

Heat Transfer in Pool Boiling with Surfactants

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Abstract

Boiling with surfactant is important in many key industrial applications such as the petrochemical processing, refining, refrigeration, hygiene and personal care, pharmaceutical, and food processing, among others.

The aims of this study are experimental determination of the heat transfer coefficient with and without the addition of surfactants to pure water and quantify the effects of surfactant concentration, ionic nature, its ethoxylation, and molecular weight on the nucleate boiling performance of water on vertical cylindrical heater.

Several different surfactants were employed: [SDS(Sodium Dodecyl Sulfate), SLES (Sodium Lauryl Ether Sulfate) (anionic)]and [Triton X-100 (Octylphenol Ethoxylate) (nonionic)], they have different molecular weights, ionic nature and number of ethylene oxide EO groups attached to its polar head.

The boiling results show that with the addition of small amounts of surfactants, the saturated nucleate pool boiling heat transfer coefficient of water is found to be altered due to reduction in the surface tension and this enhances the heat transfer. The enhancement in nucleate pool boiling depends upon wall heat flux (or temperature difference), concentration of surfactant, ionic nature, molecular weight and number of (EO) group. The heat transfer coefficient is found to increase by as much as (81.9%) over that for pure water for SDS solutions while (53 %) for SLES and (45 %) for Triton X-100 at CMC (critical micelle concentration).

The enhancement increases with concentration and the enhanced solutions are found to be with $C \leq CMC$. The optimum enhancement is at or near the CMC of surfactants. However, the maximum heat transfer enhancement is in the order of $SDS > SLES > Triton X-100$, this is also, in the reverse order of their molecular weights and number of (EO) groups.

Keywords: Nucleate Pool Boiling, Surfactant Effect.

انتقال الحرارة في الغليان الحوضي بوجود مُثبّطات الشد السطحي

الخلاصة

الغليان بوجود مُثبّطات الشد السطحي مهم في العديد من التطبيقات الصناعية مثل: الصناعات البترولية، الكيماوية، المصافي، التليج، الصحة والعناية الشخصية، الصيدلة والصناعات الغذائية. كان الهدف من البحث هو حساب معامل انتقال الحرارة تجريبياً في حالة إضافة مُثبّطات الشد السطحي أو عدم إضافتها للماء النقي وكذلك للتكهن بمدى تأثير كلاً من تركيز مُثبّطات الشد السطحي، طبيعتها الأيونية، عدد مجاميع أوكسيد الاتلين المرتبطة برأسها ووزنها الجزيئي على سلوك الغليان المتتوي للماء.

تم استخدام عدد من مُثبّطات الشد السطحي مثل SDS و SLES (الأيونية) و Triton X-100 (الغير أيونية) والتي تختلف في الوزن الجزيئي، الطبيعة الأيونية وعدد مجاميع أوكسيد الاتلين. لقد

بينت نتائج الغليان بأنه عند إضافة كميات صغيرة من مثبطات الشد السطحي فإن معاملات انتقال الحرارة في الغليان المتنوي المشبع للماء تتغير نتيجة لتقليل الشد السطحي وبذلك يُحسن انتقال الحرارة. لوحظ أن التحسن في الغليان الحوضي المتنوي يعتمد على الفيض الحراري (أو الاختلاف بدرجات الحرارة)، تركيز مثبطات الشد السطحي، طبيعتها الأيونية، أوزانها الجزيئية، وعدد مجاميع أوكسيد الأثلين.

وجد أن نسبة التحسن في معامل انتقال الحرارة هو (81.9%) لمحاليل SDS بينما تكون (53%) لمحاليل SLES و (45%) لمحاليل Triton X-100 مقارنة مع الماء النقي عند التركيز الحرج (CMC).

التحسن يزداد مع التركيز، حيث وجد أن تحسن المحلول عند $C \leq CMC$ وأفضل تحسن هو عند أو حول التركيز الحرج لمثبطات الشد السطحي. من ناحية أخرى، أقصى تحسن في انتقال الحرارة هو في الترتيب $SDS < SLES < Triton X-100$ وكذلك في ترتيب معكوس من ناحية أوزانها الجزيئية وعدد مجاميع أوكسيد الأثلين.

Nomenclature

A	Heat transfer surface area	$[m^2]$
C	Concentration of surfactants	$[ppm]$
d_b	Bubble departure diameter	$[m]$
I	Current	$[Amp]$
L	Heater length	$[mm]$
h	Heat transfer coefficient	$[kW/m^2.K]$
M	Molecular weight	$[kg/kmol]$
P	Pressure	$[N/m^2]$
q_w''	Wall heat flux	$[kW/m^2]$
T	Temperature	$[K]$
V	Voltage	$[Volt]$
ΔT_{sat}	Wall superheat or temperature difference	$[K]$
	$[T_w - T_{sat}]$	

Greek Symbols

	Enhancement	
α	heat transfer coefficient in equation (9)	$[-]$
ρ	Density	$[kg/m^3]$
σ	Surface tension	$[N/m]$
f	Contact angle in equation (7)	$[deg]$

Abbreviation

CMC	Critical Micelle Concentration	$[ppm]$
EO	Ethylene Oxide	$[-]$
SDS	Sodium Dodecyl Sulfate	$[-]$
SLES	Sodium Lauryl Ether Sulfate	$[-]$
Triton X-100	Octylphenol Ethoxylate	$[-]$

Subscripts

b	Bulk
l	Liquid
v	Vapor
Sat.	Saturation

1. Introduction

The existence of several regimes of boiling was first clearly discussed by Nukiyama as cited in [23]. These regimes include the nucleate boiling, transition boiling and the radiation zone.

With its ability to transfer large amounts of heat in relatively small temperature differences, nucleate boiling has attracted considerable research attention [22].

Boiling with surfactants is generally a very complex process and it is influenced by a larger set of variables in comparison to the phase-change process of pure water. Besides the wall heat flux or (temperature difference), heating surface geometry, and bulk concentration of surfactants, the nucleate boiling behavior is also dependent upon, among others, the role played by surface tension, interfacial stresses and the nucleation process. Furthermore, it appears that the boiling mechanism itself is influenced by the nature of surfactant, and its chemistry in solution [10].

The nucleate boiling of surfactants solutions has become one of the most interesting subjects in the scope of heat and mass transfer for the last twenty years because of its importance in the following fields: The petrochemical processing, liquefaction, air separation, refrigeration, power plant and electric equipment [1, 2].

Surfactants are essentially low-molecular weight chemical compounds, with molecules consisting of a combination of a water-soluble (hydrophilic) and a water insoluble (hydrophobic) part, Figure (1). The hydrophobic part is generally a long hydrocarbon chain, whereas the hydrophilic part of the

molecule may be ionic or non-ionic and usually contains only one polar group [3, 4].

Depending upon the nature of the hydrophilic head group, surfactants can be primarily classified as anionics, nonionics, cationics, and zwitterionics [5].

Surface tension reduction of an aqueous solution decreases continually with increasing concentrations till the critical micelle concentration CMC is reached, at which point the surfactant molecules cluster together to form micelles. All surfactants in their solutions show significant changes in adsorption behavior at or around their respective CMC. The CMC is characterized by micelle formation, or micellization, which is the property of surface-active solutes that leads to the formation of colloid-sized clusters, i.e., at a particular concentration, additives form aggregates in the bulk phase or a surfactant cluster in solution that are termed micelles [6, 7].

2. Experimental Work

2.1 Systems Studied

Aqueous solutions of anionic surfactants (SDS, SLES) and nonionic (Triton X-100) having different concentrations (measured as the ppm) were prepared by dissolving weighted samples in pure water.

The boiling curve for pure water was first established. The water data provide the baseline reference for the surfactant solution results.

The concentrations of each surfactant that have been used in this study were:

1). Anionic surfactants:

SDS :(300, 600, 900, 1250, 2500, 5000, 10000) ppm.

SLES :(250, 500, 1000, 2000, 4000) ppm.

2). Nonionic surfactant:

Triton X-100 (100,200, 400, 600, 800) ppm.

2.2 Experimental Procedure:

1. The unit was charged with water until the level of water in the cylinder was (20 – 30) mm above the top of the heater.
2. The electric heater was adjusted to about (30) watts and the water flow rate was adjusted until the desired pressure was about (1atm) and then the voltage, current, vapor pressure, liquid temperature and metal temperature were observed.
3. The power was increased to (100) watts; and the cooling water flow rate was adjusted to give the desired pressure. When water started to boil vigorously, the pressure release valve steam was pulled out to release any air in the cylinder.
4. When water reached saturation temperature and steady state conditions, the current, voltage, liquid temperature, and wall temperature were recorded. The power input was then increased at an equal intervals and the same operation was repeated.

2.3 Determination of Heat Flux and Nucleate Pool Boiling Heat Transfer Coefficient:

All the heat generated in these experiments was from the heater. The energy generated by the heater can be calculated using the current (I) and the voltage (V).

$$\text{Power (J/sec)} = I \text{ (Amperes)} \cdot V \text{ (volts)} \quad \dots (1)$$

At steady state, heat from the heater is transferred to the test fluid while some is lost through natural convection from the glass this can be translated into the following energy balance.

$$\text{Power} = q_{\text{losses}} + q_{\text{liquid}} \quad \dots (2)$$

The heat transfer term for liquid (q_{liquid}) can be determined from its heat capacity (C_{PL}) and temperature difference as shown below:

$$q_{\text{liquid}} = m C_{PL} (T_{\text{out}} - T_{\text{in}}) \quad \dots (3)$$

The heat transfer due to natural convection (q_{losses}) can be determined from Newton's law :

$$q_{\text{losses}} = h_{\text{air}} A_{\text{glass}} (T_{\text{bulk}} - T_{\text{ambient}}) \quad \dots (4)$$

$$\begin{aligned} \text{The net of heat} &= \text{Power} - q_{\text{losses}} \\ &= m C_{PL} (T_{\text{out}} - T_{\text{in}}) \quad \dots (5) \end{aligned}$$

Since the capacity of the electric heater is (300) watt and the area of the heater is equal to (0.001986) m², the heat flux ($q_w'' = q_w/A$) is designed to vary uniformly in six different levels as follows (38.10, 48.66, 61.35, 74.08, 86.78, 101.60) kW/m², so that the heat transfer coefficient can be solved using the following equation

$$h = q_w'' / (T_w - T_{\text{sat}}) \quad \dots (6)$$

More experimental details are found in Ref. [21].

3. Results and Discussion:

Nucleate pool boiling experiments and the measured heat transfer performance of aqueous solutions of the three different surfactants are described.

The results of solutions of different concentrations are presented, and the optimum enhancement in heat transfer is identified. In addition, the effects of the molecular weight and ionic nature and ethylenoxide (EO) of the surfactants are delineated.

3.1 Pool Boiling without Surfactants:

Figure (4) shows the saturated nucleate boiling data for pure water, and its comparison with the cylindrical steel - heater/water data available due to Borishanskii [8] and

other researchers such as Shakir et al. [9]; Wesekar [10] and Zhang [11].

Borishanskii's data is based on the principles of thermodynamic similitude.

The experimental data of present work agree very well with both Borishanskii's data and other researchers' data, and they provide an accurate baseline reference for the nucleate boiling performance of the surfactant solutions described in the next section.

Figure (5) shows the measured heat transfer coefficient in the present work as a function of heat flux. The results illustrate that the heat transfer coefficient increases as heat flux increases. In Figure (5), comparisons are also made with the Peyghambarzadeh et al. data [12], and found the experimental data of this study agree very well with his data (maximum error of 15%).

3.2 Pool Boiling with Surfactants:

The experimental data for pool boiling of various concentrations of aqueous anionic (SDS and SLES) and nonionic (Triton X-100) surfactant solutions are presented, respectively, in Figures (6, 7, and 8).

In general, with the addition of surfactant to water, the nucleate boiling curve shifts to the left indicating enhancement in heat transfer. This can be seen, in Figures (6, 7, and 8) for SDS, SLES and Triton X-100 aqueous solutions respectively.

Boiling with surfactant solutions, when compared with that in pure water, was observed to be more vigorous. The surfactant additive reduces significantly the tendency of coalescence between vapor bubbles. The bubbles grow continuously and collapse on the surface heater. The bubbles are smaller but much larger in

number than in the case of 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 pure water.

Lower values of σ allow departure of smaller-sized bubbles because of the reduction in surface tension force at the heater surface that counters the buoyancy force trying to pull the bubble away from the surface.

This is consistent with the well-established Fritz equation [13],

$$d_b = 0.0208 f \sqrt{\frac{s}{g(r_l - r_v)}} \quad \dots (7)$$

which suggest bubble departure diameter is directly proportional to σ .

These mechanism vapor bubbles contribute significantly towards enhancing heat transfer.

3.3 Optimum Heat Transfer and Critical Micelle Concentration (CMC):

A closer inspection of Figures (9, 10 and 11), reveals that an optimum heat transfer enhancement is typically obtained over a concentration range around CMC of the respective surfactant.

The concentration of surfactant at which micellization begins is called the critical micelle concentration (CMC).

The process of micelle formation characterizes this range of concentration [14], and for the surfactants tested in this work, this concentration range is (2500 - 4000 ppm for SDS, 1000 - 1500 ppm for SLES, and, 200 - 300 ppm for Triton X-100).

Several investigators have developed empirical relationships

between the CMC and the structural features of surfactants. Becher calculated the coefficients for the linear relationship between the logarithm of the CMC, the number of ethylene oxide (EO) and the number of carbon atoms (C) in hydrophobic part for surfactants

$$\log CMC = a - b C + d EO \dots\dots (8)$$

With $a = (1.646 \pm 0.082)$, $b = (0.496 \pm 0.08)$ and $d = (0.0437 \pm 0.0094)$.

The CMC is affected by several factors like as hydrophobic group, hydrophilic group, and temperature [15].

The markedly different behavior of heat transfer performance for pre- and post-micellar surfactant solutions can be seen from Figures (9,10 and 11) which give a typical enhancement plot quantifying the extent of heat transfer enhancement in nucleate boiling of SDS,SLES and Triton X-100 solutions.

The results are graphed in the form of heat transfer coefficient defined as:

$$\frac{h - h_{water}}{h_{water}} = \frac{(q''_w / \Delta T_{sat}) - (q''_w / \Delta T_{sat})_{water}}{(q''_w / \Delta T_{sat})_{water}} = a \dots\dots (9)$$

Figure (9) shows a maximum enhancement of (81.9%) for 2500 ppm aqueous SDS solution while (53 %) for SLES and (45 %) for Triton X-100 at CMC Figure (10 and 11) .The repeated decreases and increases are probably connected with the hydrodynamic situation prevailing.

In addition to improving heat transfer in solutions with $0 < C \leq CMC$, Figure (9) clearly shows the decrease in boiling heat transfer enhancement in 5000 ppm and 10000 ppm SDS solutions at ($C > CMC$).

3.3.1 Effect of Concentration:

The experiments were carried out to study the effect of concentration on nucleate pool boiling heat transfer coefficient.

Figures (12, 13 and 14) show different influence of SDS concentration on nucleate boiling heat transfer coefficient for heat different fluxes. It was observed that on increasing the concentration of surfactants the nucleate boiling heat transfer coefficient increases and the optimum heat transfer enhancement is found to be around CMC.

At low concentration, surfactant molecules arrange themselves at the interface in the form of monomers with their hydrophilic part inside water and the hydrophobic part away from the interface. This results in an appreciable reduction in the surface tension at the interface. This process continues with increasing concentrations until CMC is reached, at which point no more molecules can be arranged at the interface. The surfactant molecules then cluster together inside water to form micelles.

In addition, it was found that temperature difference (ΔT_{sat}) decreases with increasing amount of surfactant and tends to increase heat transfer coefficients and the optimum heat transfer enhancement is at CMC.

Figure (15), shows that at (2500 ppm) CMC gives less temperature difference and optimum heat transfer enhancement. A similar trend can be obtained for SLES (CMC=1000 ppm) and Triton X-100 (CMC=200 ppm) in Figures (16 and 17).

3.3.2 Effect of Surfactant Molecular

Weight:

Figure (18) provides insights on the role of surfactant molecular weight and ethoxylation, of their solutions and show the maximum heat transfer enhancement is in the order of SDS >SLES >Triton X-100. This is in the reverse order of their respective molecular weights and EO groups.

The rate of relaxation and hence the value of the surface tension is a function of surfactant molecular weight and number of EO group present in it [16,17].

It can be observed that in the entire range of concentrations employed in this study departure diameter for SDS is always less than SLES. The main reason for this occurrence is the difference in molecular weight and EO groups among the anionic surfactants. The surfactant molecules with lesser molecular weight (and no EO group) diffuse faster than their heavier counterpart towards the rapidly growing and departing interface [17]. This results in faster relaxation of surface tension at the liquid-vapor interface in the case of SDS (as compared with SLES) resulting in smaller bubbles departing quickly. This correlates well with the greater enhanced heat transfer observed in SDS as compared with SLES. The departure diameter for SDS and SLES continues to decrease even after reaching the CMC.

3.3.3 Effect of Ethoxylation:

Furthermore, except for SDS, the [SLES and Triton X-100] surfactants tested in the present study have EO group in their hydrocarbon chain.

The presence of ethylenoxide (EO) group increases the overall size

of the polar head and makes the surfactant more hydrophilic Such that they occupy a larger area at the interface than the SDS molecule [16].

Consequently, in comparison with SDS, lower concentrations of SLES, Triton X-100 are required to depress σ by the same amount.

For the present data, the addition of EO groups decreases the CMC value and increases σ at CMC for anionic surfactants, Figure (18).

Both σ and CMC values increase with increasing number of EO groups in nonionic surfactants [10].

The EO groups in a molecule of polyoxyethylated sulfate (SLES in the present work) act as a hydrophobic group, in contrast to the situation of nonionic surfactants [18]. this hydrophobicity of EO groups in anionics could be caused either by genuine contribution to hydrophobicity or by an enlargement of the distances between the charged sulfate groups from each other [19].

3.3.4 Effect of Ionic Nature:

In general, nonionics show higher σ relaxation and lower CMC values in comparison to anionics. The CMC for the three cases are (200 ppm for Triton X-100, 1000 ppm for SLES, and 2500 ppm for SDS) in Figures (14, 13, and 12) respectively. The lower values of CMC observable with nonionic surfactants have been attributed to the absence of any electrical repulsion, which could oppose micelle formation unlike that associated with anionic surfactants [16, 20].

4. Conclusions:

The salient features of this work can be summarized as follows:

1. The heat transfer in saturated nucleate boiling of aqueous surfactant solutions is found to be enhanced considerably. The

optimum nucleate boiling heat transfer performance enhancement is generally observed to be at or around CMC of the surfactant in the order SDS > SLES > Triton X-100, which is in the reverse order of their respective molecular weights and EO groups.

2. The maximum enhancement in nucleate pool boiling is found to be dependent upon wall heat flux (or temperature difference), surfactant concentration, molecular weight and its EO groups.
3. The heat transfer generally increases with surfactant concentration (C) up to a $C \leq CMC$. Depending on C, the heat transfer coefficient is found to increase by as much as (81.9%) over that for pure water for SDS (a low molecular weight ionic surfactant and zero EO group) solutions. With $C > CMC$, the enhancement decreases and the heat transfer coefficients approach those for pure water.

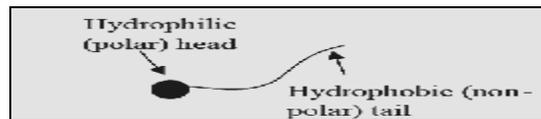
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Table (1) Physio-chemical properties of various surfactants analyzed in this study [16].

Surfactant (Chemical Name)	<i>SDS</i>	<i>SLES</i>	<i>Triton X-100</i>
Chemical Formula	$C_{12}H_{25}SO_4Na$	$C_{12}H_{25}(OCH_2CH_2)_3SO_4Na$	$C_{14}H_{21}(OCH_2CH_2)_{9-10}OH$
Ionic Nature	Anionic	Anionic	Non-ionic
(EO group)	(0)	(3)	(9-10)
Appearance	White Powder	Slightly yellow viscous liquid	Clear liquid
Molecular weight	288.3	422	624(average)
Manufacturer	Fisher	Henkel	Union Carbide
Melting point	>206 C°	-	-
Specific gravity	0.4	1.03	1.065

**Figure (1): Schematic illustration of the primary structure of a surfactant molecule**

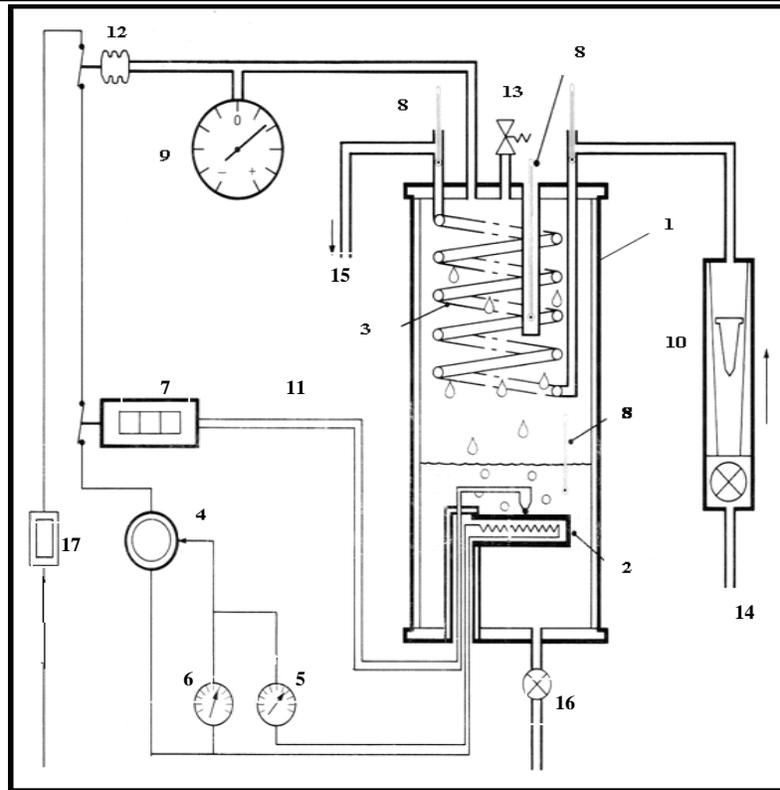


Figure (2) Schematic Diagram of the experimental setup

- | | |
|-----------------------|------------------------------|
| 1. Glass chamber | 10. Rotameter |
| 2. Heating element | 11. High temperature cut-out |
| 3. Condenser | 12. High pressure cut-out |
| 4. Variac | 13. Relief valve |
| 5. Voltmeter | 14. Cooling water inlet |
| 6. Ammeter | 15. Cooling water outlet |
| 7. Digital reader | 16. Drainage valve |
| 8. Glass thermometers | 17. Switch |
| 9. Pressure gauge | |



Figure (3): General View of Experimental setup

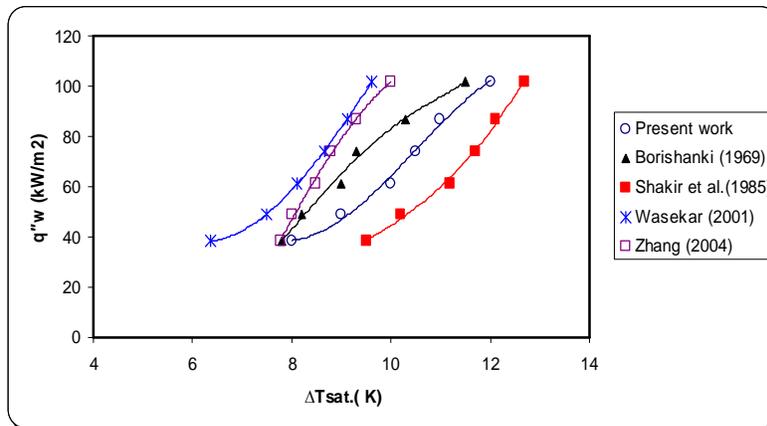


Figure (4): Variation in heat flux with temperature difference for pure water.

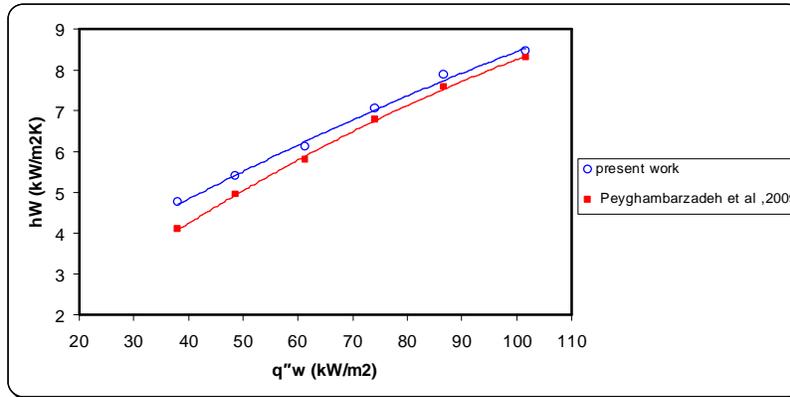


Figure (5): Pool boiling heat transfer coefficients of pure water.

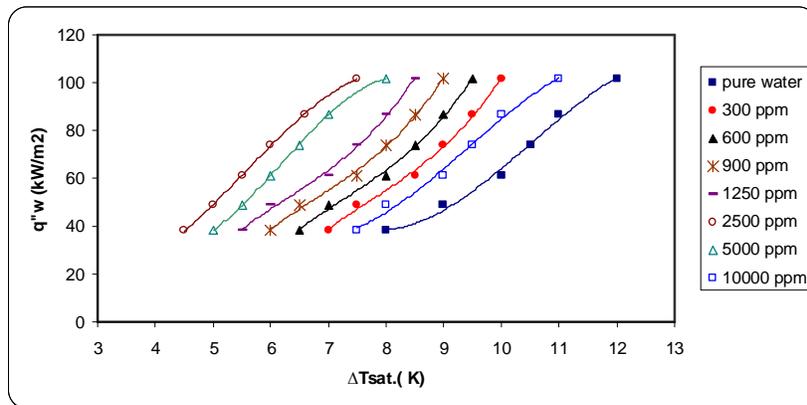


Figure (6): Pool boiling data for aqueous solutions of SDS (an anionic surfactant)

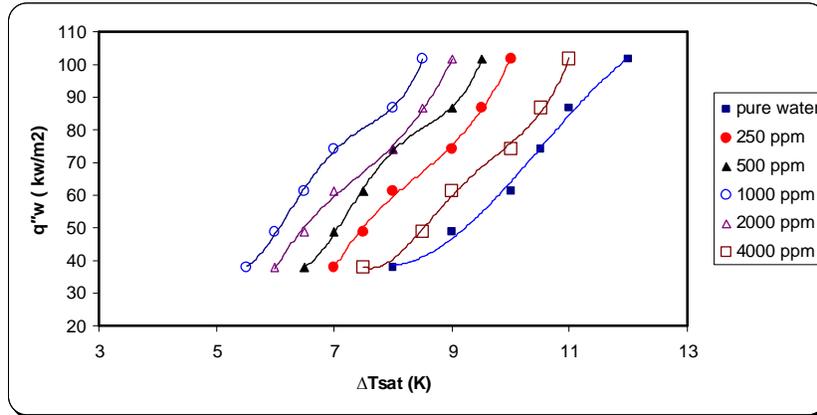


Figure (7): Pool boiling data for aqueous solutions of SLES (an anionic surfactant)

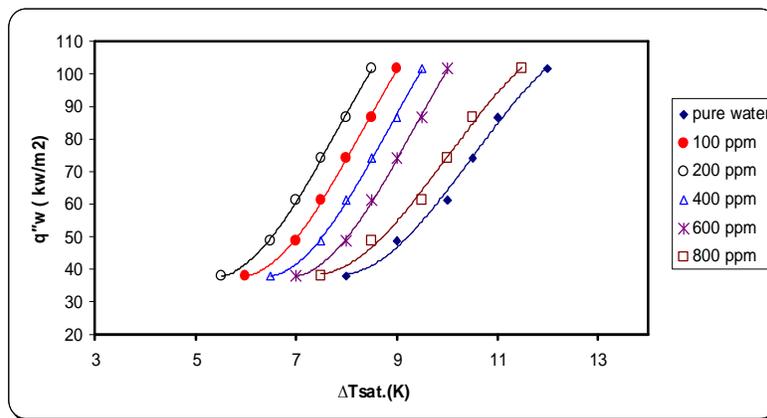


Figure (8): Pool boiling data for aqueous solutions of Triton X-100 (nonionic surfactant)

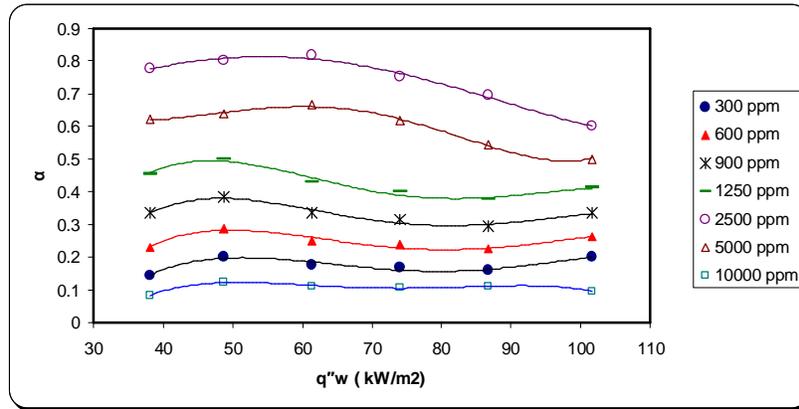


Figure (9): Heat transfer enhancement of aqueous SDS solutions and its variation with heat flux and surfactant concentration.

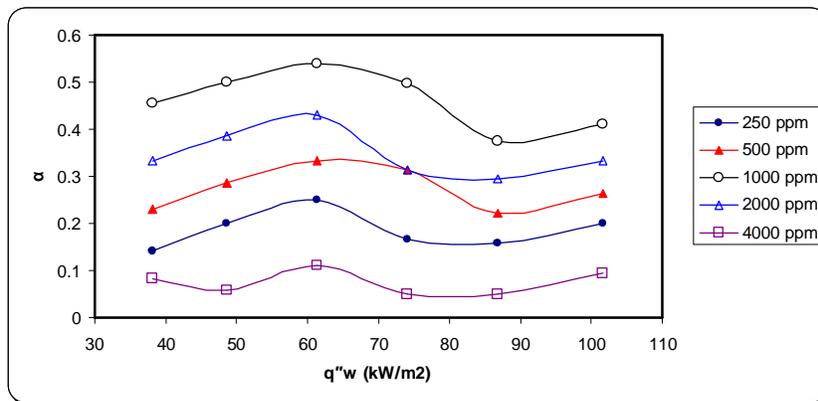


Figure (10): Heat transfer enhancement of aqueous SLES solutions and its variation with heat flux and surfactant concentration.

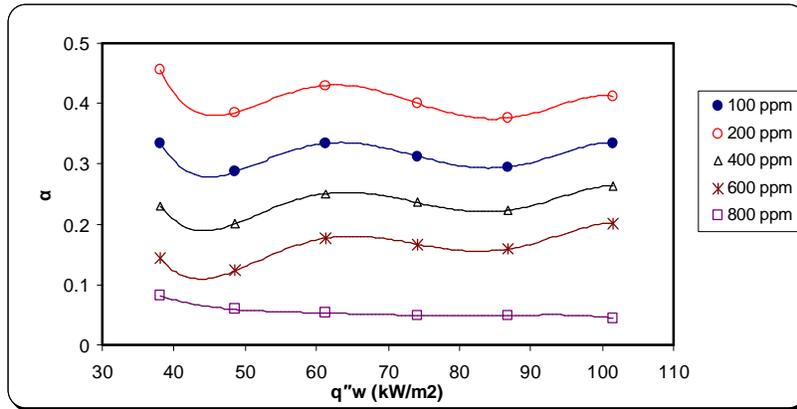


Figure (11): Heat transfer enhancement of aqueous Triton X-100 solutions and its variation with heat flux and surfactant concentration

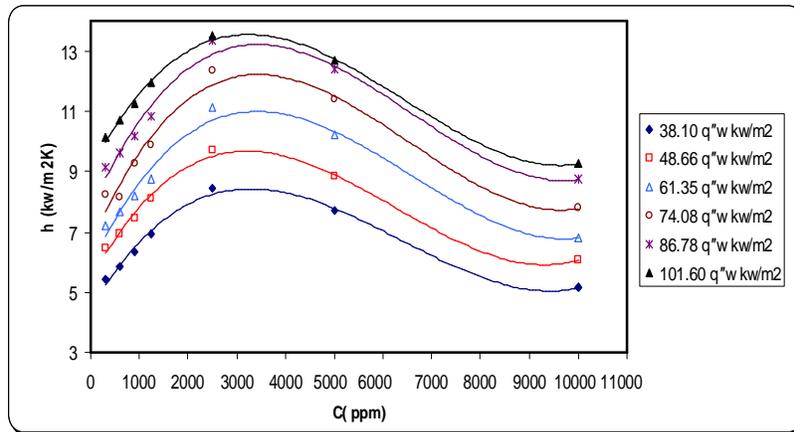


Figure (12): The effect concentration of surfactants on heat transfer coefficient at different heat fluxes of SDS

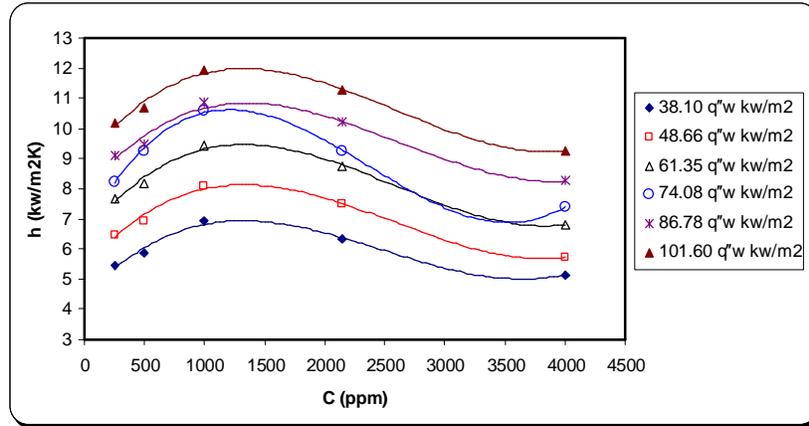


Figure (13): The effect concentration of surfactants on heat transfer coefficient at different heat fluxes of SLES.

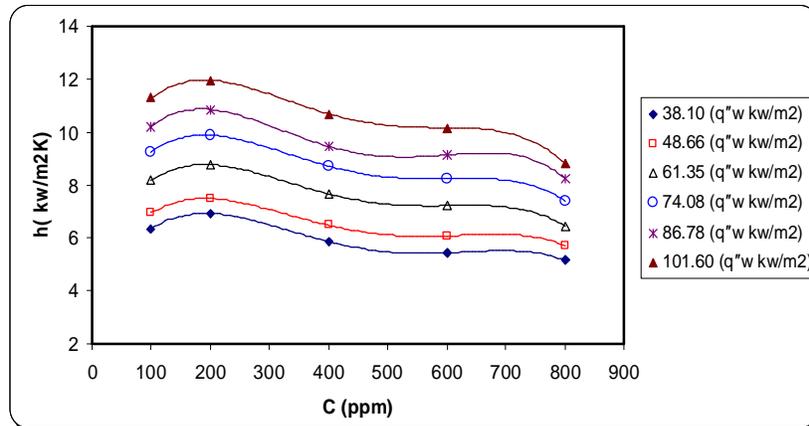


Figure (14): The effect concentration of surfactants on heat transfer coefficient at different heat fluxes of Triton X-100.

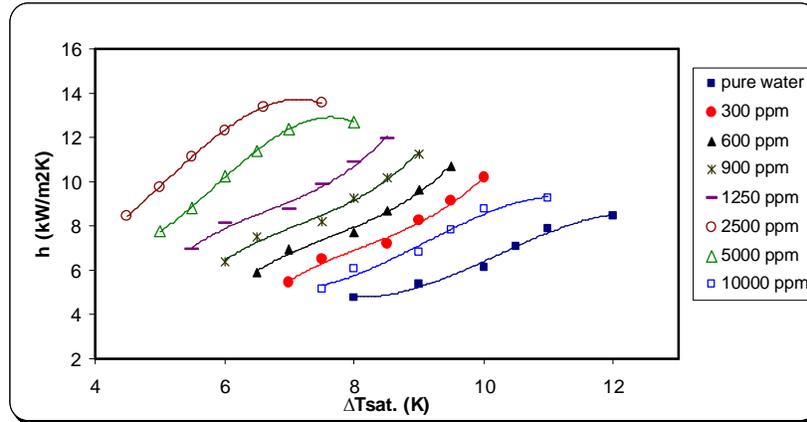


Figure (15): Nucleate boiling heat transfer coefficient as a function of temperature difference for aqueous solutions of SDS.

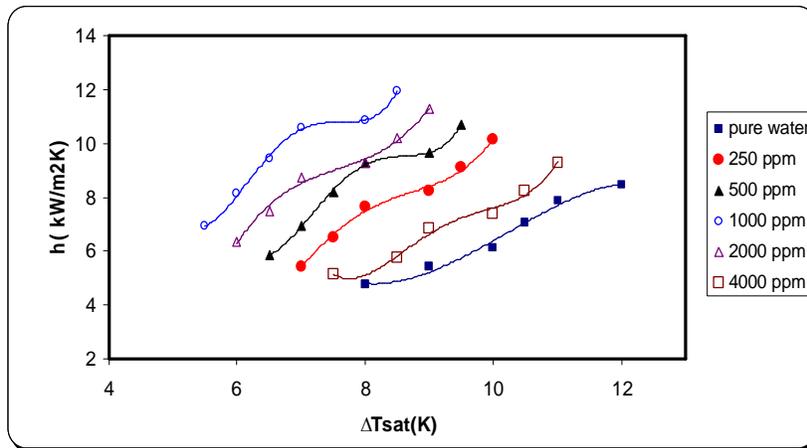


Figure (16): Nucleate boiling heat transfer coefficient as a function of temperature difference for aqueous solutions of SLES.

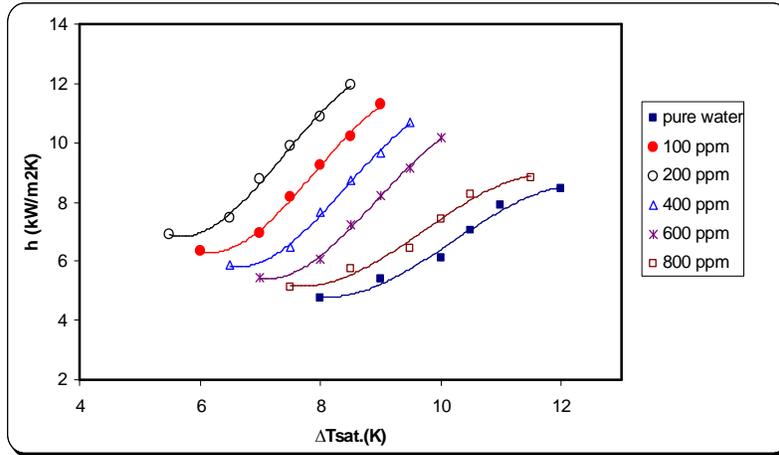


Figure (17): Nucleate boiling heat transfer coefficient as a function of temperature difference for aqueous solutions of Triton X-100.

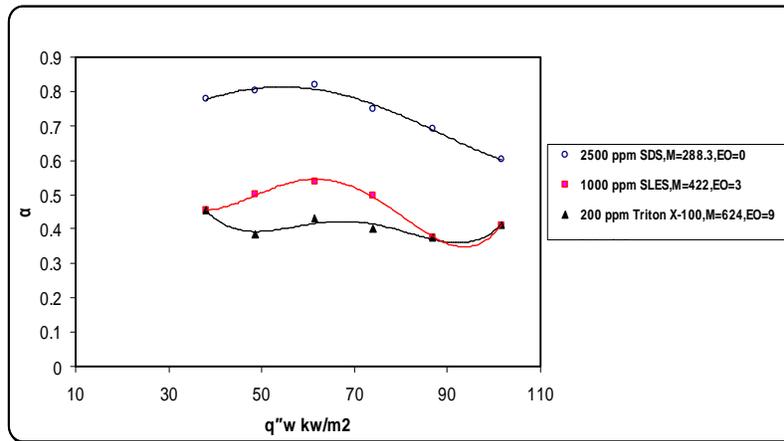


Figure (18): Effect of surfactant molecular weight and its ethoxylation on the heat transfer coefficient enhancement at variation of heat flux at CMC.