PERGAMON

International Journal of Heat and Mass Transfer 45 (2002) 483–493

International Journal of
HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

The influence of additive molecular weight and ionic nature on the pool boiling performance of aqueous surfactant solutions

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Received 29 November 2000; received in revised form 9 May 2001

Abstract

Saturated nucleate pool boiling on a horizontal cylindrical heater in aqueous solutions of surfactants, which have different molecular weights and ionic character, has been experimentally investigated. Two anionic surfactants, sodium dodecyl sulphate (SDS) and sodium lauryl ether sulfate (SLES), and two nonionic surfactants, Triton X-100 and Triton X-305, were used; their molecular weights are 288.3, 422, 624 and 1526, respectively. The boiling performance, characterized by an early onset of nucleate boiling, is significantly enhanced, and the maximum enhancement increases with decreasing surfactant molecular weight. Also, the heat transfer coefficient, normalized by dynamic σ (at 50 ms, 80°C), scales as $h \propto M^n$ with $n = -0.5$ and 0 for anionics and nonionics, respectively. This scaling follows from the postulation that the solution's dynamic surface tension is determined by the surfactant concentration and its interfacial activity in the sublayer around the growing bubble. Correspondingly, boiling of these solutions is directly influenced by the ionic character and molecular makeup of this sublayer. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Surfactants in aqueous solutions promote appreciable enhancement in nucleate boiling heat transfer of pure water [1–4]. This improvement is generally brought about by an early incipience and modified bubble dynamics (smaller-sized bubbles with increased departure frequencies and reduced coalescence). Moreover, there are several other factors that have been identified in the literature [1,3–6] for their influence on the boiling mechanisms in surfactant solutions, and these include dynamic surface tension, Marangoni convection, increased number of active nucleation sites, and the surfactant's ionic nature and molecular weight.

Phase change during boiling is a local phenomenon that is associated with the heat transfer and hydrodynamics in the vicinity of a growing vapor bubble. Because of their adsorption characteristics at an interface, surfactants form a concentration sublayer around the boiling bubble in their aqueous solutions. Consequently, the molecular makeup of this sublayer can significantly influence the boiling behavior of surfactant solutions. The concentration sublayer also determines the dynamic surface tension at the interface [7], which in turn directly influences the bubble dynamics [5]. Increasing surfactant molecular weight, accomplished by either an increase in the hydrocarbon chain length or an addition of a functional group, tends to decrease the surface tension as well as the concentration for beginning of colloidal phase (micelle) separation or micellization, commonly referred to as critical micelle concentration (c.m.c.) [8,9]. The decrease due to the hydrocarbon chain length is caused by closer packing of surfactant molecules, whereas the additional functional group such as ethoxy or ethylene oxide (EO) increases the overall size of the polar head group, thereby increasing the interface area occupied per surfactant molecule. Furthermore, surface tension measured under near-boiling conditions

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Nomenclature

A	heater surface area ($=\pi DL$) (m^2)
C	surfactant bulk concentration (wppm)
D	cylindrical heater outer diameter (mm)
h	boiling heat transfer coefficient (kW/m^2 K)
I	current (A)
k	thermal conductivity of heater material (kW/m K)
L	length of heated cylinder (mm)
M	molecular weight
n	exponent
q''_w	wall heat flux (kW/m^2)
r	radius or radial location (mm)
T	temperature (K)
ΔT_w	wall superheat (K)
V	voltage (V)
Greek symbols	
Γ_m	maximum surface-excess concentration
σ	surface tension (mN/m)
$\sigma_{50\ \mathrm{ms},80^\circ\mathrm{C}}$	surface tension at a surface age of 50 ms and 80°C temperature (mN/m)
$\sigma_{\mathrm{eq},80^\circ\mathrm{C}}$	equilibrium surface tension at 80°C (mN/m)
Subscripts	
c.m.c.	at critical micelle concentration
dyn	at dynamic condition
eq	at equilibrium condition
i	at inner surface of heater
o	at outer surface of heater
sat	at saturation temperature
SDS	pertaining to sodium dodecyl sulfate
SLES	pertaining to sodium lauryl ether sulfate
surf	pertaining to a surfactant
Triton X-100	pertaining to Triton X-100
Triton X-305	pertaining to Triton X-305
w	at heater-wall
water	pertaining to water

(elevated temperature and higher bubbling frequency) shows significant differences in surfactant adsorption kinetics relative to those under equilibrium conditions at room temperature [1,7].

Cooper [10] has suggested that the heat transfer coefficient in nucleate boiling of most pure liquids shows an inverse molecular weight dependence that scales as $h \propto M^{-0.5}$. This result is based on an extensive literature data for water, refrigerants, hydrocarbons, and cryogens, with molecular weights ranging from 2 to 200. A similar dependence appears to be applicable for boiling of two anionic surfactants (sodium dodecyl sulphate (SDS) and sodium lauryl ether sulfate (SLES)), provided the heat transfer coefficient is normalized by their respective dynamic σ [5]. However, the kinetics of surfactant adsorption and desorption, associated with its diffusion in the bulk fluid and the vapor–liquid interface, is altered by the different electrostatic interactions induced by its ionic nature [11–13]. These interactions also tend to govern the development of the interfacial concentration sublayer, thereby influencing the boiling behavior. The generalization of the molecular weight effect on the boiling heat transfer coefficient, therefore, may perhaps be dependent upon the ionic character of the surfactants as well.

This paper presents the results of a study that investigates the dependence of nucleate boiling heat transfer coefficients 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 are used in varying concentrations. The respective molecular weights of SDS, SLES, Triton X-100, and Triton X-305 are 288.3, 422, 624, and 1526. The dynamic surface tension measurements of their solutions at a surface age of 50 ms and 80°C are presented, along with their saturated nucleate pool boiling performance for both pre- and post-micellar concentrations. Finally, the normalization and scaling of the enhanced heat transfer coefficient with dynamic surface tension and molecular weight are discussed.

2. Experimental setup and procedure

2.1. Surface tension measurements

Surface tension measurements were carried out using a SensaDyne QC6000 surface tensiometer (CSC Scientific Company) that employs the maximum bubble pressure method. Dry air at 3.4 bar is slowly bubbled through a small and a large orifice probe immersed in the test fluid, which produces a differential pressure signal proportional to the fluid surface tension. The time interval between the newly formed interface and the point of bubble break-off is referred to as *surface age*, and it gives the measure of bubble growth time corresponding to the dynamic surface tension value at a given operating bubble frequency. Depending upon the bubble frequencies, the surface age can vary from as much as 50–100% of the bubble interval. By altering the bubble frequencies of air through the two probes, both static and dynamic surface tension can be measured with ±0.1 mN/m accuracy. The instrument is interfaced with a PC, and the surface tension data are recorded using Sensa-Dyne QC6000 – 5.3 software. Detailed descriptions of the solution preparation, instrument calibration, measurement uncertainties and measurement and validation procedures can be found in [7]. For the four surfactants used in this study, the relevant physico-chemical properties are listed in Table 1.

2.2. Pool boiling experiments

The experimental setup used for the pool boiling studies is shown schematically in Fig. 1(a). The inner glass tank ($230 \times 170 \times 310$ mm^3) contains the liquid pool of the aqueous surfactant solutions and the cylindrical heater. The outer glass tank ($300 \times 300 \times 290$ mm^3) has circulating mineral oil, which is fed from a constant-temperature recirculating bath (not shown in figure), to ensure that the test pool is maintained at its saturation temperature at atmospheric pressure. A water-cooled reflux condenser, along with a second coiled-tube water-cooled condenser, helps cool the excess vapor and maintain an atmospheric-pressure pool. A pressure gage (±0.0025 bar precision) is mounted on top of the boiling vessel to monitor the pressure in the pool throughout the experiment. The heating test section consists of a horizontal, gold plated, hollow copper cylinder of 22.2 mm outer diameter, 9.5 mm inner diameter, with a length of 95 mm, as shown in Fig. 1(b). The 0.0127 mm thick gold plating mitigates any surface degradation and oxidation from chemicals in the test fluids. A 240 V, 1500 W cartridge heater, with insulated lead wires, is press-fitted with conductive grease to fill any remaining air gaps and provide good heat transfer to the inside of the tube. The 88.9 mm long cartridge heater, with 6.25 mm long inactive heating zones at each end, is centrally located inside the copper tube and the gaps at each end are filled with silicone rubber to prevent water contact. The heater surface roughness, measured by an atomic force microscope has r.m.s. values ranging from 0.076 to 0.347 μm (see [1] for details).

The primary measurements for the boiling experiments consist of the heater-wall and pool-bulk temperatures, and power input to the heater. All temperature measurements were recorded using a HP-75000 data acquisition system, with an in-built ice junction and calibration curve, that was interfaced with a PC. A variac-controlled AC power supply, a current shunt (0.15 Ω with 1% accuracy), and two precision multimeters (for current and voltage measurements) provided the controls and measurements of the input electric power. At each incremental value of heat flux, the dissipated wall heat flux q''_w and the wall superheat ΔT_w were computed from the measured values of V, I, and the four wall thermocouple readings ($T_{i,r}$), from the following set of equations:

$$q''_w = (VI/A), \tag{1}$$

$$T_w = \left\{ \sum_{i=1}^{4} \left[T_{i,r} - \left(q''_w r_o / k \right) \ln(r_o/r) \right] / 4 \right\}, \tag{2}$$

$$\Delta T_w = (T_w - T_{sat}). \tag{3}$$

Here r is the radial location of thermocouples, and r_o the outer radius of the cylindrical heater. The maximum experimental uncertainties in the measured values of q''_w and ΔT_w were ±1.5% and ±0.5%, respectively, as computed using the single-sample error propagation method outlined by Moffatt [15]. Details of the experimental procedure and uncertainty analysis, along with the boiling data validation for water are given in [1].

Table 1
Physico-chemical properties of surfactants

Surfactant (Trade name)	SDS –	SLES (STANDAPOL ES-3)	Triton X-100 (TRITON X-100)	Triton X-305 (TRITON X-305)
Chemical formula	$C_{12}H_{25}SO_4Na$	$C_{12}H_{25}(OCH_2CH_2)_3SO_4Na$	$C_{14}H_{21}(OCH_2CH_2)_{9-10}OH$	$C_{14}H_{21}(OCH_2CH_2)_{30}OH$
Source	Fisher Scientific	Henkel Corporation	Union Carbide	Union Carbide
Ionic nature	Anionic	Anionic	Nonionic	Nonionic
Form	White dry powder	Water white to slightly yellow viscous liquid	Clear liquid	Transparent colorless
Molecular weight	288.3	422	624 (average)	1526 (average)
Specific gravity	0.4	1.03	1.065	1.095
Viscosity[a], cps (25°C)	–	500	240	470
Krafft point[b]	16°C	0°C	–	–
Cloud point[b]	–	–	65°C	>100°C

[a] Brookfield viscometer.

[b] See [14].

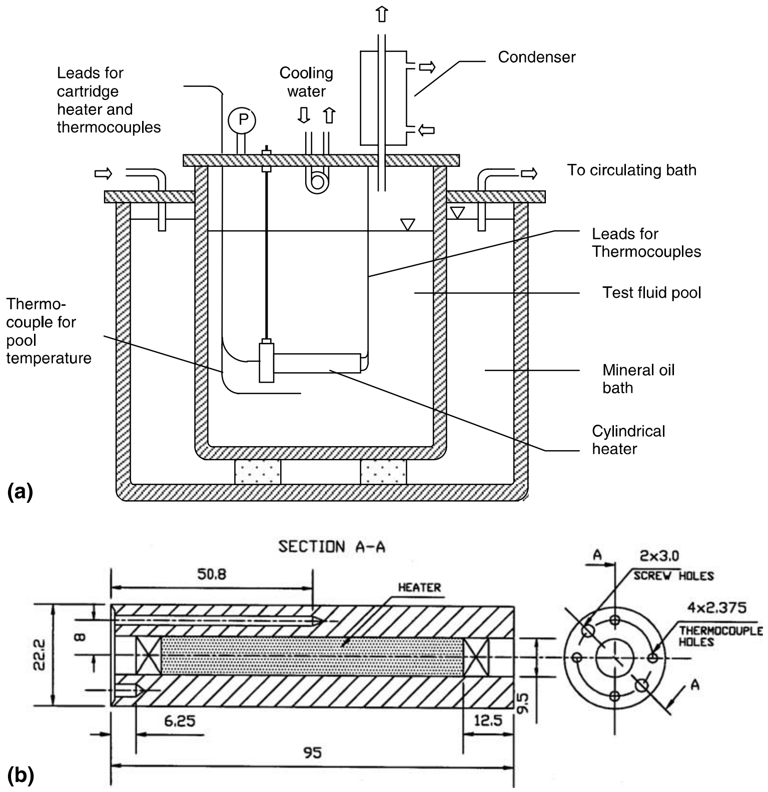

Fig. 1. (a) Schematic of pool boiling apparatus, and (b) construction details of cylindrical heater assembly.

3. Results and discussion

3.1. Dynamic surface tension

Fig. 2(a) gives a comparison of the equilibrium and dynamic surface tension σ at 23°C for the four different surfactants. Relative to anionics in general, nonionics show higher σ relaxation and lower c.m.c. values. The c.m.c. for the four surfactants (obtained from the equilibrium adsorption isotherms as a value at which the slope of the isotherm changes sharply) are ~200 wppm for Triton X-100, ~1000 wppm for Triton X-305, ~1000 wppm for SLES, and ~2500 wppm for SDS. The lower c.m.c. values of nonionic surfactants has been attributed to the absence of any electrical repulsion, which could oppose micelle formation unlike that associated with anionic surfactants [16]. Except for SDS, all the surfactants that were tested have ethoxy or EO groups in varying proportions. The presence of EO group increases the overall size of the polar head and makes the surfactant more hydrophilic [9,14]. For the present data, while addition of EO groups decreases c.m.c. and increases σ at c.m.c. for anionic surfactants, both σ and c.m.c. increase with increasing number of EO groups in nonionic surfactants. Furthermore, Fig. 2(a) shows a distinctly large difference in σ values between dynamic (50 ms, which is comparable to the boiling bubble growth time) and equilibrium conditions for Triton X-100 compared to other surfactants. This indicates a significantly slow σ relaxation to equilibrium for Triton X-100 surfactant, i.e., at a given bulk concentration, it usually takes more time for Triton X-100 solutions to attain an equilibrium value than other surfactants presented in Fig. 2(a). Ferri and Stebe [17] suggest that because Triton X-100 is highly surface active (depresses σ maximally and has high value of surface-excess concentration Γ_m), an adsorption layer is formed at low bulk concentrations such that the time required to establish the equilibrium is very long.

The effect of increased bulk temperature (80°C) on both the dynamic and equilibrium σ for the different surfactant solutions is depicted in Fig. 2(b). Comparisons with respective values at room temperature (23°C) indicate overall reductions in both dynamic and equilibrium σ values at higher temperature. Also, surfactants with EO groups present in their hydrocarbon chain show larger reductions in σ compared to SDS. These reductions, however, are not uniform over both the dynamic and equilibrium conditions. While an increase in number of EO groups, is found to depress dynamic σ

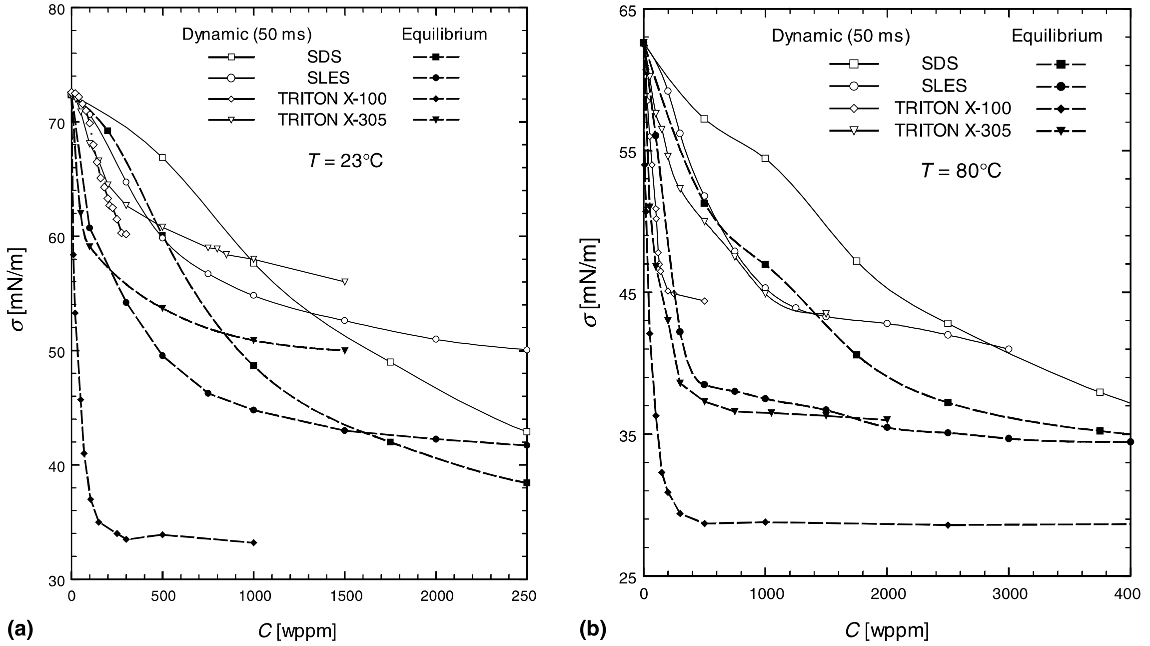

Fig. 2. Equilibrium and dynamic surface tension measurements for aqueous surfactant solutions at: (a) 23°C, and (b) 80°C.

in both anionic and nonionic surfactants, equilibrium σ tends to be much higher for Triton X-305 compared to Triton X-100 (the number of EO groups in the two samples are 30 and 9–10, respectively). This behavior reflects a completely different adsorption–diffusion kinetics at elevated temperature during the short as well as long transients. The values of c.m.c. at 80°C for the four surfactants can be identified from their equilibrium σ–C isotherms as ~3000 wppm for SDS, ~500 wppm for SLES, ~200 wppm for Triton X-100, and ~500 wppm for Triton X-305. In general, it is observed that the process of micelle formation takes place over a range of concentrations [18,19] and in the present work this range is found to be 2500–3750 wppm for SDS, 500–2000 wppm for SLES, 150–250 wppm for Triton X-100, and 400–800 wppm for Triton X-305.

3.2. Nucleate boiling heat transfer

The experimental data for pool boiling of various concentrations of aqueous anionic (SDS and SLES) and nonionic (Triton X-100 and Triton X-305) surfactant solutions are presented in Figs. 3 and 4, respectively. The boiling behavior was observed to generally have an early onset of nucleate boiling (ONB), except in solutions with surfactant concentrations higher than c.m.c. when there was a delay in incipience. Also, a significant thermal hysteresis is seen in the solutions of surfactants that have EO groups in their hydrocarbon chain. This contrasts with the results for aqueous solutions of SDS (absence of EO group) shown in Fig. 3(a), where the exception is the 10,000 wppm solution ($\gg$c.m.c.) that shows some hysteresis. As pointed out earlier, the presence of EO groups makes the surfactant more hydrophilic and hence these solutions have better wetting characteristics in comparison to SDS solutions. This would explain to some degree the observed temperature overshoot in the former cases. As such, the thermal hysteresis behavior of these surfactant solutions is similar to that seen in boiling of pure fluids, such as CFC refrigerants and FC-72, that also have low surface tension and high wettability [20,21].

Boiling in surfactant solutions, when compared with that in pure water, was observed to be more vigorous with clusters of smaller-sized and more regularly shaped bubbles. In both surfactant solutions and pure water, the bubbles mostly originate from the underside of the cylindrical heater, and then slide along the heater surface before departure. These sliding bubbles tend to knock off the bubbles growing on the top surface of the heater causing their early departure, and this tendency is found to increase with increasing bubble departure frequency. With surfactant solutions, the lowering of surface tension promotes nucleation of smaller-sized bubbles and activation of nucleation sites in a clustered fashion, especially at lower heat fluxes. The bubbles depart at much higher frequencies and the coalescence between two neighboring bubbles or between the sliding bubbles along the heater surface is minimal. The departing bubbles were seen to reach the pool free surface and

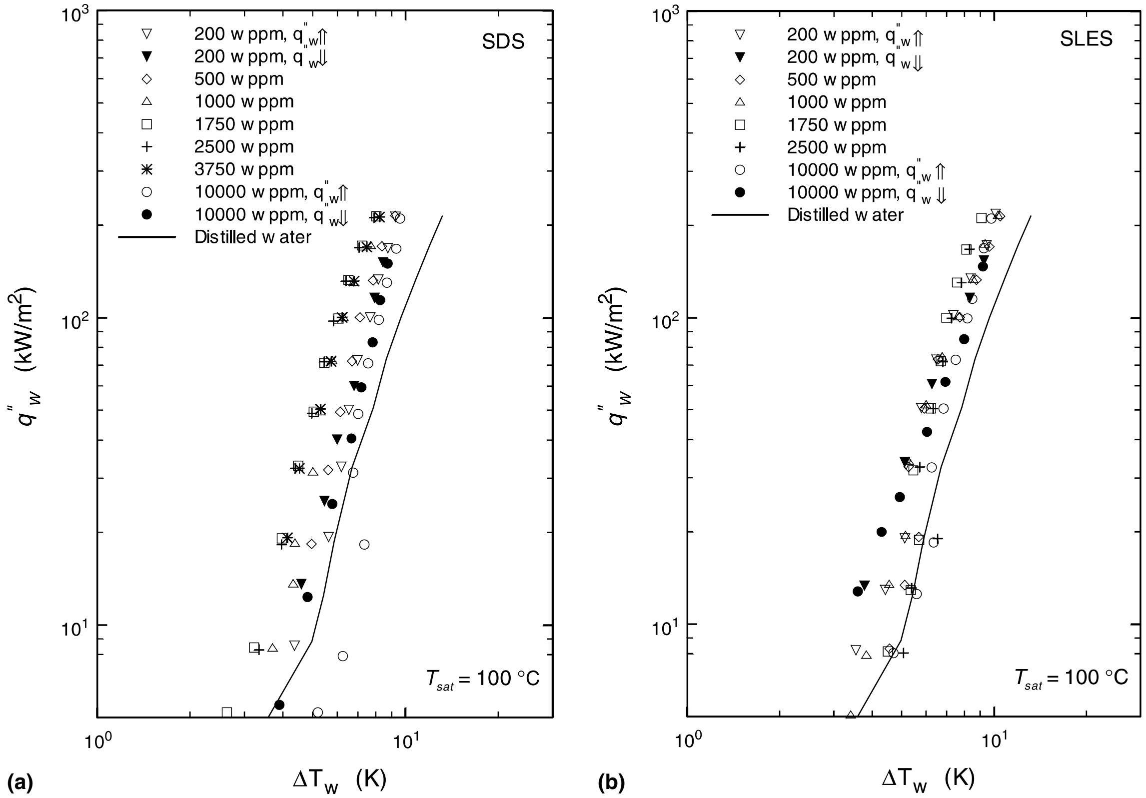

Fig. 3. Pool boiling data for aqueous solutions of anionic surfactants: (a) SDS, and (b) SLES; all data are for increasing heat flux except as otherwise indicated.

form a foam layer, whose thickness increased with increasing heat flux. With nonionic surfactant solutions, this foam was much finer. At high heat fluxes ($\sim$200 kW/m^2), due to the vigorous bubbling motion, the liquid free surface in the pool oscillated mildly; this was also observed with the boiling of pure water. Furthermore, no significant differences were observed in the boiling evolution (bubble incipience, growth, and detachment) in surfactant solutions having concentrations below and above c.m.c.

A closer inspection of Figs. 3 and 4 reveals that an optimum heat transfer enhancement is typically obtained over a concentration range around c.m.c. of the respective surfactant. As discussed earlier, the process of micelle formation characterizes this range of concentration. Such an optimum in heat transfer enhancement around c.m.c. of the surfactant has also been observed by Hetsroni et al. [2] for the saturated pool boiling of aqueous solutions of Habon G (a cationic surfactant having molecular weight of 500). The boiling envelope, however, varies in shape and size, representing varying degrees of enhancement depending upon the choice of surfactant. Between surfactants in each ionic category, an increase in surfactant molecular weight generally narrows down the performance envelope with a reduction in the optimum level of enhancement. This behavior to a certain extent can be explained from Fig. 5, which presents for each surfactant the values of dynamic σ at 80°C normalized by its equilibrium surface tension obtained at c.m.c. and 80°C; likewise, the concentration is normalized by its equilibrium c.m.c.. For the two surfactants that have higher molecular weight in each ionic category (SLES and Triton X-305), the range of σ reduction over the entire concentration range is appreciably smaller than that for their low molecular weight counterparts (SDS and Triton X-100). This occurs perhaps due to the lower mobility of heavier molecules, which also results in significantly higher c.m.c. values under dynamic conditions for these surfactants (see Fig. 2(b)). This parallel behavior observed between the dynamic surface tension variations and nucleate boiling curves, suggests a direct contribution of dynamic σ in characterizing the nucleate boiling heat transfer enhancement in surfactant solutions.

Fig. 6 gives the optimum enhancement in heat transfer coefficients (over that for pure water) for various surfactants for $q''_w > 30\ \mathrm{kW/m^2}$. The lower q''_w range, which represents the partially developed nucleate boiling

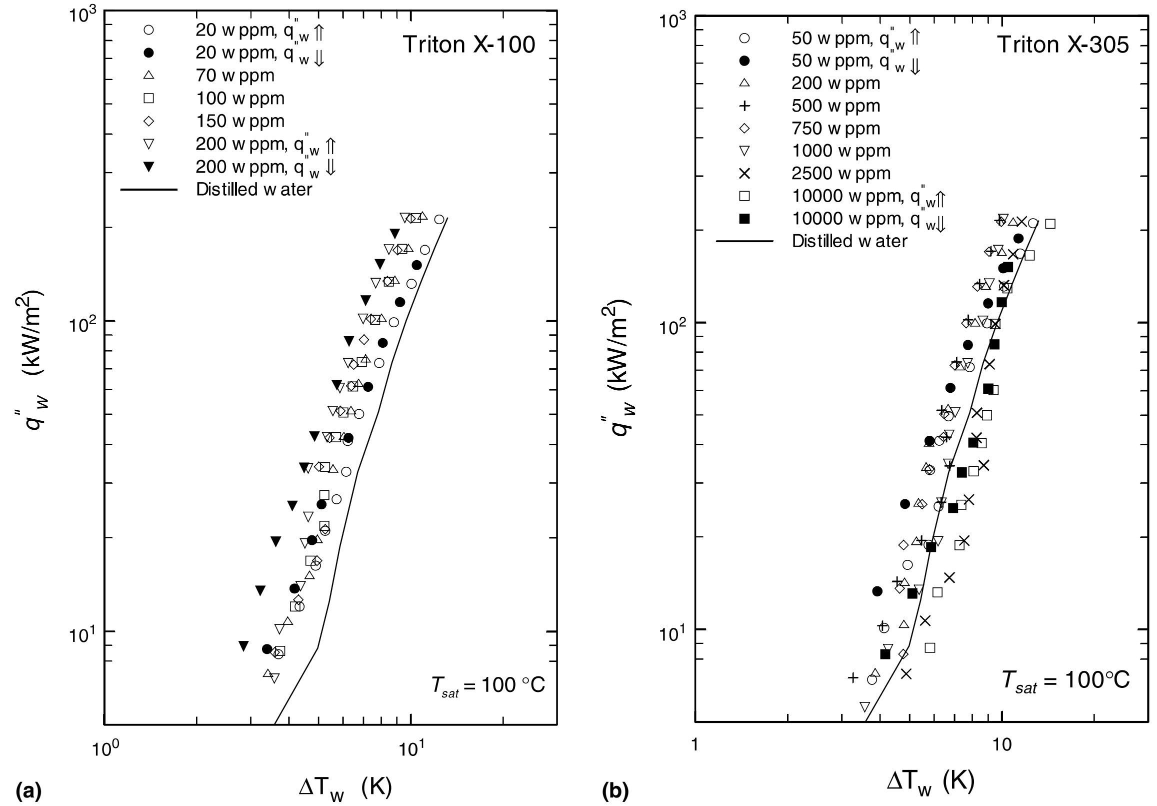

Fig. 4. Pool boiling data for aqueous solutions of nonionic surfactants: (a) Triton X-100, and (b) Triton X-305; all data are for increasing heat flux except as otherwise indicated.

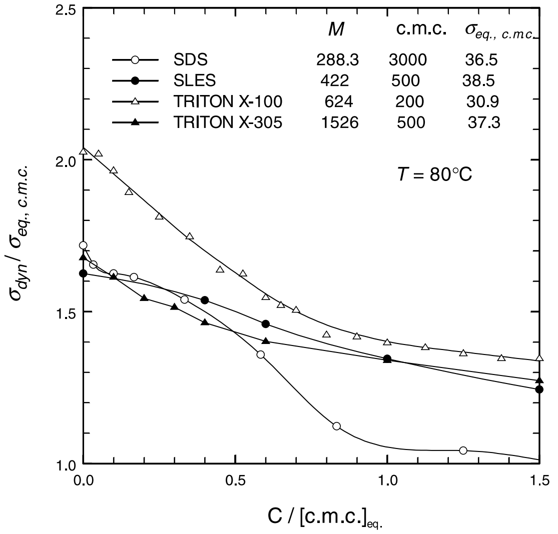

Fig. 5. Effectiveness of dynamic surface tension relaxation of different surfactant additives in aqueous solution at 80°C.

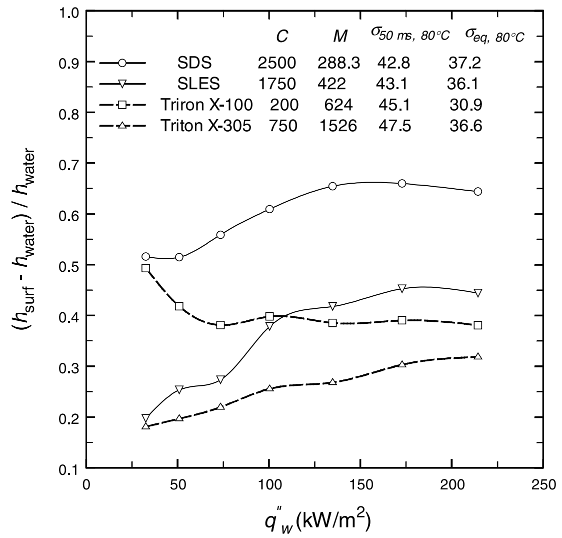

Fig. 6. Surfactant molecular weight dependence of the maximum enhancement in heat transfer coefficient.

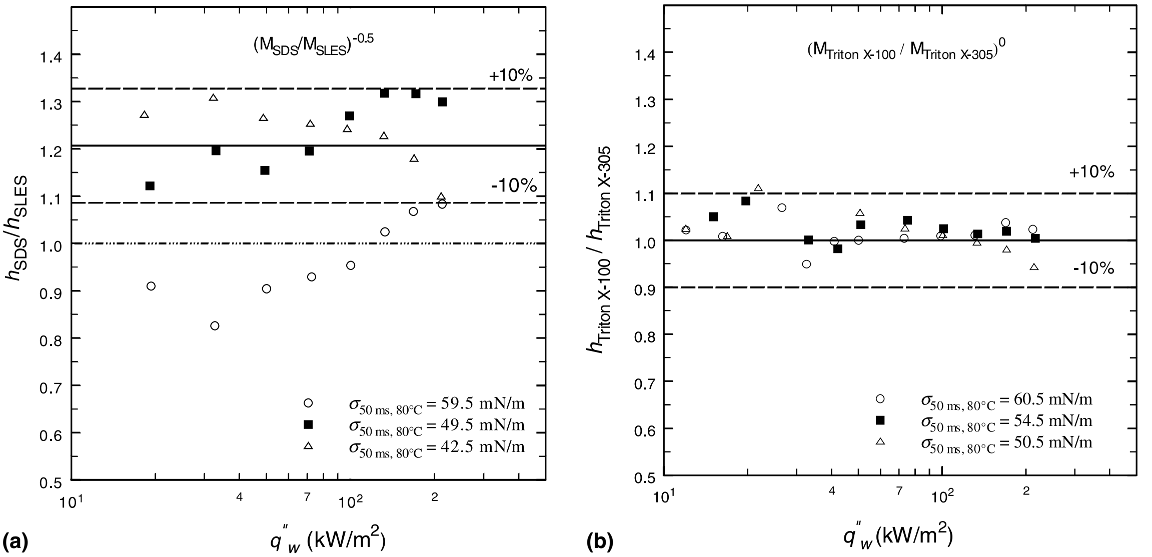

Fig. 7. Effect of molecular weight on the nucleate boiling heat transfer coefficients of aqueous solutions of: (a) anionic surfactants, and (b) nonionic surfactants.

regime, is characterized by the thermal hysteresis and wetting behavior of the surfactant solution. At higher heat fluxes, typically in the fully developed nucleate boiling regime ($q''_w > 100$ kW/m^2), however, the maximum heat transfer enhancement is in the order of SDS > SLES > Triton X-100 [1] > Triton X-305. This is in the reverse order of their respective molecular weights (Fig. 6). Furthermore, the values of dynamic σ (at 50 ms, 80°C), measured for concentrations that are representative of the optimum enhancement, are lower for anionics compared to nonionics and follow the same order as that of molecular weights of the surfactants. The equilibrium σ values at 80°C, in contrast, do not show any correlative dependence on both the boiling heat transfer coefficient and surfactant molecular weight. These results therefore suggest that the selection of a surfactant for an optimum nucleate boiling heat transfer enhancement can be made based upon its molecular weight, ionic nature, and the dynamic surface tension characteristics under the given operating conditions.

To further delineate the effect of molecular weight on the nucleate boiling performance of surfactant solutions, a comparison of the data on the basis of dynamic surface tension values rather than surfactant concentrations is quite revealing. Fig. 7 gives such a comparison, where the ratios of heat transfer coefficients for anionics (h_{SDS}/h_{SLES}) and nonionics ($h_{Triton\ X\text{-}100}/h_{Triton\ X\text{-}305}$) are graphed against the wall heat flux for three different dynamic surface tension values. In order to minimize the influence of temperature hysterisis at lower heat fluxes (<25 kW/m^2), the data acquired with descending levels of heat flux are used. The solution concentrations typically cover the range up to the c.m.c. of respective surfactants, and the corresponding concentrations for the given values of dynamic σ for each surfactant are listed in Table 2. As seen from Fig. 7(a) for anionic surfactants, the boiling performance of SDS is superior to that of SLES for solutions with lower dynamic surface ten-

Table 2

Values of dynamic σ (at 50 ms, 80°C) and corresponding surfactant concentrations in Figs. 7(a) and (b)

$\sigma_{50\ ms,80°C}$ (mN/m)	Concentration (wppm)	
	SDS	SLES
Fig. 7(a) (anionics)		
59.5	200	200
49.5	1750	500
42.5	2500	2500
	Concentration (wppm)	
	Triton X-100	Triton X-305
Fig. 7(b) (nonionics)		
60.5	20	50
54.5	70	200
50.5	100	500

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[1] In this case, when heated to the saturation temperature, clouding of the solutions was observed for concentrations above 200 wppm. Heat transfer reduction is assumed above this concentration owing to rapid micellization. This appears to be corroborated by the results of Wu et al. [4], who have also observed an optimum enhancement around 200–250 wppm on a stainless steel tubular heater ($D = 5.3$ mm, $L = 100$ mm).

sion. Although the wall heat flux appears to have some influence on this performance, the data scatter is well within $\pm 10\%$ of the molecular weight dependence that can be described by $(M_{\mathrm{SDS}}/M_{\mathrm{SLES}})^{-0.5}$. Interestingly, the exponent of -0.5 for the ratio of molecular weights in these cases is the same value suggested by Cooper [10] for pure fluids of different molecular weights (e.g., water, refrigerants, cryogens). For nonionics, however, the comparisons made at a fixed value of dynamic σ in Fig. 7(b) show almost no dependence on the surfactant molecular weights over the entire heat flux range, i.e., $(M_{\mathrm{Triton\ X\text{-}100}}/M_{\mathrm{Triton\ X\text{-}305}})^0$ holds good and the heat transfer coefficient is essentially independent of additive molecular weight.

The molecular makeup of the surfactants, their ionic nature, the dynamic surface tension characteristics of their aqueous solutions, their bulk concentrations, and the thickness of an enveloping concentration sublayer around the growing vapor bubble provide an explanation for this correlation of the heat transfer coefficient with surfactant molecular weight. In order to depress the solution's surface tension by some fixed amount, the required bulk concentration depends on the surfactant molecular mobility and its surface activity. The presence of EO groups in SLES, Triton X-100, and Triton X-305 molecules makes their polar head more bulky such that they occupy a larger area at the interface than the SDS molecule. Consequently, in comparison with SDS, lower bulk concentrations of SLES, Triton X-100, and Triton X-305 are required to depress σ by the same amount. Additionally, nonionics show further reduction in bulk concentration due to the absence of any electrostatic interactions among the surfactant molecules. This leads to a closer packing of adsorbed molecules at the interface. During boiling the surfactant molecules diffuse towards the growing bubble interface from the adjacent sublayer. The surfactant concentration in this sublayer would tend to be very close to the bulk concentration, although the weighted average molecular weight of the surfactant solution may not change appreciably. A conceptual description of the nature of concentration sublayers during boiling of aqueous SDS and SLES solutions for different dynamic σ values is schematically outlined in Fig. 8. It is expected that this concentration sublayer would determine the dynamic surface tension at the interface, and thus directly influence the bubble dynamics during boiling. Consequently, the surfactant molecular weight would indeed be an appropriate correlating parameter for the boiling heat transfer coefficient.

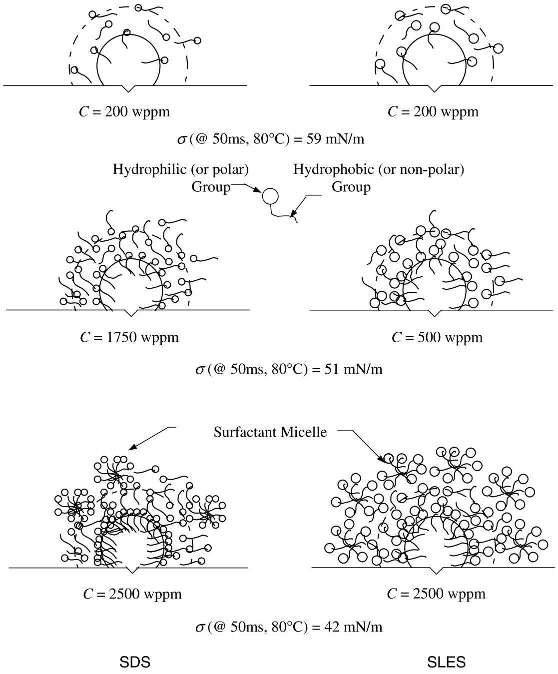

Fig. 8. Conceptualization of surfactant monomer and micellar activity in a concentration sublayer around a growing bubble during boiling.

That the molecular weight dependence may not necessarily be the same for different ionic categories of surfactants, is evident from Figs. 7(a) and (b). A lower molecular weight surfactant molecule typically diffuses faster than its higher molecular weight counterpart. Anionics in general, and those used in the present study, are low molecular weight surfactants compared to nonionics. Within a given transient time of bubble growth, the faster diffusion of lower molecular weight anionics leads to a larger number of anionic molecules approaching the growing bubble interface. The concomitant growth of concentration sublayer around the growing bubble tends to have a thickness, which is much larger than that in nonionic surfactant-solution boiling. In addition, the electrostatic repulsion between anionic surfactant molecules tends to increase the sublayer thickness further such that its character influences the vaporization at the bubble interface. The insensitivity of boiling heat transfer coefficients on the molecular weights of nonionic surfactants may, therefore, be due to an appreciably thinner concentration sublayer under dynamic conditions of bubble growth. This is also observed in very low concentrations of anionic surfactant solutions (Fig. 7(a)), where the experimental data for $\sigma = 60$ mN/m lie within $\pm 10\%$ of unity presumably due to lack of a strong sublayer effect at such concentrations.

4. Conclusions

The importance of dynamic surface tension, measured at or near boiling temperatures, as one of the primary determinants of the nucleate boiling heat transfer characteristics of aqueous surfactant solutions is established in this study. Two different categories of surfactants were considered based on their ionic nature. The optimum nucleate boiling heat transfer performance enhancement in their solutions tends to follow in a reverse order of their respective molecular weights. By normalizing the boiling performance by the respective solution's dynamic surface tension, the heat transfer coefficient is found to be correlated by $M^{-0.5}$ for anionics (SDS and SLES) and M^{0} for nonionics (Triton X-100 and Triton X-305). As a phenomenological description of this scaling, it is shown that the surfactant concentration and its interfacial activity in a sublayer around the growing vapor bubble determine the dynamic surface tension. The ionic nature of the surfactant influences the thickness and molecular makeup of the enveloping concentration sublayer, thereby affecting the bubble dynamics and boiling heat transfer.

In essence, it is shown that the presence of surfactant concentration sublayer around the growing bubble interface governs the bubble growth behavior through the mechanism of dynamic σ. For pure liquids, which are homogeneous in character, the interface molecules experience uniform behavior from the neighboring liquid molecules (in terms of intermolecular forces, which can be reasonably represented by the molecular weight). The constant exponent of -0.5 [10] for all pure fluids is indeed the result of this effect. For surfactant solutions, however, the presence of surfactant molecules at the interface will influence the exponent, which for the present case is -0.5 for anionics and 0 for nonionics. It should also be noted that the ratio of surfactant molecular weights has been considered in the correlation, instead of their absolute values. The exponent values for surfactants, therefore, reflect the surfactant molecular activity in a given ionic category with respect to the thickness of concentration sublayer, surfactant effectiveness at the interface, surfactant molecular orientation at the interface, and its interaction with the neighboring water molecules.

Acknowledgements

This study was supported by the National Science Foundation CAREER Award (Grant No. CTS – 9502128) and the Thermal-Fluids and Thermal Processing Laboratory.

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