dynamics in the nonionic surfactant solution with negligible environmental impact at various concentrations of surfactant and different heat fluxes. A comparison of the results of this study with the ones reported for cationic and anionic surfactants provides information on the influence of an ionic nature of aqueous surfactant solutions on the pool boiling.

2. Experimental

2.1. Rheological properties of surfactant solutions

The solution was prepared by dissolving the surfactant (52% active substance and 48% water) in deionized water, with gentle stirring over a period of a one-day. The measurements of the physical properties were carried out at the Department of Chemical Engineering, Ohio State University (Hetsroni et al., 2004).

The shear viscosity was determined with Rheometrics Fluids Spectrometer RFS II using a Couette system. The standard deviation is 4%. The shear viscosity of the surfactant solution for two temperatures at various concentrations is shown in Fig. 1.

The surface tension data were obtained by using a SensaDyne PC500-LV Surface Tensiometer System.

![Fig. 1. The shear viscosity of the surfactant solution: (a) T = 25 °C; (b) T = 60 °C.](image_url)
This system measures the surface tension within the body of a test fluid by blowing a bubble of gas through two probes of different diameters inside the fluid. The measurements of surface tension were carried out for different concentrations of surfactant solutions over a range of temperature from 300 to 368 K with standard deviation of 2%.

In Fig. 2 the equilibrium surface tension, $\sigma$, is plotted vs. the concentration of the surfactant solution at different temperatures. An increase in the surfactant concentration up to $C = 300$ ppm (parts per million weight) leads to significant decrease in the surface tension, whereas the surface tension is almost independent of concentration in the range $300 \leq C \leq 1200$ ppm. In all cases an increase in a liquid temperature leads to a decrease in the surface tension.

### 2.2. Apparatus

Two sets of apparatus were used. Fig. 3 shows the one designed for the study of pool boiling on a horizontal stainless steel tube. The experimental facility consists of a rectangular vessel (140 mm long, 90 mm wide and 100 mm deep) with transparent walls, a thermostat to regulate the bulk fluid temperature, the heated tube, two copper bars and electric contacts.

The heated part of the tube ($d_{\text{out}} = 1.5$ mm, $d_{\text{in}} = 1.0$ mm) was 40 mm long. It was fixed in a horizontal position along the longitudinal centerline of the pool at a distance of 40 mm from the bottom. Electric current was supplied to the heated tube through copper bars from a DC power supply. A calibrated, Teflon coated, T-type thermocouple of diameter 0.3 mm was inserted inside the heated tube. The thermocouple could be adjusted exactly to any desired position in the heated tube. The temperature of the outer surface was calculated from the power dissipation per unit volume of the tube. The measurements showed that the temperature along the tube was uniform.

The apparatus for studying the bubble growth is depicted in Fig. 4. The objective of these experiments was to study bubbles growing in a fixed cavity. The vessel was filled with the investigated liquid (water or surfactant solution) where a saturation temperature of the liquid was maintained at normal pressure. The bubble generation was studied on a horizontal stainless steel foil of 0.05 mm thickness. The natural roughness of the surface (of the order of 0.1 $\mu$m) was used to produce bubbles. The cone-shaped heater was moved up to contact with lower surface of the foil. The contact pressure was regulated by special traverse mechanism and controlled by a dynamometer.

The growth of bubbles and the bubble motion near the heated surface were recorded by a high-speed video camera with recording rate up to 10,000 frames per second. The playback speed can be varied from a single frame to 25 frames per second.

### 2.3. Procedure

The heating surface was cleaned routinely before and after each set of three data points with a sequence of operations involving application of constantan cleaner and washing with hot tap water and deionized water.
Only a soft sponge and absorbent paper tissues contacted the stainless steel foil, which remained smooth and completely wettable.

During a typical run, the boiler was loaded with 1500 ml of liquid to bring the surface to a level 70–80 mm above the heater. Steady state boiling was achieved in 10–20 min after the supplementary heater was turned on. This was determined by monitoring the temperature of the solution. Surfactant solutions were replaced with fresh samples after three runs. This precaution was taken in order to minimize changes in solution properties, which might have occurred at high temperature due to evaporation over long periods of time.

While renewing the liquid, the heater surface was examined. No visible deposits formed under the test conditions, based on observations in the test runs and after draining the boiler. Room temperature was maintained at 23°C, so that heat losses from the boiler would be nearly constant in all runs.

2.4. Uncertainty analysis

The electrical power was determined with an accuracy of 0.5%. The surface heat flux was calculated by measuring the power delivered to the heated surface and by determination of heat losses. The temperature of the heated surface and of the working fluid was measured by 0.3 mm type-T thermocouples. The thermocouples and the data acquisition system were calibrated at the steam point and ambient water temperature, and yield uncertainty values within 0.3 K at these two conditions. The estimated accuracy in the calculation of the saturation temperature is 0.1 K. In order to calculate the deviations associated with the measurement of various quantities, readings were taken for a few runs every 2 min over a period of 20 min. The uncertainty analysis was performed according to the ASME Policy on Reporting Uncertainties in Experimental Measurements and Results. The results of the uncertainty analysis are given in Table 1, where the bias limit is an estimate of the magnitude of the fixed constant error. The precision limit is an estimate of the lack of repeatability caused by random errors and unsteadiness.

### Table 1

<table>
<thead>
<tr>
<th>Item</th>
<th>Designation</th>
<th>Bias limit B</th>
<th>Precision limit P (%)</th>
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<td>1 kW/m²</td>
<td>2.0</td>
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<tr>
<td>Wall temperature</td>
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<td>0.3 K</td>
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</tr>
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<td>2.0</td>
</tr>
<tr>
<td>Saturation temperature</td>
<td>$T_s$</td>
<td>0.1 K</td>
<td>0.2</td>
</tr>
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</table>

3. Results

3.1. Boiling behavior

The evolution of vapor bubbles in a boiling liquid, in particular the growth of bubbles is one of the parameters determining the intensity of the heat transfer from a heated surface. The growth of the bubble in the liquid containing surfactants is affected by a number of specific factors. The pool boiling experiments were carried out under atmospheric pressure. The bubble behavior was recorded at 1000 frames per second by the high-speed camera. The typical pictures of bubble growth for this study are shown in Fig. 5a and b. The field of view is 40×30 mm in the horizontal and vertical directions, respectively. Fig. 5a shows a bubble forming in water. It can be seen that the bubble has a regular shape. As the bubble grows, its shape is changed to ovoid necking at the foil surface. Soon after the neck appeared, the bubble center accelerated upward. The bubble is detached when the buoyant force just overcomes the surface tension. A different situation arises with the bubble growing in surfactant solution. Fig. 5b shows the typical

![Fig. 5. Bubble growth on a flat surface in a liquid at saturated boiling, (q = 110 kW/m²); (a) water; (b) Alkyl (8–16) Glucoside of 600 ppm solution.](image-url)
bubble coalescence before detachment in 600 ppm surfactant solution. It presents a cluster of small bubbles, which rise from the cavity. These bubbles are adjacent to each other and the cluster neck is not observed.

Boiling in surfactant solutions, when compared with that in pure water, was observed to be more vigorous. Surfactant solutions promote activation of nucleation sites in a clustered mode, especially at lower heat fluxes. After the onset of nucleate water boiling on the pipe, the regime of single bubbles occurs close to the heated wall. For pure water, the average bubble size was observed to slightly increase with increasing the heat flux. Fig. 6a shows a typical picture for water boiling on the pipe of outer diameter 1.5 mm at heat flux \( q = 600 \) kW m\(^{-2}\). A population of bubbles was observed in the vicinity of the heated tube. The bubbles have an irregular shape at all values of heat flux. Fig. 6b shows boiling of the 600 ppm surfactant solution under the same conditions. The surfactant additive reduces significantly the tendency of coalescence between vapor bubbles. The bubbles grow continuously and collapse on the tube. The bubbles are smaller in size but much larger in number than in the case of pure water. They appear on the heated tube in quite an orderly manner. Here, too, there is a weak tendency toward increasing the average bubble diameter as heat flux increases. In this case, the shape of bubbles is closer to spherical, than for pure water.

A decrease in the bubble size at boiling in the surfactant solution may be attributed to a decrease in the surface tension compared to the clean water. However, it should be pointed out that the change in surface tension may not be the only explanation for the effect of surfactant (Yang and Maa, 2001).

3.2. Boiling curves

The saturated pool boiling experimental data with surfactant solution are shown in Fig. 7 as a function of the heat flux vs. the heater excess temperature (space-time average values at the fluid-solid interface). For each concentration and heat flux twelve runs were performed: six runs with increasing heat flux and six ones with decreasing heat flux. Each point in Fig. 7 represents an average value obtained from these measurements. We did not observe any signs of a hysteresis. Under conditions of nucleate boiling the pool boiling temperature, \( T_s \), of surfactant solutions did not differ from that of pure water.

The wall temperature of the heated tube decreases monotonically with an increase in the concentration of the alkyl polyglycosides solution, in contrast to SDS and Habon G solutions. Tzan and Yang (1990) demonstrated that the effect of surfactant additives on nucleate boiling heat transfer decreases, when the concentration of SDS solution was higher than 700 ppm. The analogous data on the decrease in the heat transfer for 1060 ppm Habon G solution reported by Hetsroni et al. (2001). The critical micelle concentration (c.m.c.) for the surfactant used here was obtained from the equilibrium adsorption isotherm as the value at which the slope of the isotherm finished to change abruptly. As it is seen from Fig. 2 this value is about 300 ppm. Low c.m.c. value for nonionic surfactant has been attributed to an absence of any electrical repulsion. From Fig. 7 one can

![Fig. 7. Boiling curves with nonionic surfactant solution at various concentrations.](image-url)
see that even if the concentration of surfactant solution is beyond c.m.c. further increase in the concentration affects the boiling curve and shifts it towards the left. Note, that in this case the surface tension almost does not change.

In the literature there are some contradictions about the role of surface tension. Wasekar and Manglik (2002) reported the results of a study that investigated the dependence of nucleate boiling heat transfer coefficient of aqueous surfactant solutions on the additives’ molecular weight and ionic nature. Two anionic (SDS and SLES) and two nonionic (Triton X-100 and Triton X-305) surfactants at various concentrations were used. The boiling performance, characterized by an early onset of nucleate boiling, was significantly enhanced, and the maximum enhancement increased with decreasing surfactant molecular weight, M. The heat transfer coefficient, normalized by dynamic surface tension, $h^*$, scales as $h^* \sim M^n$ with $n = -0.5$ and $n = 0$ for anionics and nonionics surfactants, respectively. It should be noted that dependence the $h^* \sim M^n$ was determined only for four surfactants considered by Wasekar and Manglik (2002).

Criteria for nucleate boiling enhancement by surfactant additives were proposed by Yang and Maa (2001). As the first criterion, it was postulated that the surfactant should be soluble in water. As the second criterion, it was postulated that the surfactant should depress the equilibrium surface tension of water significantly. As the third criterion, it was postulated that the surfactant should not depress the equilibrium contact angle significantly. According to Yang and Maa (2001), boiling heat transfer with an addition of the surfactant is enhanced by the depression of the equilibrium surface tension but suppressed by the depression of equilibrium contact angle.

4. Subcooled boiling

This study was conducted to investigate pool boiling phenomena of environmentally acceptable surfactants at various levels of subcooling. For a subcooled liquid, the system bulk temperature $T_B$ was maintained below the saturation temperature $T_s$ at a given system pressure. The difference between the saturation and system temperature is the degree of subcooling.

Tests were conducted in the same pool at three different water temperatures: $T_B = 40, 60, 80$ °C. In Fig. 8 the heat flux is plotted vs. wall excess temperature ($T_W - T_s$), where $T_W$ is the temperature of the heated surface. Previous investigators (Johannsen, 1991; Hong et al., 1997) have reported that this temperature difference allowed presenting the boiling data for all levels of subcooling by a single boiling curve. It can be concluded from Fig. 8 that boiling data for subcooling levels of 60, 40 and 20 K may be described by a single curve with a standard deviation of 12%. This merging of data indicates that the boiling curve is insensitive to the subcooling level in the range of examined temperatures. Carey (1992) reported that the boiling curve usually changes very little with an increase in the level of subcooling. Judd and Hwang (1976) observed independence of the wall temperature vs. level of subcooling in methylene chloride at boiling on a flat glass surface. Mudawar and Anderson (1989) discussed the effects of subcooling in pool boiling of FC-72 on vertically mounted flat heaters. There was no substantial difference in the boiling characteristic, during nucleate boiling for two different levels of subcooling 20 and 35 K. Our data agree well with results reported by previous investigators.

The shape of boiling curves obtained in the present study for subcooled boiling of nonionic surfactant solutions did not differ significantly from that reported by Hetsroni et al. (2002) for cationic surfactant Habon G. In both sets of experiments we did not observe any signs of S-shape boiling curve. One may conclude that ionic nature of surfactant and surface tension cannot be used for explanation of boiling behavior under subcooled pool boiling. We assume that the difference between boiling curves for saturated and subcooled boiling is due to change in the contact angle.

5. Discussion

The unusual behavior of boiling curves for solutions of nonionic surfactants raises a number of interesting questions. Is the observed S-shape of saturated boiling curve the result of an interaction between surface tension and elasticity? If so, the addition of polymer solutions to water may produce the same phenomenon. Does a decrease or an increase in the heat flux affect boiling curve in different ways depending on kind of
saturant? Another question relates to the ionic nature of surfactant.

The interesting results were presented by Hartnett (1991) for pool boiling behavior of aqueous hydroxyethyl cellulose polymer solutions (Trade name Natrosol marketed by Hercules Co.). The pool boiling behavior of the Natrosol showed that at concentration less than 1500 ppm, solutions behaved like water, but for solutions above 1500 ppm there was considerable decrease in the temperature difference \( T_w - T_s \). Photographic evidence revealed that the bubbles associated with the high concentration Natrosol solutions were generally smaller, more numerous than in the water pool boiling experiments. The same phenomenon was observed in the present study. It may be concluded that behavior of boiling curve was caused by interaction between surface tension and elasticity.

Yang et al. (2002) experimentally investigated saturated nucleate pool boiling in aqueous solutions of Triton SP-190 and Triton SP-175 on a horizontal tubular heater. During an increase in heat flux, boiling incipience excursion was found for Triton SP-190, \( C = 120 \) ppm and Triton SP-175, \( C = 110 \) ppm. Once boiling commenced, the excess superheat was quickly released by vigorous boiling, resulting in an abrupt temperature drop. The authors assumed that the temperature overshoot was due to deactivation of large nucleate sites that were penetrated by highly wetting liquid. The boiling curve of Triton SP-175, \( C = 110 \) ppm obtained during decreasing heat flux did not differ from that of water.

On the other hand the experimental results of Tzan and Yang (1990) shows a set of decreasing legs of boiling curves for water containing anionic surfactant of various concentrations. The additive used in this work was sodium lauryl sulfate (SLS). The excess superheat at concentration of \( C = 100 \) and \( C = 300 \) ppm decreases for heat flux higher than \( q = 150 \) kW/m\(^2\), i.e. the boiling curves have so-called S-shape.

Saturated nucleate boiling on a horizontal cylindrical heater in aqueous surfactant solutions, which have different molecular weights and ionic character, has been experimentally investigated by Wasekar and Manglik (2002). Two anionic surfactants, sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES), and two nonionic surfactants, Triton X-100 and Triton X-305 were used. Their molecular weights was 288.3, 422, 624 and 1526, respectively. The concentration varied from \( C = 200 \) to 10,000 ppm for SDS and SLES; from \( C = 20 \) to 200 ppm for Triton X-100, and from \( C = 50 \) to 10,000 ppm for Triton X-305. The behavior of boiling curves did not differ from that of water.

The S-shape boiling curves for solutions of cationic surfactant Habon G (molecular weight is 500) were obtained by Hetsroni et al. (2001). The concentration of solutions varied from \( C = 65 \) to 1060 ppm. For each concentration the runs were performed as for increasing heat flux as for decreasing heat flux. Any signs of hysteresis were not observed.

Comparison of studies discussed in this section indicates that the ionic nature of the surfactant and molecular weight cannot explain the unusual behavior (S-shape) of boiling curves obtained for some kind of solutions. The experiments conducted with increasing heat flux and with decreasing heat flux also did not clarify the phenomenon.

Some of the mechanisms to elucidate the S-shape behavior of boiling curve have been proposed by Sher and Hetsroni (2002). The authors developed a model of nucleate pool boiling with surfactants additives. Solid–vapor, solid–liquid, and liquid–vapor surface tensions were postulated to be surfactant diffusion controlled, and expressions for them were derived. Using these expressions the boiling curve was obtained as a function of surfactant bulk concentration. The model was compared to experimental boiling curves obtained by Hetsroni et al. (2001) for pool boiling of cationic surfactant. Comparison between theoretical and experimental results shows good agreement.

6. Conclusions

The experimental results are summarized as follows: The addition of small amount of environmentally acceptable alkyl glycosides makes the boiling behavior quite different from that of pure water. For water, bubble action is seen to be extremely chaotic, with extensive coalescence during the rise. Bubbles formed in surfactant solutions were much smaller than those in water and the surface became covered with them faster. The boiling excess temperature becomes smaller and the vapor bubbles are formed more easily. Boiling in surfactant solutions, when compared with that in pure water, was observed to be more vigorous. Surfactant solutions promote activation of nucleation sites in a clustered mode, especially at lower heat fluxes.

The boiling curves of alkyl glycosides under conditions of saturated boiling are quite different from the boiling curve of pure water. Experimental results demonstrate that the heat transfer of the boiling process can be enhanced considerably by the addition of a small amount of surfactant. The heat transfer increases monotonously at an increase in the concentration.

The study of pool saturated boiling indicates that the ionic nature of the surfactant and molecular weight cannot explain the unusual behavior (S-shape) of boiling curves obtained for some kind of solutions. The experiments conducted with increasing heat flux and with decreasing heat flux also did not clarify the phenomenon.
The boiling curve of the surfactant solution at subcooling depends on its concentration. Every surfactant solution, at given concentration, behaves as new liquid having common boiling curve at various level of subcooling.

The shape of boiling curves obtained in the present study for subcooled boiling of nonionic surfactant solutions did not differ from that reported by Hetsroni et al. (2002) for the cationic surfactant Habon G. In both sets of experiments we did not observe any signs of S-shape boiling curve. As in the case of the pool saturated boiling one may conclude that the ionic nature of surfactant and the surface tension cannot explain the boiling behavior under subcooled conditions. We assume that the difference between boiling curves for saturated and subcooled boiling is due to a change in the contact angle.

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