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# Boiling phenomena with surfactants and polymeric additives: A state-of-the-art review

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#### Abstract

This paper presents a state-of-the-art review with respect to studies of boiling phenomena of aqueous surfactant and polymeric additive solutions in the literature. Both nucleate pool boiling and flow boiling are concerned. First, the effect of surfactants and polymeric additives on the physical properties of aqueous surfactant and polymeric additive solutions is discussed. The measurement results of surface tensions and viscosities of aqueous surfactant and polymeric additive solutions by the authors and other researchers are presented to show the variation of the physical properties and interfacial phenomena affected by the concentrations and/or temperatures of surfactant and polymeric additive solutions. Then, a comprehensive review of boiling phenomena including both nucleate pool boiling and flow boiling with surfactants and polymeric additives is presented. It covers both experimental studies on boiling characteristics of various aqueous surfactant and polymeric additive solutions and theoretical studies on the boiling mechanisms such as the effect of surfactants and polymeric additives on nucleation process, bubble dynamics and interfacial phenomena by the methods of visualization and modeling. In addition, as one of the related interesting topics, the study of drag reduction by the addition of surfactants and polymeric additives in fluid flow is also mentioned. According to this review, several research directions related to boiling phenomena with surfactants and polymeric additives have been identified. Especially, a cross-research area on boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels (micro-scale boiling heat transfer) has been emphasized because the study on this topic is very scarce but very important. To identify the main research needs on this cross-research topic, a brief review of boiling phenomena in confined spaces is also presented. Incorporated with the characteristics of boiling phenomena with surfactants and polymeric additives in large spaces, some scientific hypotheses of boiling phenomena of aqueous surfactant and polymeric additive solutions in confined spaces have been proposed based on an analysis of boiling patterns (bubble behavior). It is suggested that experimental work be done to explore this research area and to verify these hypotheses as well in the future.

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Keywords: Boiling; Enhanced heat transfer; Surfactant; Polymeric additives; Drag reduction; Confined spaces; Microchannels; Boiling patterns

#### 1. Introduction

Nucleate boiling is a very efficient mode of heat transfer. It has been found in a wide range of applications in both traditional industries such as various energy conversion system, heat exchange system, air-conditioning, refrigeration and heat pump system, chemical thermal process and in highly specialized fields such as cooling of highenergy-density electronic components, micro-fabricated fluidic system, the thermal control of aerospace station, bioengineering reactors. Generally, boiling is classified as pool boiling and flow boiling. Pool boiling refers to boiling under natural convection conditions, whereas in flow boiling, liquid flow over the heater surface is imposed by

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external means. Over the past decades, a great amount of research on pool boiling and flow boiling has been carried out to understand the fundamental aspect of boiling phenomena and to provide practical knowledge for the engineering design requirements in various industries. Several mechanisms and theories of boiling phenomena have been developed and the mechanisms are not fully understood yet and still under discussion [\[1–11\]](#page-24-0). Boiling is a complex and elusive process. As such, we often rely on dimensionless groups and empirical constants when correlating data. Concurrent with the development of correlations useful for engineering applications, progress continues to be made in understanding the physics of the boiling process. Because the process is so complex and because so many heaters and fluid variables interact, completely theoretical models have not been developed to predict the boiling heat fluxes as a function of heater surface superheat temperature. In many cases, a consensus is lacking in the technical community with respect to the dominant mechanisms of the heat transfer (in nucleate and transition boiling) and the degree to which the contribution of various mechanisms to total heat flux changes with wall superheat temperature and heater geometry [\[5\].](#page-24-0) In addition, a number of studies have focused on the enhancement of heat transfer, which is called the second generation heat transfer technology [\[12–16\]](#page-24-0). In the aspect of enhancement of boiling heat transfer, quite a few of studies have been carried out over the past years to improve heat transfer rate and energy efficiency. An exhaustive compilation of the relevant literature has been presented by Bergles [\[12–14,16\],](#page-24-0) Webb and Bergles [\[15\],](#page-24-0) Bergles et al. [\[17\],](#page-24-0) Thome [\[18\]](#page-24-0), Webb and Kim [\[19\].](#page-24-0) Heat transfer enhancement technology is generally classified as active heat transfer enhancement technology, passive heat transfer enhancement technology and compound heat transfer enhancement technology which combines at least two heat transfer enhancement methods [\[19\].](#page-24-0) Of the available heat transfer enhancement technology, passive heat transfer enhancement technology is of more practical use and is easily implemented because it does not consume external power. In recent years, with rapid development of high technologies, the third generation heat transfer enhancement technology which is applied in cooling of high heat fluxes in electronic device, aerospace technology and so on has arisen as pointed out by Bergles [\[14\].](#page-24-0) As one highly efficient heat transfer mode, various boiling heat transfer enhancement methods have been developed over the past years, for example, rough surface, electrostatic field, coiled tubes, additives for fluids and so on. Among the different nucleate boiling heat transfer enhancement techniques, the use of additives such as surfactants and polymeric additives for liquids appears to be quite viable and has attracted a lot of research over the past decades. Of the available studies, aqueous surfactant and polymeric additive solutions are quite common because the surface tension of water is greater than that of many liquids with amphipathic structures. For example, typically the surface tension of refrigerants is lower than that of amphipathic liquids and therefore most of the studies focus on the boiling of water with surfactants and polymeric additives. Addition of very small amount surfactants or polymeric additives in water can enhance the nucleate boiling heat transfer remarkably. Because of their low concentration, the presence of surfactants in water causes no significant change in the solvent physical properties except for surface tension, whereas the presence of polymers or surfactants at higher concentrations in water may causes big change of the viscosity in the solvent (non-Newtonian fluidic behavior). The importance of additive enhanced

<span id="page-2-0"></span>boiling has been recognized by the heat transfer community for a long time as pointed out by Cheng and Mewes [\[11\]](#page-24-0) in their recent review of two-phase flow and flow boiling of mixtures in small and mini channels. Boiling of aqueous surfactant solutions is a kind of heat transfer enhancement technology. Due to the very small amount of the addition of surfactants and polymeric additives (at ppm grade), they did not include the topic of boiling phenomena with surfactants and polymeric additives in their review which focuses on fluidic mixtures but they realized this very important research area which should be focused on as one very important research direction. The study of boiling phenomena with surfactants and polymeric additives may go back to a very earlier research of flow boiling with surfactants by Stroebe et al. in 1939 [\[20\]](#page-24-0) and an earlier research of pool boiling with surfactants by Morgan et al. in 1949 [\[21\].](#page-24-0) After these, a lot of research of boiling phenomena with surfactants and polymeric additives has been conducted. It is still a very active research topic at present.

In order to develop the enhancement technology of boiling heat transfer with additives (mostly surfactants and polymeric additives), a number of studies have been performed to characterize and to quantify boiling heat transfer characteristics of aqueous additive solutions, and to investigate the effect of thermo-physical properties such as surface tensions and viscosities on the nucleate boiling behavior. Studies have focused particularly on nucleate pool boiling of various aqueous additive solutions although there are some studies on flow boiling with additives. Wu et al. [\[22\]](#page-24-0) provided a literature review on both pool boiling [\[20–31\]](#page-24-0) and flow boiling [\[32–35\]](#page-25-0) with surfactant additives. The latest papers cited in their review were up to 1993. Kandlikar and Alves [\[36\]](#page-25-0) provided a literature summary of some important studies of the effect of surface tension on boiling in their research paper. Apparently they only included several typical studies related to boiling phenomena with surfactants and polymeric additives. Wasekar and Manglik [\[37\]](#page-25-0) performed a comprehensive review on nucleate pool boiling of aqueous surfactant and polymeric additive solutions. The latest papers cited in their review were until 1998. Yang [\[38\]](#page-25-0) presented a literature review on boiling heat transfer enhancement by surfactants. The latest papers cited in his review were up to 2004. He attempted to show the evolution of how the practice of employing surfactant additives in liquids may develop and mature into an enhancement techniques for boiling heat transfer. From an engineering design point of view, it is desirable that the results of surfactant effect on boiling heat transfer can be analyzed, generalized and formulated into a more convenient form for calculations, as pointed out by Yang [\[38\]](#page-25-0). However, at present, only tentative criteria for a given surfactant as a competent additive in enhancing nucleate boiling heat transfer of water are available. We are still far from a systematic theory or explanation for the enhancement of boiling heat transfer caused by surfactant additives. He pointed out that some more fundamental boiling phenomena should be studied before the problems

can be elucidated and the practical application of surfactant additives in commercial plants is possible. Generally, previous studies have shown that surfactants and polymeric additives at low concentrations can enhance nucleate boiling heat transfer significantly. A number of studies have also been carried out to understand the mechanisms of nucleate boiling with surfactants and polymeric additives, which generally include the effect of physical properties on boiling behavior, nucleation process and bubble dynamics. However, there is still much fundamental work to do for both academic and practical aspects of boiling with surfactants and polymeric additives.

The present paper is aimed at providing state-of-the-art knowledge of boiling phenomena with surfactants and polymeric additives and identifying the future research requirements with respect to this interesting topic as well. An overall review on boiling phenomena (both pool boiling and flow boiling) with surfactants and polymeric additives in the literature is presented. First, the effects of surfactants and polymers on the physical properties such as the surface tension and viscosity of aqueous solutions are discussed. Then, a comprehensive review on both experimental studies of the boiling phenomena and theoretical studies of the boiling mechanisms with surfactants and polymeric additives is presented. In addition, as one of the related interesting topics, the study of drag reduction by the addition of surfactants and polymeric additives in fluid flow is also mentioned. Finally, according to the review, several research directions related to boiling phenomena with surfactants and polymeric additives have been identified.

## 2. The effect of surfactants and polymeric additives on the physical properties of aqueous additive solutions

#### 2.1. The fundamental of surfactants

Surface active substances or surfactants are amphiphilic compounds having a lyophilic, in particular hydrophilic part (polar group) and a lyophobic, in particular hydrophobic part (often hydrocarbon chain). The amphiphilic structure of surfactants is responsible for their tendency to concentrate at interfaces and to aggregate in solutions into various supramolecular structures, such as micelles and bilayers. According to the nature of the polar group, surfactants can be classified into nonionic and ionic surfactants, which may be of anionic, cationic, and amphoteric or zwitterionic nature. Nonionic surfactants have no charge, anionic surfactants have a negative molecular charge, cationic surfactants have a positive molecule charge, and amphoteric or zwitterrionic surfactants have both positive and negative charges [\[39,40\].](#page-25-0) Anionic and nonionic surfactants provide most of industrial surfactant requirements and are the most common.

Surfactants greatly reduce the surface tension of solvents, water and water-based solutions, inks, fountain solutions, adhesives and other coating formulations. To reduce the surface tension, however, surfactant molecules have to

migrate to the interface, and this takes some finite amount of time. The formulation will eventually reach equilibrium (static) surface tension after certain time. This takes several seconds or even several hours depending on the type of surfactant and the concentration of solutions. During this dynamic process before reaching equilibrium, the surface tension changes with the time and thus is defined as dynamic surface tension. In general, surfactants with smaller (lighter) molecule mass (short hydrophobic tail) diffuse more rapidly to the interface than that with larger (higher) molecule mass. Higher molecular weight surfactants affect a higher equilibrium surface-tension depression compared to lower molecular weight surfactants [\[39,40\].](#page-25-0) In addition, most surfactants at higher concentrations cause change of the physical properties of the surfactant solutions and cause strong surface films between adjacent molecules, the strength of which determines surface properties of the surfactant solutions. In general, surface tension decreases with increasing surfactant solution concentration, and dynamic surface tension is usually higher than equilibrium surface tension at a fixed concentration. Higher solution temperature results in lower surface tension in both equilibrium and dynamics conditions. Additionally for all surfactants, surface tension decreases asymptotically with increasing concentration. The asymptotic limit is commonly referred to as the critical micelle concentration (cmc) of the surfactants. Critical micelle concentration (cmc) is characterized by micelle formation, or micellization, which is the property of surface-active solutes that lends 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. Different shapes and sizes of micelles such as globular or spherical, rod-shaped or cylindrical, and lamellar or plate-like exist depending upon the surfactant type and its concentration, solution temperature, presence of other ions and water-soluble organic compounds in the solutions. The micelle is a dynamic entity and its structure and shape can change with time. Critical micelle concentration (cmc) may be determined by many different techniques. A survey of methods for cmc determination is summarized by Lange [\[40\].](#page-25-0) Popular techniques include surface tension, turbidity, self-diffusion, conductivity, osmotic pressure, solubilization, surfactant selective electrodes and fluorescence methods. Nearly all of these methods involve plotting a measurement as a function of surfactant concentration or as a function of the logarithm of surfactant concentration. The cmc is then deduced as a breakpoint. Critical micelle concentration is an important parameter in boiling phenomena with surfactants.

# 2.2. The effect of surfactants on the physical properties (surface tension and viscosity) of aqueous surfactant solutions

With respect to the boiling phenomena of aqueous surfactant solutions, the effect of surfactants on the physical properties of aqueous solutions is crucial to understand the boiling phenomena. The surface tension and viscosity of aqueous surfactant solutions are possibly the primary thermo-physical properties that are influenced by the presence of surfactants, whereas all other physical properties are remained unchanged. The extent of surface tension reduction and/or viscosity variation of aqueous surfactant solutions (possibly at higher concentrations) depend upon the chemistry of the surfactant type as well as the concentration of the aqueous solutions. Addition of surfactants to water reduces the surface tension of the aqueous surfactant solutions considerably. The reduction in the surface tension is dependent upon several factors such as surfactant bulk concentration, surfactant type and molecular weight, solution temperature, interfacial conditions and so on. In order to determine the effect of surfactants on the surface tension of aqueous surfactant solutions, we measured the equilibrium (static) surface tensions of aqueous solutions with two surfactants in the Institute of Thermodynamics at the Leibniz University of Hanover. The surfactants are SDS ( $C_{12}H_{25}NaO_4S$ ) ( $\geq 95\%$ , anionic) and Triton X-100  $(C_{33}H_{60}O_{10})$  (reinst, nonionic) supplied by Carl Roth GmbH in Germany. An optical contact angle measurement instrument manufactured by Dataphysics in Germany was used to measure the equilibrium surface tensions with the pendant-drop-method. Fig. 1 shows the variation of the measured equilibrium surface tension versus the concentration of SDS and Triton X-100 solutions at 21  $^{\circ}$ C. The surface tensions were measured by static pendant liquid drops contacted by air. The measured equilibrium surface tensions decrease with increasing of concentrations for both surfactants. The concentration of the solutions has a great effect on the surface tension of the solutions. When the concentration reaches at a critical value, the surface tension will tend to a constant value which corresponds to the critical micelle concentration (cmc) for each surfactant. However, the critical value of Triton X-100 solution is much smaller than that of SDS solution. The critical value of SDS solution is more than 1000 ppm while that of Triton



Fig. 1. Variation of the measured equilibrium surface tension versus concentration.

X-100 solution is only about 200 ppm. This manifests that the surfactant type has a great effect on the surface tension and the cmc value. Several studies have focused on the effect of surfactant types and concentrations on the equilibrium surface tension of aqueous surfactant solutions in the literature [\[22,41–47\]](#page-24-0) and similar conclusions have been reached. One typical example is the measurement of the equilibrium surface tension of solutions reported by Wu et al. [\[41\]](#page-25-0). They measured the equilibrium surface tension of aqueous solutions for nine additives including three anionic surfactants: sodium lauryl sulfate (SLS), Tergitol and Aerosol-22; one cationic surfactants: dodecyl trimethyl ammonium chloride (DTMAC) and five nonionic surfactants: Triton X-100, n-Octanol, Tween 20, Tween 40 and Tween 80 (polyoxyethylene sorbitan mono-oleate) at 25 °C. Fig. 2 shows the variation of the measured equilibrium surface tension versus the solution concentration which was measured by Wu et al. [\[41\]](#page-25-0). It can be concluded that surface tensions decrease with increasing additive concentrations for all the nine surfactants. In addition, it can also be concluded that the depression of equilibrium surface tensions increases in the order: nonionic > anionic  $>$  cationic. The molecular weights of these surfactants considered in their study also vary in the same order, which suggests that higher molecular weight surfactants affect a higher surface-tension depression in the aqueous surfactant solutions. For nonionic surfactants: Triton X- $100 >$  Tween 20, 40,  $80 > n$ -Octanol; and for anionic surfactants: SLS > Aerosol-22 > Tergitol. For nonionic surfactants, the depression of equilibrium surface tensions increases with increasing the molecular weight of surfactants while it is contrary for anionic surfactants. Obviously, the surfactant type and the molecular weight (chemistry structure) have great effect on the surface tension change of the aqueous surfactant solutions. Similar results have been obtained by Wasekar [\[44\]](#page-25-0), Zhang [\[45\],](#page-25-0) Zhang and Manglik [\[46\],](#page-25-0) and Wasekar and Manglik [\[47\],](#page-25-0) etc. as well. In addition, the surface tension decreases asymptotically with increasing the concentration of the aqueous surfactant



Fig. 2. Variation of the measured equilibrium surface tension versus concentration presented by Wu et al. [\[41\]](#page-25-0).

solutions. This asymptotic limit is the critical micelle concentration (cmc) of surfactants.

For the boiling phenomena of aqueous surfactant solutions, the knowledge of the dynamic surface tension and the corresponding adsorption behavior at boiling temperature is very crucial to understanding the boiling phenomena. The dynamic surface tension of aqueous surfactant solutions can be measured by several different techniques which are classified as direct and indirect methods. Direct methods include the maximum bubble pressure, oscillating jet, Langmuir trough methods which measure the interfacial tension of an interface undergoing steady, unsteady, or pulse expansion. Indirect methods include the surface wave, oscillating bubble, and pulsed drop methods that measure the dilatational elasticity of an interface undergoing a time-depend surface expansion [\[48\]](#page-25-0). Roll and Myers [\[24\]](#page-24-0) measured the dynamics surface tension of various aqueous surfactant solutions at a temperature of  $90^{\circ}$ C with the maximum bubble pressure method. The maximum bubble frequency employed was 30 Hz. It was observed that the surface tension of water lager than the dynamic surface tension of the aqueous surfactant solutions, and the dynamic surface tension are larger than the equilibrium surface tension. In the test range of surfactant concentrations, the dynamic surface tension decreases with increasing the concentration of aqueous surfactant solutions. Wasekar [\[44\]](#page-25-0) used the maximum bubble pressure method to measure the dynamics surface tension of several different water-soluble surfactants such as sodium dodecyl sulfate (SDS, anionic) sodium lauryl ether sulfate (SLES, anionic), Triton X-100 (octylphenol ethoxylate with 9–10 moles of ethylene oxide, nonionic) and Triton X-305 (octylphenoxypolyethoxyethanol with 30 moles of ethylene oxide, nonionic) at  $23 \text{ °C}$  and  $80 \text{ °C}$ . The dynamic surface tension measurement was made at bubble frequencies typically encountered in the nucleate boiling phenomena. The measured dynamic surface tensions at different bubble frequencies for SDS solutions at 23  $\degree$ C by Wasekar [\[44\]](#page-25-0) are shown in [Fig. 3](#page-5-0). The data for the lowest bubble frequency (0.017 Hz) represent the equilibrium surface tensions. The dynamic surface tension increases with increasing bubble frequency. At higher bubble frequencies, larger solution concentrations are needed to initiate micelle formation and cmc. This was also obtained by Iliev and Dushkin [\[49\]](#page-25-0) for SDS and Veranol H-10 (nonylphenol polyglycol ether with 10 moles of ethylene oxide, a nonionic surfactant) solutions. Similar to the observation of Roll and Myers [\[24\],](#page-24-0) the dynamic surface tensions are generally higher than the equilibrium surface tensions at all concentrations of the aqueous surfactant solutions. In addition, the dynamic surface tension curves for SDS solutions approach the equilibrium values much faster (rapid relaxation of surface tension) than those for Triton X-100 and Veranol H-10 solutions, indicating a lower surface activity and a smaller characteristic diffusion time of SDS monomers. A number of measurements of the dynamic surface tension of aqueous surfactant solutions were also reported

<span id="page-5-0"></span>

Fig. 3. Variation of the measured dynamic surface tension versus concentration presented by Wasekar [\[44\].](#page-25-0)

by Wu et al. [\[22\]](#page-24-0), Manglik et al. [\[42\],](#page-25-0) Zhang [\[45\]](#page-25-0) and so on. In addition, the surface tension of the aqueous surfactant solutions has also been found to be temperature dependent. Zhang [\[45\]](#page-25-0) compared the variation of equilibrium surface tensions of various surfactant solutions and water with temperature. As shown in Fig. 4, the equilibrium surface tension decreases with increasing temperature for all the aqueous surfactant solutions and water. Generally the surface tension-temperature variation tends to be linear for surfactants at various concentrations. Similarly, different reductions of surface tensions with increasing temperatures were reported by Wang and Hartnett [\[50\]](#page-25-0) for aqueous solutions of SLS and Tweem-80 and by Huplik and Raithby [\[25\]](#page-25-0) for aqueous FC-176 solutions. Wang and Hartnett's data also suggest that there is no induced change in the surface tension-temperature characteristics due to boiling, i.e., the surface tension prior to and after boiling remains the same at room temperature (20–25 °C). This occurs with the qualititative observations made by Morgan et al. [\[21\]](#page-24-0) for aqueous solutions of Drene (triethanolamine alkyl sulfate) and sodium lauryl sulfonate (SLS).

The viscosity of aqueous surfactant solutions may also be affected by the addition of surfactants in some cases. In



Fig. 4. Variation of surface tension versus temperature presented by Zhang [\[45\]](#page-25-0).

order to determine the effect of surfactants on the viscosity of aqueous surfactant solutions, we measured the dynamic viscosities of aqueous surfactant solutions for SDS and TritonX-100 at the maximum solution concentrations for respective surfactants in the Institute of Process Engineering at the Leibniz University of Hanover. We also measured the dynamic viscosity of deionized water which is used as a reference for comparison to the measured dynamic viscosities of the surfactant solutions. A Rheometrics Fluids Spectrometer II (RFS) manufactured by Rheometric Scientific GmbH in Germany was used to measure the dynamic viscosities of aqueous SDS solution at the concentration of 1035 ppm, aqueous Triton X-100 solution at the concentration of 1203 ppm and deionized water at three different temperatures at atmospheric pressure. Fig. 5 shows the measured dynamic viscosities of SDS solution, Triton X-100 solution and deionized water at three different temperatures. There is no obvious difference among the dynamic viscosities for the three fluids at the same temperature. This manifests that both SDS and Triton X-100 solutions reveal the Newtonian fluidic behavior as that of water. Especially for aqueous Triton X-100 solution, even the test concentration of 1203 ppm is much higher than the cmc (about 300 ppm), the solution still reveals the Newtonian fluidic behavior. Thus, it can be concluded that the addition of Triton X-100 does not change the viscosity of the aqueous solutions at higher concentrations. This is different from some measured results by other researchers in the literature, for example, the measured results of the aqueous Habon G solutions by Hetsroni et al. [\[43\]](#page-25-0) as shown in [Fig. 6](#page-6-0) where the solution viscosity increases with increasing the solution concentration at the same temperature. The aqueous Habon G solutions reveal non-Newtonian fluidic behavior except for the case at very low solution concentrations. The reason is possibly due to the effect of the surfactant type. Several studies have also concluded that surfactants with pre-micellar or dilute concentrations cause no significant change in the dynamic viscosity of solution [\[50,51\].](#page-25-0) The measured viscosities for both SLS and Tween-80 aqueous solutions at room temperature are constant and independent of shear rates. Therefore, these two surfactant solutions show the Newtonian



Fig. 5. Variation of the measured dynamic viscosity versus temperature.

<span id="page-6-0"></span>

Fig. 6. Variation of the measured kinematic viscosity versus temperature presented by Hetsroni et al. [\[43\]](#page-25-0).

fluidic behavior in a wide concentration range of 125– 500 ppm for polymeric surfactant solutions [\[52\]](#page-25-0). Post-micellar solutions, however, may show appreciable increases in dynamic viscosity [\[53\]](#page-25-0) and tend to be viscoelastic [\[54,55\]](#page-25-0), which behave like polymers as discussed in the next section. Hetsroni et al. [\[56\]](#page-25-0) measured the shear viscosities of aqueous Alkyl (8–16) Glucoside (Plantacare 818 UP) solutions at 25 and  $60^{\circ}$ C. The increased trend of the measured shear viscosity with increasing shear rate indicates that aqueous Plantcare 818 solutions reveal the non-Newtonian fluidic behavior at higher concentrations. The measured concentrations ranging from 600 ppm to 7000 ppm, mostly exceed the cmc of the surfactant. It is reasonable that the solutions behave like the non-Newtonian fluids. In addition, Hetsroni et al. [\[43\]](#page-25-0) studied the effect of temperature on the dynamic shear viscosity of aqueous Habon G solution over a temperature range of  $25-60$  °C. The concentration of the aqueous Habon G solution was around its cmc. For a given shear rate, the viscosity decreases with the increase of solution temperature. Moreover, the change in shear viscosity at a temperature of 333 K over the shear rate range of 1–1000 per second was negligible. They also measured the kinematic viscosities for various concentrations of Habon G over a temperature of 55–95 °C, as shown in Fig. 6. At the same temperature, the kinematic viscosity increases with the increases of the concentration of the surfactant solution. This is contradiction to our measured results presented in [Fig. 5](#page-5-0) and also does not follow the general law if the solutions are the Newtonian fluids. The reason is unclear but could be the effect of the surfactant type. Furthermore, at the near boiling temperature, the kinematic viscosities approach the value of pure water for both pre-micellar and micellar solutions. Such a behavior is more pronounced with decreasing the solution concentrations.

## 2.3. The effect of polymeric additives on the physical properties of aqueous polymeric additive solutions

In addition to enhancing boiling heat transfer by adding surfactants in water, trace amounts of polymers dissolved in water can also enhance boiling heat transfer as reported firstly by Potchaphakdee and Williams [\[57\].](#page-25-0) They concluded that surface tension was only a minor variable and the enhancement of heat transfer seemed to be ultimately limited by the effect of viscosity (A detailed review on this point is presented in the next section.). Therefore, in the case of boiling of aqueous polymeric additive solutions, variation of the viscosity (the non-Newtonian fluidic behavior) of aqueous polymeric additive solutions related to the solution concentrations and the polymer molecular weights may play an important role. It results in that some polymeric additives can enhance nucleate boiling heat transfer while others cannot or depress nucleate boiling heat transfer. Therefore, it is of primary importance to understand the effect of polymeric additives on the physical properties of dilute aqueous polymeric additive solutions in investigating the boiling phenomena with polymeric additives.

Polymers are typically large molecules, macromolecules, or agglomerates of small chemical units called monomers, and are broadly classified as biological and non-biological macromolecules. Addition of polymers in water primarily increases the solution viscosity, which tends to increase with increasing the concentration of aqueous polymeric additive solutions as well as the molecular weight of the polymers. The polymeric additive solutions often display a shear-rate depended shear-thinning rehology [\[54\]](#page-25-0) with the exception of some surface-active polymers (or polymeric surfactants) such as hydroxyethyl cellulose (HEC) and polyethylene oxide (PEO), most aqueous polymeric additive solutions do not show any significant change in surface tension [\[42,52,57\]](#page-25-0). The viscosity of aqueous polymeric additive solutions, however, can influence the surface tension measurement considerably, especially at higher viscosities and bubble frequencies. The reduced surface tensions in aqueous polymeric additive solutions are largely brought about by the molecular adsorption of the polymeric additives to the vapor–liquid interface. The time scales of this process vary from the order of seconds to minutes depending upon the polymer chemistry and the solution concentration, which is possibly due to the slow process of diffusion transport of polymer molecules to the interface and their subsequent reorientation. This dynamic adsorption process, along with time scales of 10–100 ms for the boiling bubble dynamics in water, thus results in a rather complex interfacial behavior, which significantly alters the nucleate boiling in polymeric additive solutions. Zhang and Manglik [\[108\]](#page-26-0) measured the surface tensions at different bubble frequencies for the various polymeric concentrations of HEC QP-300 solutions at  $23^{\circ}$ C and 80  $\degree$ C. [Fig. 7](#page-7-0) shows the variation of his measured dynamic surface tensions of HEC QP-300 solutions at various bubble frequencies at a temperature of  $23^{\circ}$ C versus the concentration of the aqueous solutions. Similar to that of surfactants, the dynamic surface tension of the polymeric additive solutions is found to increase with increasing the bubble frequency and decreasing the solution concentration. A critical polymer concentration (cpc) akin to cmc

<span id="page-7-0"></span>of surfactants is observed. It must be pointed out that HEC is a kind of polymeric surfactant which can depress the surface tension of aqueous polymeric additive solutions. However, most polymers generally have little effect on the surface tensions of solutions. Therefore, it is important to select those polymers which can depress the surface tension of aqueous polymeric additive solutions when study the boiling phenomena with polymeric additives.

As the viscosity of aqueous polymeric additive solutions has critical effect on the boiling phenomena of the aqueous polymer solutions, a lot of researchers measured the viscosity of aqueous polymeric additive solutions in their studies of the boiling phenomena of aqueous polymeric additive solutions. Fig. 8 shows the measured viscosities for HEC 250HHR at various solution concentrations by Hu et al. [\[52\]](#page-25-0) and that for HEC-QP300 at various solution concentrations and water by Zhang [\[45\]](#page-25-0). It can be seen that aqueous HEC solutions are more viscous than pure water, and the viscosity of the aqueous polymeric additive solutions increases with increasing concentration for each polymer. Actually the polymeric additive solutions behave like the Newtonian fluids at lower solution concentrations as the viscosities at solution concentrations remain constant with increasing shear stresses. By comparison, the HEC-QP300 solutions at the concentration of 3000 ppm show the Newtonian fluidic shear-constant behavior while the HEC 250HHR solutions at the concentration of 1000 ppm show the non-Newtonian fluidic shear-thinning behavior. This attributes to the effect of molecular weights and degrees of polymerization of the HEC family polymers. HEC 250HHR has a higher molecular weight  $(M = 1.3 \times 10^6)$ and a higher degree of polymerization as compared with HEC-QP300  $(M = 4-6 \times 10^5)$ . Similar results were obtained by Maestro et al. [\[58\].](#page-25-0) Their data for the lower molecular weight HEC9 ( $M = 9 \times 10^4$ ) reveal the Newtonian fluidic characteristics even at a very high concentration (10% by weight), and the non-Newtonian fluidic shear-thinning behavior for the higher molecular weight HEC130 ( $M = 1.3 \times 10^6$ ) solution at a concentration of



Fig. 8. Variation of the measured dynamic surface tension versus concentration for HEC-QP300 presented by Zhang [\[45\]](#page-25-0) and for HEC250HHR presented by Hu et al. [\[52\]](#page-25-0).

0.75% by weight. The results clearly indicate that molecular weight and the degree of polymerization play a role in the rheological behavior of polymeric additive solutions. As mentioned above, HECs are polymeric surfactants, they behavior like Newtonian fluids at low concentrations. Zhang and Manglik [\[108\]](#page-26-0) also measured the viscosities of Carbopol 934 solutions at various concentrations and compared the results with those of water. As shown in Fig. 9, the polymeric additive solutions show the non-Newtonian fluidic shear-thinning behavior apparently, even at lower solution concentrations. The reason is that Carbopol 934 has a higher molecular weight ( $M = 3 \times 10^6$ ) and a higher degree of polymerization as compared with HEC QP-300. Therefore, it has confirmed that a higher viscosity of a polymeric solution reflects a high degree of polymerization of the polymer.

Like that in the boiling of aqueous surfactant solutions, dynamic surface tension is also a critical parameter in the



Fig. 7. Variation of the measured dynamic surface tension versus concentration by Zhang and Manglik [\[108\].](#page-26-0)



Fig. 9. Variation of the measured viscosity versus shear rate presented by Zhang and Manglik [\[108\]](#page-26-0).

<span id="page-8-0"></span>boiling of aqueous polymeric additive solutions. In dynamic process, higher surface tension is primarily obtained due to the viscous resistance offered by the fluid against the growing bubble interface. The higher surface tension of aqueous polymeric additive solutions has been found to be dependent upon the fluid viscosity, capillary radius and surface age. To predict the apparent increase in surface tension, Fainermann et al. [\[59\]](#page-25-0) give the following correlation based on the Stokes' flow approximation:

$$
\Delta \sigma = 1.5 \left( \frac{\mu r_{\rm cap}}{\tau} \right) \tag{1}
$$

with this relation, it is able to determine the variation of the surface tension with the fluid viscosity in polymeric additive solutions which normally display the non-Newtonian fluidic shear-thinning behavior. It is critical to predict the surface tension change in the boiling process of polymeric additive solutions when study the boiling phenomena with polymeric additives.

## 3. Comprehensive review of the studies of boiling phenomena with surfactants and polymeric additives

Over the past decades, a number of experimental and theoretical studies of boiling phenomena with surfactants and polymeric additives have been carried out to understand the very complex boiling process and the boiling mechanisms. Emphasis has been placed on investigating nucleate pool boiling with surfactants and polymeric additives. In addition, relatively less studies of flow boiling with surfactants and polymeric additives have been carried out as well. In this section, a comprehensive review on the studies of boiling phenomena with surfactants and polymeric additives is presented. The studies of boiling phenomena with surfactants and polymeric additives are separately described according to their respective different effects on the physical properties of aqueous surfactant and polymeric additive solutions.

#### 3.1. Boiling phenomena with surfactants

One of the earliest research works concerning the effect of surfactants on boiling phenomena is the study on flow boiling of water with a surfactant in a long-tube vertical evaporator performed by Stroebe et al. [\[20\]](#page-24-0) in 1939. They found that flow boiling heat transfer coefficients were enhanced by addition of a surfactant-Duponol, and surface tension had a strong effect on the boiling heat transfer of water. Although there are much more studies on nucleate pool boiling with surfactants than those on flow boiling with surfactants in the literature, one of the earliest studies on nucleate pool boiling with surfactants is the research work by Morgan et al. [\[21\]](#page-24-0) in 1949, which is much later than the study of flow boiling with a surfactant by Stroebe et al. [\[20\].](#page-24-0) They conducted experiments of nucleate pool boiling of aqueous Drene and SLS (sodium lauryl sulfonate) solutions and found that the nucleate pool boiling heat transfer coefficients increased qualitatively with the decrease in surface tension of the liquid for temperature differences below the critical value. In addition, they have realized that, since the formation of bubbles in boiling involves the continue formation of new surface, the condition of equilibrium surface tension is never truly attained although it may be closely reached in some cases. This viewpoint has been widely accepted by the later researchers as indicated in the previous section that most researchers studied the effect of surfactants on the dynamic surface tension of aqueous surfactant solutions. Yang [\[60\]](#page-25-0) took dynamics surface tension as one critical parameter in his study and investigated the effect of dynamic surface tension on the boiling of aqueous surfactant solutions. It was recognized long time ago that surface tension plays an important role in boiling process. Considering the role of surface tension in boiling heat transfer, Westwater [\[61\]](#page-25-0) assumed the following heat transfer coefficient relationship with surface tension:

$$
h \propto \sigma^n \tag{2}
$$

As pointed out by Lowery and Westwater [\[62\],](#page-25-0) earlier literature is contradictory about the role of surface tension during boiling process. Some researchers have reported that surface active agents in water increase heat transfer at a given temperature difference driving force, while others have reported a decrease. A dozen values have been published for the exponent *n*, which has values of  $-2.5$ ,  $-2$ ,  $-1$ .  $+0.25$ ,  $+1.275$  [\[62\].](#page-25-0) Apparently it is contradictory for the role of surface tension in the boiling process. With negative exponent values, the reduction in surface tension increases boiling heat transfer coefficient whereas with positive exponent values, the reduction in surface tension decreases boiling heat transfer coefficient. However, theoretically surface tension is an important variable in boiling process. Rate of formation of vapor nuclei in the boiling of a liquid is proportional to surface tension as [\[61\]](#page-25-0):

$$
N \propto \mathrm{e}^{-\sigma^3} \tag{3}
$$

Thus, small decrease in surface tension should causes large increase in the number of nuclei. This has been confirmed by the visualization of nucleate boiling process conducted by a lot of researchers. For example, Zhang [\[45\]](#page-25-0) observed the nucleate boiling process by means of a high-speed camera and compared the observed results for water and surfactant solutions. His observation has firmly confirmed this point. In addition, cavitation theory predicts that force required to rupture a liquid in tension is proportional to surface tension as [\[61\]:](#page-25-0)

$$
F \propto \sigma^{3/2} \tag{4}
$$

Thus, liquids with large surface tensions should be difficult to fracture.

A number of studies have been performed to investigate boiling phenomena with surfactants including both nucleate pool boiling and flow boiling. [Table 1](#page-9-0) lists the summary of the studies of boiling phenomena with surfactants in the <span id="page-9-0"></span>Table 1

Summary of studies on boiling phenomena with surfactants in the literature in chronological order

Author/year	Boiling mode	Heating surfaces	Surfactants	Results and remarks
Stroebe et al. (1939) $\lceil 20 \rceil$	Flow boiling of water with surfactant	Tube	Duponol	Heat transfer was enhanced. Surface tension has a strong effect on heat transfer
Morgan et al. (1949) $[21]$	Pool boiling of water with surfactants	Cylindrical surface	Drene and SLS	Heat transfer was enhanced with decreasing surface tension
Lowery and Westwater (1957) [62]	Pool boiling of methanol with surfactants	Cylindrical surface	Span 20, Lot 1759C, sorbitan monolaurate, Hyamine 1622, Lot 379A, diisobutyl phenoxyethoxyethyl dimethyl benzyl ammonium chloride, Aerosol OT, Lot A6839 and dioctyl sodium sulfosuccinate	Surfactants did not change the surface tension at boiling point. However, heat transfer was increased
Jontz and Myers $(1960)$ [23]	Pool boiling of water with surfactants	Plate surface	Tergitol and Aerosol-22	The dynamic surface tension was changed for Tergitol solutions but not for aerosol solutions. Heat transfer increased by 50% with tergitol and by 400% with Aerosol
Dunskus and Westwater (1961) [63]	Pool boiling of isopropanoal with additives	Cylindrical surface	Additives	Bubble frequency increased with additives, surface viscosity with higher molecular weight additives was identified as a factor
Roll and Myers $(1964)$ [24]	Pool boiling of water with surfactants	Plate surface	Aerosols: OT, AY, IB, and MA; Hyonics: PE-200	Bubble volume, growth time and delay time decrease with surface tension, bubble frequency increased by an order of magnitude
Frost and Kippenhan $(1967)$ [32]	Flow boiling of water Channel with surfactants		Ultra Wet 60L	With the additive, more sites were nucleated, bubble growth was lower and heat transfer was enhanced
Huplik and Raithby $(1972)$ [25]	Pool boiling of water with surfactant	Plate surface	$FC-176$	Small amount of surfactant added to the liquid results in dramatic changes in boiling mechanism. At high heat fluxes, a substantial improvement in the heat transfer was achieved
Shah and Darby $(1973)$ [33]	Falling film flow (evaporation) of water with surfactant	Plate surface	Joy	Heat transfer was enhanced due to the increased foaming under nucleate boiling conditions
Shibayama et al. $(1980)$ [34]	Film flow of water (evaporation) with surfactants	Plate surface	Sodium oleate, Rapisool B80, Piluronic: F98, F88 and F208	Flow boiling heat transfer was enhanced
Podsushnyy et al. $(1980)$ [64]	Pool boiling of water with surfactants	Cylindrical surface	PVS-6 polyvinyl alcohol, NP-3 sulfonol, and SV1017 wetting agent	Enhancement of heat transfer has an optimum value for a surfactant concentration corresponding to cmc
Filippov and Saltobov (1982) [26]	Pool of water with surfactant	Cylindrical surface	Octadecylamine	Addition of the surfactant can enhance boiling heat transfer by 100%
Yang and Maa (1983) Pool of water with	surfactant	Plate surface	SLS and SLBS	As surface tension decreased, the heat transfer coefficient increased
Saltanov et al. (1986) $\lceil 28 \rceil$	Pool of water with surfactant	Cylindrical surface	Octadecylamine	For an optimum level of surfactant concentration, maximum enhancement up to 100% was obtained
Chang et al. (1987) $\left[35\right]$	Flow boiling of water with surfactant	Tube	<b>SLS</b>	Flow boiling heat transfer was enhanced by the addition of SLS
Tzan and Yang $(1990)$ [29]	Pool boiling of water with surfactant	Cylindrical surface	<b>SLS</b>	The bubble density was increased and boiling heat transfer was enhanced
Liu et al. (1990) [65]	Pool boiling of water with surfactants	Plate surface	BA-1, BA-2, BA-3, BA-4, DPE- 1, DPE-3; Gelatine, Oleic acid, trimethyl octadecyl ammonia chloride, and polyvinyl alcohol	Maximum heat transfer enhancement in the range of 200–700% was obtained with BA-1, BA-2 and BA-3, while no effect with other additives
Yang (1990) [60]	Pool boiling of water with surfactants	N/A	No specific surfactant mentioned	Theoretical study. Dynamic surface effect may play an in portent role in the boiling process of aqueous surfactant solutions
Chou and Yang $(1991)$ [30]	Pool boiling of water with surfactant	Plate surface	<b>SLS</b>	Maximum heat transfer enhancement is around $150%$
Wu and Yang $(1992)$ [66]	Pool boiling of water with surfactant	Cylindrical surface	<b>SLS</b>	Incipient superheat and bubble size were decreased and heat transfer was enhanced (continued on next page)

Table 1 (continued)



Table 1 (continued)



literature in chronological order. The table is organized by the contents of author/year, boiling mode, heating surfaces, surfactants, and results and remarks. It clearly shows the research status of boiling phenomena with surfactants from 1939 to 2005 in the literature. The latest studies have been included in this review. There are much more studies on nucleate pool boiling with surfactants [\[21–31,41–](#page-24-0) [47,50,56,60,62–86\]](#page-24-0) whereas there are relatively less studies on flow boiling with surfactants [\[20,32–35,87–89\]](#page-24-0) as indicated in the table. The available studies of boiling phenomena with surfactants include both experimental and theoretical aspects which are described, respectively, in the following.

In the experimental aspect of nucleate pool boiling with surfactants, the available studies have generally identified the type of heating surfaces and surfactant additives employed in each study and their effects on the boiling heat transfer behavior. The nucleate pool boiling heat transfer has generally been observed to increase with increasing the concentration of aqueous surfactant solutions. However, when the solution concentration is larger than critical micelle concentration (cmc), there will be reduction in boiling heat transfer enhancement. As just mentioned, Morgan et al. [\[21\]](#page-24-0) studied saturated nucleate pool boiling of water with surfactants (Drene and SLS, respectively) very early. Since then, a lot of studies on saturated nucleate pool boiling have been performed as summarized in [Table 1](#page-9-0). Just to present one example here, Hetsroni et al. [\[43\]](#page-25-0) studied the saturated nucleate pool boiling of aqueous Habon G solutions on an electrically heated constantan plate experimentally. They have concluded that heat transfer coefficient can be enhanced by the addition of Habon G, depending upon the Habon G concentration. The heat transfer increases with increasing the solution concentration and reaches a maximum value at a certain solution concentration, and decreases with further increasing the solution concentration. The effect of both the surface tension and the kinematic viscosity of aqueous Habon G solutions can explain the features of boiling heat transfer of the solutions. The enhancement of nucleate boiling heat transfer is connected to the decrease in surface tension, whereas the decrease in boiling heat transfer enhancement at higher concentration is related to the increase in viscous characteristics. There appears to be a critical concentration value of 530 ppm, beyond which there is reduction in the extent of heat transfer enhancement at high heat fluxes. This concentration value appears to be around the critical micelle concentration (cmc) of the surfactant. Fig. 10 shows the experimental results of the boiling heat transfer enhancement for various surfactant solutions at different heat fluxes versus the solution concentration by Hetsroni et al. [\[43\]](#page-25-0) and Tzan and Yang [\[29\]](#page-25-0). Similar results were reported by Fillipov and Saltanov [\[26\]](#page-25-0), Yang and Maa [\[27\],](#page-25-0) Saltanove et al. [\[28\]](#page-25-0), Chou and Yang [\[30\]](#page-25-0), Wu et al. [\[41\],](#page-25-0) Wasekar [\[44\],](#page-25-0) Zhang [\[45\]](#page-25-0), Zhang and Manglik [\[46\],](#page-25-0) Wasekar and Manglik [\[47,78\]](#page-25-0), Podsushnyy et al. [\[64\],](#page-25-0) Liu et al. [\[65\]](#page-25-0), Manglik [\[73\],](#page-26-0) Yang et al. [\[77,80\]](#page-26-0) and so on. It is generally concluded that the enhancement of saturated nucleate pool boiling heat transfer by the addition of small amounts of surfactants in water is due to the reduction of surface tension in the aqueous surfactant solutions. However, some researchers have reached different results from the generally accepted conclusions. Jontz and Myers [\[23\]](#page-24-0) studied saturated nucleate pool boiling of water with surfactants on a plate surface. They found that dynamic surface tension changed for Targitol solutions but did not change for aerosol solutions, and the nucleate boiling heat transfer was increased by 50% with Targitol and by 400% with aerosol. Lin et al. [\[68\]](#page-25-0) reported that some surfactants could enhance



Fig. 10. Heat transfer enhancement versus concentration for Habon G solutions presented by Hetsroni et al. [\[43\]](#page-25-0) and for SDS presented by Tzan and Yang [\[29\]](#page-25-0).

saturated nucleate pool boiling heat transfer while some did not. Wang and Hartnett [\[70\]](#page-26-0) studied saturated nucleate pool boiling of water with surfactants on a wire. They reported that nucleate boiling heat transfer of aqueous SLS solutions was similar to that of water, and nucleate boiling heat transfer of aqueous tween-80 solutions was lower than that of water although surface tensions were decreased by the addition of the surfactants. Their results are contradictory to the general conclusions reached by other researchers, and to the theoretical analysis according to Eqs. [\(3\) and \(4\)](#page-8-0) as well. Yang et al. [\[80\]](#page-26-0) studied saturated nucleate pool boiling of water with surfactants (Triton SP-190 and Triton SP-75, respectively) on a cylindrical surface. They reported that while both equilibrium surface tension and contact angle were depressed, the nucleate pool boiling heat transfer was hardly affected. The possible reason could be the opposite functions of surface tension and contact angle. The reason why some surfactants can depress surface tension of aqueous surfactant solutions but cannot enhance nucleate boiling heat transfer is unclear. The possible reason could be the effect of surfactant type. Besides a lot of studies of saturated nucleate pool boiling heat transfer, there are several studies on critical heat flux (CHF) of nucleate pool boiling and subcooled pool boiling with surfactants in the literature. Lin et al. [\[68\]](#page-25-0) studied nucleate pool boiling of water with SLS on a sphere. They concluded that the surfactant reduced film and transition boiling and both minimum and critical heat fluxes decreased with increasing the surfactant concentration. Wu et al. [\[69\]](#page-26-0) studied saturated nucleate pool boiling of aqueous SLS solutions on a sphere and reported that CHF was decreased by the addition of SLS. Inoue et al. [\[85,86\]](#page-26-0) studied nucleate pool boiling of water and water/ethanol mixtures with perfluoroalkyl compound on a wire and concluded that the surfactant has little effect on CHF. Near the CHF, huge amount of vapor is generated so that the surfactant may be diffused on the bubble surface and may be absent from the vicinity of the heated wire. As a result, the surfactant would hardly influence the CHF. The experimental results of CHF by Inoue et al. [\[85,86\]](#page-26-0) are shown in [Fig. 11.](#page-13-0) It is obvious that the critical heat flux of ethanol/ water mixture with surfactant has no big difference from that of ethanol/water mixture without surfactant. In the case of a sphere, cylindrical surface and plate surface heaters, CHF could be decreased due to the blanket of the huge amount of vapor on the surface. Therefore, addition of surfactants can enhance saturated nucleate pool boiling heat transfer of water, but it cannot enhance CHF. It seems to be quite reasonable that all the available studies have reached similar conclusions. In addition, Hetsroni [\[56,82\]](#page-25-0) studied subcooled pool boiling of water with surfactants. They have concluded that neither equilibrium surface tension nor viscosity may explain the subcooled boiling phenomena with surfactant. Subcooled boiling heat transfer is enhanced by the addition of surfactants, but boiling hysteresis has been found for degraded solutions as shown in [Fig. 12](#page-13-0). In addition, some researchers investigated the

<span id="page-13-0"></span>

Fig. 11. Comparison of the experimental critical heat flux versus mass fraction for binary mixture (ethanol/water) at different surfactant concentrations presented by Inoue et al. [\[85,86\].](#page-26-0)



Fig. 12. Boiling hysteresis for degraded surfactant solutions in subcooled boiling presented by Hetsroni et al. [\[82\]](#page-26-0).

saturated nucleate pool boiling of mixtures or organic fluids by the addition of surfactants. Lowery and Westwater [\[62\]](#page-25-0) studied saturated nucleate pool boiling heat transfer of methanol with surfactants on a cylindrical surface. They found that the surfactants did no change the surface tension of the solution at boiling point but the nucleate pool boiling heat transfer of methanol was increased. Dunskus and Westwater [\[63\]](#page-25-0) studied saturated nucleate pool boiling of isopropanoal with additives. They reported that the bubble frequency with additives increased and surface viscosity with higher molecular weight additives was a critical parameter. Tan and Wang [\[67\]](#page-25-0) studied saturated nucleate pool boiling heat transfer of mixture fluids (ethanol/water and methanol/water, respectively) with a surfactant on a GEWA-T tube. They concluded that the saturated nucleate pool boiling heat transfer of organic-water solutions was effectively enhanced by the addition of the surfactant. But they did not measure the physical properties such as the surface tension and viscosity of the solutions. Therefore, they were not able to explain the enhancement mechanism of nucleate boiling heat transfer in their study. Inoue et al. [\[85,86\]](#page-26-0) studied saturated nucleate pool boiling of ethanol/water mixtures with a surfactant on a wire. They concluded that heat transfer was enhanced by the addition of the surfactant but was hardly enhanced by surfactant concentrations over 1000 ppm. This is closely connected with the depression of surface tension up to 1000 ppm and the corresponding boiling heat transfer behavior. Kedzierski [\[76\]](#page-26-0) reported the study of saturated nucleate pool boiling of refrigerant-123 (R-123) with N-hexane on a GEWA-T surface. It should be mentioned that N-hexane is not a surfactant. He concluded that the saturated nucleate pool boiling heat transfer was enhanced with a simultaneous reduction in the bubble diameter and an increase in the site density. The pool boiling heat transfer enhancement mechanism is presumably due to an accumulation of hexane at the boiling surface in the channels. Apparently, the excess layer reduces the surface-energy between the liquid and the heat transfer surface causing the production of small diameter bubbles. Smaller bubbles induce higher site densities than larger bubbles. The site density is increased enough to more than compensate for the loss in bubble size and result in a net heat transfer enhancement. Wu et al. [\[74\]](#page-26-0) studied pool boiling of LiBr solution with surfactants on a cylindrical surface. They concluded that the surface tension of the surfactant solutions was depressed and saturated nucleate pool boiling heat transfer was enhanced. It seems that the addition of small amounts of surfactants in mixture fluids and organic fluids can enhance saturated nucleate pool boiling as well. However, Wen and Wang [\[81\]](#page-26-0) obtained the opposite conclusion in their experimental study of nucleate pool boiling of acetone with surfactants (SDS and Triton X-100, respectively). They concluded that surfactants have little influence on nucleate boiling heat transfer of acetone. Although they tried to explain the boiling heat transfer phenomena by considering the change of surface wettability (actually it should be contact angle, they did not mention this important parameter in their paper.). Apparently they were not able to give a reasonable explanation of the boiling heat transfer phenomena as they did not measure the physical properties of the solutions under their test conditions. Generally, most of the available experimental studies have indicated that addition of surfactants can enhance nucleate pool boiling heat transfer of water, mixture and organic fluids except some studies as indicated.

In the theoretical aspect of saturated nucleate pool boiling with surfactants, a lot of studies have focused on exploring bubble dynamics affected by addition of surfactants and the enhancement mechanism of saturated nucleate pool boiling with surfactants. It was recognized that surface tension had a strong effect on boiling heat transfer with surfactants in one of the earliest research [\[20\].](#page-24-0) Without exception, the following studies of saturated nucleate boiling heat transfer mechanisms have emphasized on the effect of the solution physical properties such as surface

tension and viscosity on bubble dynamics, nucleate process and boiling heat transfer behavior. As the first step, a lot of studies have been performed to measure the physical properties of aqueous surfactant solutions as described Section [2.](#page-2-0) Then, the effect of the physical properties of the aqueous surfactant solutions on nucleate pool boiling heat transfer behavior, nucleate process and bubble behavior have been investigated, and visualizations of the nucleate boiling process have been performed by means of high-speed video cameras. For example, in earlier studies, Roll and Myers [\[23\]](#page-24-0) observed the nucleate boiling process of aqueous surfactant solutions and found that bubble frequency was increased by an order of magnitude. Dunskus and Westwater [\[63\]](#page-25-0) observed the bubble performance and also noticed that bubble frequency was increased with surfactants. Visualization of nucleate boiling process was also carried out by a number of researchers such as Tzan and Yang [\[29\],](#page-25-0) Wasekar [\[44\],](#page-25-0) Zhang [\[45\]](#page-25-0), Wasekar and Manglik [\[47\]](#page-25-0), Frost and Kippenhan [\[32\]](#page-25-0), Yang [\[60\],](#page-25-0) Wu and Yang [\[66\]](#page-25-0), Zhang and Manglik [\[84\],](#page-26-0) Inoue et al. [\[85,86\]](#page-26-0) and so on, and similar conclusions have been reached. Of these studies, one typical example is the study of the effect of surface tension on saturated nucleate pool boiling carried out by Yang [\[60\].](#page-25-0) Based on systematic experiments, he concluded that the dynamic surface tension rather than the static or equilibrium surface tension was perhaps the more appropriate correlating parameter. In addition, the surfactant concentration variation at the bubble interface creates a surface-tension gradient, which leads to Marangoni convection in the adjacent liquid and may influence the bubble growth behavior greatly. Generally, the nucleate boiling heat transfer behavior with surfactants is dependent upon surface tension, interfacial stresses, the nucleation process, Maragoni effect and foam. Furthermore, the nucleate boiling heat transfer mechanisms are influenced by the nature of surfactants and their chemistries in the aqueous surfactant solutions. Several studies also reported the effect of surfactant types and concentrations on the dynamic and equilibrium surface tension of solutions [\[21–24,29,41–](#page-24-0) [46,70\]](#page-24-0). It has been further confirmed that surfactants greatly change the nucleate boiling heat transfer behavior of water by modifying nucleation process and the concomitant bubble dynamics and changing of the aqueous surfactant solution properties at the vapor–liquid interface. Based on the experimental studies on the nucleate boiling heat transfer behaviors and boiling process observations, several different mechanisms of nucleate boiling with surfactants were postulated in the literature. Much of the reported work focused on documenting bubble incipience, growth, detachment and coalescence by means of visualization [\[22,28–30,43–45,65,66,71,75,85,86\]](#page-24-0). Some researchers attempted to correlate the enhanced boiling heat transfer performance with changes of solution properties and the modified bubble dynamics through their observation [\[66,83\].](#page-25-0) Wu and Yang [\[66\]](#page-25-0) studied the effect of surfactants on boiling incipience and bubble growth dynamics from a stable nucleation site using a high speed motion picture

camera. Sodium lauryl sulfate (SLS) was used as a surfactant with its concentration in the aqueous solutions ranging from 0 to 500 ppm. Contact angles for the different concentrations were measured on stainless steel flat plate at room temperature  $(28 \text{ °C})$ . The contact angle had a maximum value of  $75^{\circ}$  at 200 ppm and the overall variation was within  $10\%$  with a minimum value of 68 $\degree$  for pure water as well as 400 ppm solution. The incipient superheat was found to decrease significantly by the addition of the surfactant. This was attributed to surface tension depression and contact angle change. Also, the bubble growth period was observed to increase slightly, while the waiting period and the time interval between two consecutive bubbles were reduced drastically. Similar observations of the increased bubble frequency in boiling of surfactant solutions were reported by Podsushnyy et al. [\[64\]](#page-25-0), Liu et al. [\[65\]](#page-25-0), Ammerman and You [\[71\]](#page-26-0), Wasekar and Manglik [\[78\]](#page-26-0), Wasekar [\[44\]](#page-25-0), Zhang and Manglik [\[84\],](#page-26-0) Zhang [\[45\]](#page-25-0), Hetsroni et al. [\[43,56,82\]](#page-25-0) and so on. Another aspect of the effect of surfactants on the bubble dynamics is that the departure diameter decreases considerably with increasing solution concentration and heat flux as compared to that of boiling in pure water. As observed by Saltanov et al. [\[28\]](#page-25-0), the minimum detachable bubble diameter and its maximum departure frequency correspond to the maximum nucleate boiling heat transfer coefficient. The departing bubbles are more regular in shape and have a reduced tendency to coalesce. In addition, bubble rise velocity is reduced due to the Marangoni effect, which then reduces the internal circulation. A reduction in bubble rise velocity was obtained with a method of LDA measurement by Ammerman and You [\[71\].](#page-26-0) Furthermore, in the presence of surfactants and at higher heat fluxes, bubbles were found to meander less owing to their higher departure frequency. Similar conclusions have been reached by other researchers [\[43–46,82,85,86\]](#page-25-0). [Fig. 13](#page-15-0) shows the observed results of bubble performance for different solution concentrations by Inoue et al. [\[85,86\].](#page-26-0) In addition, considering the effect of viscosity, Hestroni et al. [\[43\]](#page-25-0) concluded that viscosity decreases heat transfer which is important in correlating heat transfer with viscous solutions showing the non-Newtonian fluidic behavior. Hestroni et al. [\[56,82\]](#page-25-0) also studied subcooled pool boiling heat transfer with surfactants. They concluded that neither surface tension nor viscosity was able to explain the subcooled boiling phenomena of aqueous surfactant solutions. In addition to the studies of nucleate pool boiling of water with surfactants, the effect of surfactants on saturated nucleate pool boiling of mixtures and the effect of N-hexane (not a surfactant) on nucleate boiling of organic fluids such as refrigerant-123 and lithium bromide were studied as described above. Similar boiling mechanisms were obtained for mixtures and organic fluids. For example, Kedzierski [\[76\]](#page-26-0) observed that bubble diameter was reduced and the nucleate site density was increased in his study of saturated nucleate pool boiling of refrigerant-123 by the addition of N-hexane. This is in accordance with the observation for saturated nucleate pool boiling of



<span id="page-15-0"></span>

Fig. 13. Comparison of bubble performance for different solution concentrations presented by Inoue et al. [\[85,86\].](#page-26-0)

water with surfactants. In addition, some researchers tried to model the boiling process and bubble performance. Wasekar [\[44\]](#page-25-0) carried out computational modeling to understand and estimate the surfactant effects on the Marangoni convection for boiling nuclei under short-time transients which correspond to and cover the characteristic times for boiling bubble growth and surfactant diffusion. Zhang [\[45\]](#page-25-0) developed a computational model for the complex single bubble dynamics that addresses the effects of surface tension, viscosity, microlayer, wall superheat, and apparent contact angle on the bubble dynamics. Sher and Hetsroni [\[83\]](#page-26-0) developed an analytic model for nucleate boiling with surfactants. Their model fits to the test data of Hetsroni et al. [\[43\]](#page-25-0) well. However, whether the model fits to others' test data or not has not been verified. Due to the very complex process of saturated nucleate boiling with surfactants, it is definitely a difficult task to develop a general model for boiling with surfactants. Therefore, most of the available studies on the mechanisms of nucleate boiling phenomena with surfactants emphasized on the effect of surfactants of the bubble dynamics nucleate boiling process and heat transfer behavior by the means of visualization.

With respect to flow boiling with surfactants, there are much less studies on this topic as compared to that of nucleate pool boiling with surfactants. Of the large number of studies listed in [Table 1](#page-9-0), only eight studies are related to flow boiling. However, the limited studies of flow boiling with surfactants have confirmed certain positive results with respect to the enhancement of flow boiling heat transfer by the addition of surfactants. Stroebe et al. [\[20\]](#page-24-0) found that flow boiling heat transfer was enhanced by the addition of a surfactant. Frost and Kippenhan [\[32\]](#page-25-0) also found that more boiling sites were nucleated and bubble growth was lower and thus flow boiling heat transfer was enhanced with Ultra wet 60L. Similar results have been obtained by Shah and Darby [\[33\]](#page-25-0), Shibayama et al. [\[34\]](#page-25-0), Chang et al. [\[35\],](#page-25-0) Hetsroni et al. [\[87,88\]](#page-26-0) and Klein et al. [\[89\]](#page-26-0). Especially, Klein et al. [\[89\]](#page-26-0) seem to be the first to study flow boiling with surfactants in microchannels, which combined both the heat transfer enhancement by the addition of surfactants and flow boiling heat transfer in microchannel (micro-scale heat transfer). In addition, they used a kind of environmentally friendly surfactants and considered the environmental aspect. They concluded that an optimal value of mass flux was found for the flow boiling heat transfer. In general, previous studies of flow boiling with surfactants have confirmed that flow boiling heat transfer can be enhanced by the addition of surfactants. However, flow boiling heat transfer enhancement mechanisms which should be related to the feature of flow boiling have not really been investigated. The heat transfer mechanisms similar to that of saturated nucleate pool boiling were used to explain the flow boiling phenomena with surfactants. Apparently, the explanation of flow boiling phenomena according to the nucleate pool boiling mechanisms cannot satisfactorily explain the real situation of flow boiling with surfactants. Possibly due to the more complex phenomena involved in flow boiling with surfactants as compared to that of nucleate pool boiling with surfactants, both the experimental and theoretical studies of flow boiling with surfactants are rather less than these of saturated nucleate pool boiling with surfactants. Therefore, emphasis should be placed on this aspect to understand flow boiling phenomena with surfactants in both normal size and small channels in the future, especially, to explore the heat transfer enhancement mechanisms of flow boiling with surfactants.

#### 3.2. Boiling phenomena with polymeric additives

Over the past decades, a number of the studies have been conducted to investigate boiling phenomena with polymeric additives. [Table 2](#page-16-0) lists the summary of studies of boiling phenomena with polymeric additives in the literature in chronological order. The table is organized by the contents of author/year, boiling mode, heating surface, additives, and results and remarks. It clearly shows the research status in this aspect. Both pool boiling [\[45,50,](#page-25-0) [57,58,90,91,93,95–100,103–108\]](#page-25-0) and flow boiling [\[92,94\]](#page-26-0) <span id="page-16-0"></span>Table 2





Table 2 (continued)

Author/year	Boiling mode	Heating surfaces	Additives	Results and remarks
Chen et al. $(1993)$ [103]	Pool boiling of polymer solutions	flask	N/A	Boiling has a pronounced effect on the course of chemical reaction. Boiling of an inert solvent can accelerate the apparent reaction rate due to mass-transfer phenomena arising in the vicinity of the continuously generated vapor-liquid interface
Shulman et al. $(1993)$ [104]	Pool boiling of aqueous polymer solutions	N/A	High-molecular compounds	Effects of elastic viscosity and diffusion resistance during the growth of vapor bubbles in a superheated polymer solution are studied
Shulman and Levitskiy $(1996)$ [105]	Pool boiling of polymer solutions	N/A	High-molecular compounds	Effects of elastic viscosity and diffusion resistance during the growth of vapor bubbles in a superheated polymer solution are studied
Levitskiy et al. $(1996)$ [106]	Pool boiling of polymeric solutions	Plate surface	PAA, HEC and PEO	The reasons for the (with respect to a pure solvent) changes in the heat transfer coefficient in bubble boiling of polymer solutions were discussed
Bang et al. $(1997)$ [107]	Pool boiling of polymeric solutions	Sphere	PEO (polyethylene oxide polymer)	Quenching experiments were conducted to study the physical mechanisms of the suppression of vapor explosions in polymer solutions
Zhang $(2004)$ [45]	Pool boiling of water with surfactants	Cylindrical surface	DTAC, CTAB, Ethoquad O/12 PG and Ethoquad 18/25.	Saturated nucleate boiling was studied. Bubble behaviors were visualized. Modeling of single bubble was performed
Zhang and Manglik $(2005)$ [108]	Pool boiling of water with polymer	Cylindrical surface	HEC-QP300 and Carbopol 934	In HEC solutions, boiling is enhanced with increasing concentration till an optimum value near the critical polymer concentration. In Carbopol solutions, boiling is deteriorated with increasing concentration

are included. In addition, some theoretical analysis on bubble performance which is related to boiling phenomena of polymer solutions has been presented [\[101,102\]](#page-26-0). However, there are only two papers related to the research of flow boiling with polymeric additives available in the literature so far. In addition, compared to that of boiling phenomena with surfactants, studies of boiling phenomena with polymeric additives are much less. The reason is possibly due to the very complex boiling phenomena involved in the boiling process of polymeric additive solutions. In addition, aqueous polymeric additive solutions generally reveal the shear-thinning non-Newtonian fluidic behavior except for some polymeric surfactants as already mentioned in the previous section. The enhancement of nucleate boiling heat transfer is generally affected by the viscosity of aqueous polymeric additive solutions.

Potchaphakdee and Williams [\[57\]](#page-25-0) are perhaps the first to study nucleate pool boiling with polymeric additives including acrylamide, polyacrylamides (PA-10, PA-20) and hydroxyethyl cellulose (HEC). They concluded that trace amounts of polymers dissolved in water led to substantial increases in nucleate boiling heat flux. Surfactant polymers such as HEC seem to be more effective in this regard than non-surface-active polymer at equal viscosities or concentrations. But like low molecular weight surfactants, the peak heat flux (critical heat flux) are not significantly improved. In addition, foam can be a serious problem. Polymer PA leads to significantly improve boiling heat transfer coefficients and peak heat fluxes would be considerably higher than that for water. This is typical for non-surfactant polymers. No foaming occurs. However, the enhancement of nucleate boiling heat transfer seems ultimately limited by the effect of viscosity for all polymers. For a polymer composed of certain chemical group, an optimum solution viscosity which is influenced by the solution concentration and the molecular weight of the polymer may be selected. Similar conclusions were reached by Gannet and Williams [\[90\]](#page-26-0), Miaw [\[91\]](#page-26-0), Paul and Abdel-Khalik [\[96\],](#page-26-0) Ulicny [\[97\]](#page-26-0), Hu [\[100\],](#page-26-0) Zhang [\[45\]](#page-25-0) and Zhang and Manglik [\[108\].](#page-26-0) However, not all polymers can enhance boiling heat transfer as already pointed out in the previous section. Yang and Maa [\[93\]](#page-26-0) reported that no boiling heat transfer enhancement was found with HEC in their study. This is contradictory to the studies by Kotchaphakdee and Williams [\[57\]](#page-25-0), Miaw [\[91\],](#page-26-0) Hu [\[100\]](#page-26-0) Zhang [\[45\]](#page-25-0), Zhang and Manglik [\[108\]](#page-26-0), who used HEC as well. The reason why they obtained contrary results is unclear. Paul and Abdel-Khalik [\[95\]](#page-26-0) also reported that no boiling heat transfer enhancement was observed in their study. They concluded that polymer type, concentration

and molecular weight were important as they affected the solution viscosity, and boiling heat transfer generally decreased with increasing viscosity. Hu [\[100\]](#page-26-0) reported that boiling heat transfer was reduced with PA-30. Zhang [\[45\]](#page-25-0) and Zhang and Manglik [\[108\]](#page-26-0) found that boiling with Carbopol 934 was deteriorated with increasing the solution concentration. It seems that some polymers can enhance nucleate pool boiling heat transfer whereas others can not. Figs. 14 and 15 show the experimental results for nucleate pool boiling of aqueous polymeric additive solutions of HEC-QP300 and Carbopol 934, respectively, by Zhang and Manglik [\[108\].](#page-26-0) HEC-QP300 generally increases boiling heat transfer with increasing the solution concentration except for higher concentrations whereas Carbopol 934 decreases boiling heat transfer for all solution concentrations. The reason is due to the effect of polymer types and their chemical structures on the boiling phenomena. As already described in the previous section, HEC is a type of polymeric surfactant and it shows the surfactant behavior while Carpbopol 934 shows a polymer behavior. The reason why Carpbopol decreases boiling heat transfer is due to the effect of its chemistry and molecular weight. In addition, the only two available studies of flow boiling with polymers indicated that flow boiling heat transfer could be enhanced by the addition of small amounts of polymeric additives [\[92,94\]](#page-26-0). However, it is difficult to reach such a general conclusion from the only two studies as it has already confirmed that some polymers can enhance nucleate pool boiling while others can not. Obviously, the study of flow boiling with polymeric additives is rather scarce. In addition, there is no study of the heat transfer mechanisms with respect to flow boiling with polymeric additives so far. The study of the heat transfer mechanisms is also limited by the very little available experimental work on the flow boiling with polymeric additives.

In the aspect of heat transfer mechanisms of nucleate boiling with polymeric additives, several studies were carried out to investigate the boiling process and bubble



Fig. 14. The variation of heat flux versus superheated temperature for HEC-QP300 presented by Zhang and Manglik [\[108\]](#page-26-0).



Fig. 15. The variation of heat flux versus superheated temperature for Carbopol 934 presented by Zhang and Manglik [\[108\]](#page-26-0).

performance by the methods of visualization [\[45,57,96,](#page-25-0) [97,108\]](#page-25-0). The nucleate pool boiling of aqueous polymeric additive solutions is always accompanied by the hydrodynamic patterns which are quite different from those for water. Bubbles are smaller, release faster and rise in a more orderly fashion, with reduced coalescence. These observations resemble those for certain low molecular weight additives which are not surfactants. All these observations are directly related to the increased heat transfer behavior, but yet do not tell why it occurs for polymer in particular. Kotchaphakdee and Williams [\[57\]](#page-25-0) proposed a synthesis of several mechanisms. First, the great number of bubbles is probably due to the fact that polymers are notoriously less soluble than small molecules and therefore prefer to aggregate or adsorb on surfaces when solubility is further reduced at high temperatures. This in turn could lead to a large of number of new potential nucleate sites and thus more bubbles. Reduced bubble size is very likely a consequence of increased liquid viscosity, which would retard bubble growth rates. This tendency would be further enhanced by elastic stresses in the liquid, a phenomenon unique to polymeric systems. In addition, evaporation of the water into bubble serves to concentrate the solute locally, and the viscous and elastic liquid properties (which retard bubble growth) are known to be extremely sensitive to slight changes in polymer concentration. In addition, the surface viscosity may be an important parameter, but it seems rarely to be measured. It is distinctly possible that bubble dynamics and gross convection are altered by the viscoelastic nature of the solution. The existence of fluid viscoelasticity is known to give rise to unusual secondary flows which could affect boiling phenomena. But this point is needed to be further confirmed through experimental work. Due to the limited study of nucleate pool boiling phenomena with polymeric additives, the mechanism of nucleate boiling phenomena with polymeric additives has not been understood completely and there is still too much to do. Further research in this aspect is encouraged in the future.

## 3.3. Other studies related to surfactants and polymeric additives

Some surfactants and polymeric additives can be used to reduce the drag in turbulent flow. For polymeric additive solutions and some surfactant solutions at higher concentrations, the fluids reveal the non-Newtonian fluidic behavior. In this situation, the fluid viscoelasticity becomes critical important. The existence of fluid viscoelasticity is known to give rise to unusual secondary flows and to produce anomalous drag reduction in turbulent pipe flow. For example, HEC and PA are able to act as drag reducers and thus be particularly interesting. A lot of studies have been carried out to investigate the drag reduction during the flow and heat transfer [\[109–112\].](#page-26-0) However, there is no study of the effect of surfactants and polymeric additives on drag reduction in flow boiling in the literature so far. Whether the addition of surfactants and polymeric additives can decrease the drag in flow boiling or not is unknown. As the addition of surfactants and polymeric additives in water can enhance flow boiling heat transfer, without doubt, it is of great interest to conduct the research on the drag reduction of surfactants and polymeric additives in the flow boiling process. Especially, the research in this aspect should be connected to the heat transfer mechanisms of flow boiling with surfactants and polymeric additives. It is suggested that the research in this aspect be conducted in the future.

### 3.4. Discussion

A large number of studies on boiling phenomena with surfactants and polymeric additives have been conducted over the past years. Most of the studies have concerned the effect of surfactants and polymeric additives on the physical properties (surface tension and viscosity) of the aqueous surfactant and polymeric additive solutions. Both experimental and theoretical studies have been conducted. However, through the present comprehensive review on this interesting topic, several important aspects have not been fully considered in the previous studies and are still needed to be emphasized in the future.

First, it is well known that pressure is a critical parameter in the study of boiling phenomena because it has great effect on the nucleate process, bubble diameter and saturation temperature. Obviously, there is a lack of systematic study of boiling phenomena with surfactants and polymeric additives in a wide range of pressures. Some researchers even did not mention the test pressures used in their studies. In addition, surface tension varies with temperature (corresponding to saturation pressure) for liquids. Surface tension decreases with increasing pressure and tends to be zero at critical pressure. However, how the surface tensions of aqueous surfactant and polymeric additive solutions vary with the saturation temperature (corresponding to the saturation pressure) is lacking in the literature. Because there are so many surfactants and polymers and the effect of surfactants and polymeric additives on surface tension is quite different for various surfactants and polymers, it is necessary to measure the surface tension for a specific aqueous surfactant or polymeric additive solution at the saturation temperature. Although a lot of researchers measured the surface tensions of the solutions, The surface tension data in a wide range of pressures are lacking. Therefore, it must be pointed out that pressure should be considered as one key parameter in the study of boiling phenomena with surfactants and polymeric additives.

Second, contact angle is a very important parameter in exploring the mechanisms of boiling phenomena. Of the available studies, most researchers measured the surface tensions of aqueous additive solutions but did not consider the effect of the contact angles on the boiling phenomena. As shown in Fig. 16, contact angle  $\theta$  is the angle between the liquid and solid interface. Contact angle is one of the most important parameters in understanding boiling phenomena since it characterizes the wettability of the solid surface by the liquid. The liquid–solid system can be either completely wetting  $(\theta = 0^{\circ})$ , or have different degrees of wetting  $(0 < \theta < 180^\circ)$ , or be complete non-wetting  $(\theta = 180^{\circ})$ . Knowledge of the intermolecular interactions, both within the liquids, and across the liquid–vapor (or liquid–gas) and liquid–solid interfaces, is an important part of characterizing surface wettability or contact angle. The degree of the liquid spreading on the solid surface is governed by the surface tension of the liquid and vapor  $\sigma_{\text{LV}}$ , the surface tension of the solid and vapor  $\sigma_{SV}$  (usually referred to as the surface free energy), and the interfacial tension of the solid and liquid  $\sigma_{SL}$ . These forces essentially represent the liquid–vapor, solid-vapor, and solid–liquid interfacial tensions, and their interactions are depicted in Fig. 16. At equilibrium state, the resultant force is thus zero. The Young's equation [\[113\]](#page-26-0) is the basis for understanding the phenomenon of contact angle or surface wetting on solid surfaces as

$$
\theta = \arccos\left(\frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}\right) \tag{5}
$$



Fig. 16. The contact angle at the equilibrium of three interfacial tensions of at the vapor–liquid, vapor–solid and liquid–solid interfaces.

In the available studies, a number of researchers measured contact angles for surface-liquid–air rather than surfaceliquid–vapor. To understand the heat transfer mechanisms, it is important to measure the surface of tension of surfaceliquid–vapor at the boiling temperature.

Finally, with respect to the theoretical study, how to model the boiling phenomena of aqueous surfactant and polymeric additive solutions by incorporating the key parameter-surface tension and contact angle and how to explain the heat transfer mechanisms are still a big challenge. As pointed out by Yang [\[38\]](#page-25-0), we are still far from a systematic theory or explanation for the enhancement of boiling heat transfer caused by surfactant additives. Apparently, there is still much work to do to understand the boiling phenomena with surfactants and polymeric additives.

## 4. A new cross-research area related to boiling phenomena with surfactants and polymeric additives

A new cross-research area on boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels (micro-scale boiling heat transfer) has been identified through the present comprehensive review. One the one hand, a lot of experimental and theoretical studies of boiling phenomena with surfactants and polymeric additives have been conducted to understand the boiling behavior and the heat transfer mechanisms over the past decades. On the other hand, emphasis has been placed on the study of the boiling phenomena (both pool boiling and flow boiling) in confined spaces and microchannels to investigate the effect of confined spaces and microchannels on boiling behavior and the heat transfer mechanisms in recent years. With the urgent needs in highly specialized fields such as the cooling of electronic equipment, the thermal control of space station, the development of micro-electro-mechanical-systems (MEMS), micro-fabricated fluidic system, bioengineering and so on, as a new cross-research area, the study of boiling phenomena (both nucleate pool boiling and flow boiling) in confined spaces and microchannels is becoming increasingly important. Because the boiling heat transfer and transport phenomena in confined spaces and microchannels are quite different from those in large spaces and conventional channels, quite a number of studies have been conducted to understand the boiling phenomena in confined spaces and microchannels [\[114–141\]](#page-26-0). These include the studies of boiling heat transfer, bubble performance (boiling patterns), flow patterns, and critical heat flux (CHF) in narrow spaces and microchannels of various sizes and geometries under various peripheral conditions. However, as for the study of boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels (micro-scale boiling heat transfer), which is a new cross-research area, there is little information in the literature. To identify the main research requirements in this cross-research area, a brief review of boiling phenomena in confined spaces is present here. As for flow boiling in microchannels, four reviews were done by Kandlikar [\[131\]](#page-27-0), Thome [\[132,133\]](#page-27-0) and Cheng and Mewes [\[11\]](#page-24-0) in the literature in recent years. Therefore, only the studies of nucleate pool boiling in confined spaces are reviewed. Then, several important research directions are pointed out. Some scientific hypotheses have also been proposed based on the literature review and analysis.

#### 4.1. Boiling phenomena in confined spaces: a brief review

A number of studies have been conducted to investigate the boiling phenomena in confined spaces so far. These include the studies of boiling heat transfer, bubble performance and critical heat flux (CHF) in narrow spaces of various sizes and geometries under various peripheral conditions. Ishibashi and Nishikawa [\[114\]](#page-26-0) performed experiments at rather low heat flux in a vertical annuli of a heated core and unheated external shroud with both ends open for a gap size ranging from 0.6 to 2 mm. They identified the isolated bubble region and the coalesced bubble region. Compared to the unconfined situation, the enhanced heat transfer coefficient is attained in the coalesced bubble region and an empirical correlation was proposed for this region. Katto et al. [\[115\]](#page-26-0) carried out experiments on nucleate boiling of water in the space between two horizontal co-axial disks with the lower heated for different distances from 0.1 to 2 mm and they classified the boiling behavior depending on gap size into three regions as: unheated bubbles, depressed bubbles and oppressed bubbles. They investigated in detail the region of depressed bubbles and pointed out the thin film evaporation as a dominant heat transfer mechanism of this region. The general trend of these previous studies shows under low heat flux that the heat transfer coefficients increases as gap size decreases, when it is not too small. The results of Katto et al. showed a very fast decrease in the heat transfer coefficient for water when the distance is 0.1 mm. The increase in the heat transfer coefficient for confined boiling is explained by Katto et al. as the results of evaporation of the liquid film between the bubble and the heating wall, in the case of flattened bubbles, because with the narrow gap the surface area of the thin liquid film is increased. Yao and Chang [\[117\]](#page-27-0) studied pool boiling in a vertical annuli with a closed bottom for various gap sizes (0.32, 0.8 and 2.58 mm), fluids, and heat fluxes and distinguished three boiling regimes of isolated deformed bubbles, slightly deformed bubbles, and coalesced deformed bubbles on a boiling map where the Bond number and the boiling number are chosen as coordinates. As for the critical heat flux in a confined space, Chang and Yao [\[118\]](#page-27-0) modified the flooding model of Wallis to correlate their data in a vertical annuli with a closed bottom. Fujita et al. [\[119\]](#page-27-0) investigated the pool boiling heat transfer in a confined narrow space for saturated water at the atmospheric pressure between heated and unheated parallel rectangular plates. Experiments were conducted at heat flux from boiling

inception to CHF on heating surfaces with gap sizes of 0.15, 0.6, 2 and 5 mm under three surfaces peripheral conditions with all-open edges, closed side edges and closed side and bottom edges. Their experimental results indicated that the heat transfer increases up to a certain maximum value as the gap size decreases at a moderate heat flux, while degradation occurs for further decrease of the gap size over the whole heat flux range. For the enhanced boiling heat transfer, a predictive method was proposed based on the consideration of heat transfer mechanisms. Bonjour and Lallemand [\[120\]](#page-27-0) conducted an experimental study investigating the CHF during natural convective boiling of R113 in vertical channels. They used a vertical channel having gap sizes ranging from 0.3 to 2.5 mm with a fixed height. They confirmed that, at any pressure, reducing the gap size reduces the CHF. Especially, they developed a correlation by modifying the Monde et al. [\[121\]](#page-27-0) correlation to take into account the influence of pressure. Finally, they reported that a more fundamental study of the triggering mechanisms of the CHF in confined boiling is necessary in order to understand the phenomena observed during their study. Bonjour and Lallemand [\[122\]](#page-27-0) performed experiments to identify the different regimes of natural convective boiling of R113 in narrow rectangular vertical channels (confined spaces) with the gap size ranging from 0.5 to 2 mm. Three boiling regimes were observed: nucleate boiling with isolated deformed bubbles, nucleate boiling with coalesced bubbles and partial dryout. Both the former two regimes result in a heat transfer enhancement whereas the latter implies heat transfer deterioration. They also developed a new flow pattern map for confined boiling based on the Bond number and reduced heat flux (ration of the heat flux to the critical heat flux). Geisler and Bar-Cohen [\[123\]](#page-27-0) analyzed the nucleate boiling and critical heat flux inside vertical channels for FC-72 with gap sizes between 0.3 and 1.6 mm. The similar conclusions have been reached. As for CHF, it is highly dependent on the confinement and the general trend is its decrease with a decrease in gap size.

In sum, for nucleate boiling in confined spaces, with low heat flux, heat transfer can be enhanced up to 6 times, while in the case of high heat flux, heat transfer could be deteriorated and the critical heat flux is greatly reduced with decreasing the gap size. The intensity of heat transfer increases with decreasing confined space size and there exists an optimum value of the gap size for heat transfer enhancement. The bubble behaviors (boiling patterns) are very important to understand the heat transfer mechanism and to model the nucleate boiling heat transfer in confined spaces.

## 4.2. Boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels: research directions

As indicated in the foregoing, there are a large number of studies on both nucleate boiling with aqueous surfactant and polymeric additive solutions and boiling phenomena in confined spaces and microchannels over the past years. Both heat transfer behaviors including CHF and heat transfer mechanisms including bubble performance (boiling patterns) have been explored. However, as for the study of boiling phenomena of aqueous surfactant solutions in confined spaces, there is little information on the crossresearch topic in the literature so far. In addition, there is little information of flow boiling with surfactants and polymeric additives in microchannels as well. Therefore, it is essential to conduct studies on this cross-boundary combining both boiling with surfactants and polymeric additives and boiling in confined spaces and microchannels.

On the one hand, the research in this new cross-area is able to meet the practical demands for the development of compact and micro thermal components such as micro heat exchangers, cooling technology for electronic system and so on. On the other hand, boiling process is generally a complex process and there are still many unsolved problems such as the heat transfer mechanisms and models. Especially modeling boiling phenomena is a difficult issue but a very important one. The research on this topic is expected to bring advancement of new scientific knowledge in this cross-area from the academic viewpoint. Therefore, the study of boiling phenomena of aqueous surfactant and polymeric additive solutions in confined spaces and microchannels is of great significance to both practical and academic aspects. By considering the main effect factors in boiling of aqueous surfactant and polymeric additive solutions and boiling in confined spaces and microchannels, the following experimental and theoretical research directions have been identified and should be studied in the future:

- (1) Experiments of boiling heat transfer behavior including CHF of aqueous surfactant and polymeric additive solutions in confined spaces and microchannels (both the effect of surfactants and polymeric additives, and space gap and channel sizes should be considered).
- (2) Boiling phenomena such as bubble generation, bubble departure size and frequency, bubble coalescence, boiling patterns (flow patterns for flow boiling), and bubble rising velocity (volumetric vapor flow rate) related to surfactant or polymeric additive concentrations and gap (channel) sizes by the methods of flow visualization and a LDA.
- (3) Heat transfer mechanisms related to boiling patterns (flow patterns for flow boiling) and modeling of boiling heat transfer and critical heat flux (CHF) by incorporating key effect factors based on the observed phenomena and measured data including bubble velocity, Marangoni convection, natural convection and others. For flow boiling, the heat transfer mechanisms and models should be related to the flow patterns. Flow pattern based heat transfer models should be developed.

# <span id="page-22-0"></span>4.3. Boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels: scientific hypotheses

Despite of extensive studies of boiling phenomena over the past 50 years, the underlying mechanism of boiling is still far from being fully understood, due to the extreme complexity of the phenomena. The parameters affecting boiling heat transfer (both nucleate pool boiling and flow boiling) are heat flux, saturation pressure, and thermophysical properties of a working fluid, surface characteristics such as thermo-physical properties of the material, dimensions, surface finish, microstructure, contact angles, bubble performance and space and channel sizes. As for boiling phenomena of aqueous surfactant and polymeric additive solutions in confined spaces and microchannels, several key parameters have been identified as indicated in the above. The surfactant type, concentration of the surfactant in the solution, surface tension, heat flux, the confined space gap and microchannel sizes have great effect on the heat transfer behavior, nucleation process, bubble performance, boiling patterns (flow patterns for flow boiling) and critical heat flux (CHF). Surface tension is an important parameter in the study of boiling phenomena of aqueous surfactant and polymeric additive solutions. The boiling processes of aqueous surfactant and polymeric additive solutions in confined spaces and microchannels become much more complex as the combined function of surfactants and polymeric additives, the confined space gap and micro channel sizes plays a key role in the heat transfer behavior and mechanisms. Therefore, to understand the boiling phenomena and heat transfer mechanisms, it is important to know how surfactants and polymeric additives together with the confined space gap and microchannel sizes affect the bubble performance, boiling patterns (flow patterns for flow boiling), heat transfer behavior and critical heat flux. As indicated in the above-review of nucleate pool boiling, due to the effect of confined space gap sizes, the boiling patterns are more important to affect the heat transfer behavior and CHF. As for flow boiling in microchannels, flow patterns are very important in understanding the heat transfer behavior and mechanisms. The channel sizes have main effect on the flow patterns. For flow boiling in microchannels, the reviews by Kandlikar [\[131\]](#page-27-0), Thome [\[132,133\]](#page-27-0) and Cheng and Mewes [\[11\]](#page-24-0) are recommended to be referred to. As nucleate pool boiling may be considered as a kind of flow boiling with a flow velocity of zero, it is a fundamental to understand the flow boiling phenomena. Hence, here only the nucleate pool boiling in confined spaces is focused on to propose some scientific hypotheses.

To describe the effect of the gap size on boiling phenomena in a confined space, Bond number  $(B<sub>o</sub>)$  is introduced and defined as the ratio of a characteristic dimension (gap size  $e$ ) of the confined space to the bubble departure diameter of an isolated bubble [\[117\]](#page-27-0):

$$
Bo = e \left[ \frac{\sigma}{g(\rho_L - \rho_V)} \right]^{-1/2} \tag{6}
$$

where  $\sigma$ , g,  $\rho$ <sub>L</sub> and  $\rho$ <sub>V</sub> represent the surface tension, the acceleration due to gravity, the liquid and vapor densities, respectively. Bond number represents the squeezing effect of a bubble due to the confinement. For low bond number (of the order of unity or less), the squeezing effect is important since bubble cannot grow naturally because channels are narrower than the bubble diameter. For high Bond number, boiling can almost be considered as unconfined. For a fixed confined gap size, if the surface tension is reduced, the bubble departure diameter will reduce. This results in a change from confined boiling to unconfined boiling due to the addition of surfactants and polymeric additives. As schematically shown in Fig. 17, different boiling patterns (bubble performance) may be observed due to the effect of surfactants and polymeric additives and the confined space gaps. Boiling patterns caused by squeezed bubbles and coalesced bubbles due to the confinement are very important to understand the nucleate boiling behavior and heat transfer mechanisms and to model the boiling process as well. In the boiling process of aqueous surfactant and polymeric additive solutions, bubble departure diameter becomes much smaller than that without surfactant additives as indicated in [Fig. 18.](#page-23-0) The frequency of



Fig. 17. Schematic diagram of boiling patterns without and with surfactants and polymeric additives in unconfined and confined spaces: (a) boiling patterns of boiling without surfactants and polymeric additives in unconfined space; (b) boiling patterns of boiling with surfactants and polymeric additives in unconfined space; (c) boiling patterns of boiling without surfactants and polymeric additives in confined space; (d) boiling patterns of boiling with surfactants and polymeric additives in confined space.

<span id="page-23-0"></span>

Fig. 18. Schematic diagram of boiling patterns with surfactants and polymeric additives in confined spaces for various heat fluxes: (a) low heat flux; (b) moderate heat flux; (c) high heat flux.

bubble generation becomes larger and the rising velocity of bubble could become larger in confined spaces as well. With the increase of heat flux, much smaller bubbles will be generated and these bubbles may be coalesced as large deformed bubbles, possibly slugs and larger blanket of flattened bubbles. The bubbles occupy fully the space gap and thus can result in partial dryout as shown in Fig. 18. The coalesced bubble performance would affect the rising velocity and results in both heat transfer enhancement and deterioration as well. Therefore, it is important to verify how the boiling patterns affect the heat transfer behavior under various conditions. According to Eq. [\(6\),](#page-22-0) it is hypothesized that the heat transfer coefficient of nucleate boiling of aqueous surfactant and polymeric additive solutions in confined spaces may be improved greatly as compared to that without a surfactant for a fix gap size at certain conditions. In addition, it is also hypothesized that CHF would be increased at certain conditions of combination of aqueous surfactant solution concentrations and space gap sizes. However, the heat transfer coefficient and CHF would be decreased as well at some conditions such as smaller channels and higher heat fluxes. To verify these hypotheses and to determine the optimal conditions for both heat transfer behavior and CHF, it is suggested that experiments on nucleate boiling of aqueous surfactant and polymeric additive solutions in confined spaces for a wide range of test conditions be conducted. In addition, the study of flow boiling of aqueous surfactant and polymeric additive solutions in microchannels should be conducted as well.

## 4.4. Boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels: mechanisms and models

The heat transfer mechanisms of boiling phenomena are very complex with several factors contributing to the high heat transfer rates. For nucleate pool boiling, four different modes of heat dissipation are generally considered to comprise the total heat removal from a boiling surface: latent heat, natural convection, Marangoni flow and micro-convection. Latent heat removal takes places when liquid vaporizes and leaves the surface. Natural convection occurs when sensible energy is removed from non-nucleating portions of the heated surface due to currents established by density gradients. Marangoni flow is induced by the surface tension gradient that exists at the bubble liquid/vapor interface while the bubble is still attached to the heated surface. Microconvection heat transfer results from sensible energy being removed by entrainment of the superheated liquid in the departing bubbles wake. For flow boiling, nucleate boiling and convection boiling are generally the two main heat transfer mechanisms. Flow patterns are very important in understanding and modeling the heat transfer process [\[133,135\].](#page-27-0) As for the heat transfer mechanisms of boiling phenomena of aqueous surfactant and polymeric additive solutions in confined spaces and microchannels, further understanding of these components is needed to enable the development of heat transfer mechanisms and accurate boiling heat transfer and CHF models.

Modeling of boiling process is a very difficult task because boiling phenomena are rather complex. Over the past years, a number of empirical heat transfer and CHF correlations have been developed according to experimental data. All the available correlations are empirical predictive methods and without the boiling pattern (flow pattern for flow boiling) information. As boiling patterns (nucleate pool boiling) and flow patterns (flow boiling) become very important for confined spaces and microchannels, it can be foreseen that the available correlations are not applicable to boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels. Therefore, modeling of boiling heat transfer and CHF should be based on the experimental data. Especially the heat transfer models should be related to the boiling patterns for nucleate pool boiling in confined spaces and flow patterns for flow boiling in microchannels.

## 5. Conclusions

State-of-the-art overall review on boiling phenomena with surfactants and polymeric additives is presented in

<span id="page-24-0"></span>this paper. First, the effect of surfactants and polymeric additives on the physical properties such as the surface tension and viscosity of aqueous surfactant and polymeric additive solutions are discussed. Then, a comprehensive review on both experimental and theoretical studies of boiling phenomena (nucleate pool boiling and flow boiling) with surfactants and polymeric additives is presented. The study of drag reduction by the addition of surfactants and polymeric additives in fluid flow is also mentioned. To identify the main research directions in this cross-research area, a brief review of nucleate boiling in confined spaces is presented. In addition, some scientific hypotheses have been proposed. According to this review, several important research directions related to boiling phenomena with surfactants and polymeric additives in confined spaces and microchannels have been identified as:

- (1) Experiments of nucleate pool boiling of aqueous surfactant and polymer solutions should be further emphasized to investigate the heat transfer mechanisms of boiling phenomena with surfactants and polymers. Systematic studies should be performed in a wide range of pressures.
- (2) Study of flow boiling with surfactants and polymeric additives should be experimentally conducted and the heat transfer mechanisms of flow boiling with surfactants and polymeric additives should be explored.
- (3) Study of drag reduction in flow boiling by the addition of surfactants and polymeric additives should be developed and be connected to the heat transfer mechanisms of flow boiling with the surfactants and polymeric additives.
- (4) Study of boiling phenomena (nucleate pool boiling and flow boiling) with surfactants and polymeric additives in confined spaces and microchannels (micro-scale heat transfer) should be conducted in the future.
- (5) In the long run, effort should be made to develop heat transfer models of boiling phenomena with surfactants and polymeric additives by considering the critical parameters such as contact angle, surface tension, pressure, viscosities and others.

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