THE EFFECT OF SURFACE ACTIVE SOLUTES ON THE BEHAVIOUR OF MICROBUBBLES IN AN ULTRASONIC FIELD

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A b s t r a c t

This thesis reports on an investigation into the effect of surface active solutes on the behaviour of acoustic bubbles in aqueous solutions and its relevance to sonochemistry.

The effect that surface active solutes, such as aliphatic alcohols and the surfactant sodium dodecylsulfate (SDS), have on the extent of bubble coalescence in liquids under different ultrasonic conditions was investigated by measuring the volume change of the solution following a period of sonication. In general, the adsorption of surface active solutes at acoustic bubble/solution interface retards bubble coalescence. Within the limitations of the measurement method and the systems studied, bubble coalescence does not appear to be dependent on the applied acoustic power. Dependence on the applied acoustic frequency is apparent in some cases.

The study of bubble coalescence also provides insights into the dynamics of SDS adsorption at the acoustic bubble/solution interface. It was found that SDS does not reach an equilibrium adsorption level under the sonication conditions used. A method for estimating this nonequilibrium surface excess value is proposed and further employed to estimate the maximum lifetime of bubbles in a multibubble field. It was found that the bubble lifetime decreases with increasing frequency, ranging from up to 0.35 ± 0.05 ms for 213 kHz to 0.10 ± 0.05 ms for 1062 kHz. These estimated lifetimes equate to a bubble in a multibubble field undergoing an upper limit of 50–200 oscillations over its lifetime for applied ultrasound frequencies between 200 kHz and 1 MHz.

The intensity of multibubble sonoluminescence (MBSL) emitted under various conditions was measured to complement the coalescence results. The effect of
Aliphatic alcohols and SDS on MBSL intensity was found to be highly dependent on the applied acoustic power, and the observed MBSL behaviour have been interpreted in terms of a combination of solute evaporation into the bubble, rectified diffusion, bubble clustering and bubble coalescence. The effect of acoustic frequency on MBSL intensity was also investigated, and the results were interpreted in terms of the dynamics of solute adsorption at the bubble/solution interface. The necessity of solute molecules to evaporate into the bubble interior in order to observe MBSL quenching was demonstrated in the study involving hydrogen-bonded solutes.

Emission from electronically excited sodium atoms (Na*) from aqueous solutions containing NaCl or SDS is often observed, in addition to the MBSL emission continuum, when the solution is sonicated. Evidence presented strongly suggests that Na* emission arises from a population of bubbles that are sonochemically active but not producing SL. Results indicate that Na* emission intensity is mainly dependent on the concentration of Na+ ions near the bubble/solution interface.

The feasibility of utilising aqueous sonochemical reactions in the food processing area was explored. The yield of sonochemically generated •OH was found to vary with acoustic frequency. It was shown that the yield of these radicals can be controlled by selecting the appropriate frequency or by introducing additives into the solution. The possibility of sonochemical hydroxylation of food materials to enhance their antioxidant activity was also investigated. Whilst it was shown to be possible with the model food compound, phenol, hydroxylation attempts with some actual food materials were not successful. It was concluded that the potential of this hydroxylation may be highly compound dependent.
DECLARATION

This is to certify that

(i) the thesis comprises only my original work,

(ii) due acknowledgment has been made in the text to all other material used,

(iii) the thesis is less than 100,000 words in length, exclusive of tables, bibliographies, appendices and footnotes.

Devi Sunartio

March 2008
Writing these acknowledgements turned out to be much more difficult than I thought it would be because words just cannot express my deep gratitude to those people who have helped me through the ups and downs of my PhD life.

First and foremost, my sincere thanks to my supervisors, A/Prof. Muthupandian Ashokkumar and Prof. Franz Grieser, without whose patient and expert guidance I would not have made it this far. To Ashok, thanks for always having your door open whenever I needed a helping hand or just someone to discuss ideas with. Franz, your drive and enthusiasm are simply infectious. Thank you for always challenging me to do my best – it is a real privilege to have had you both as my mentors.

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Finally, a very warm and special thank you to my dear family, for their love and steadfast support throughout these years, I am forever grateful.
Preface

Sections of the following chapters of this thesis have been published in a different form in the following articles:

Chapter 3
“Study of the Coalescence of Acoustic Bubbles as a Function of Frequency, Power, and Water-Soluble Additives”
Devi Sunartio, Muthupandian Ashokkumar and Franz Grieser

Chapter 4
“The Influence of Acoustic Power on Multibubble Sonoluminescence in Aqueous Solution Containing Organic Solutes”
Devi Sunartio, Muthupandian Ashokkumar and Franz Grieser

“Sonoluminescence Quenching in Aqueous Solutions of Hydrogen–Bonded Solutes”
Devi Sunartio, Muthupandian Ashokkumar and Franz Grieser
(submitted to Ultrason. Sonochem.)

Chapter 5
“Correlation between Na” Emission and ‘Chemically Active’ Acoustic Cavitation Bubbles”
Devi Sunartio, Kyuichi Yasui, Toru Tuziuti, Teruyuki Kozuka, Yasuo Iida, Muthupandian Ashokkumar and Franz Grieser
Chapter 6

“Modification of food ingredients by ultrasound to improve functionality: A preliminary study on a model system”

Muthupandian Ashokkumar, Devi Sunartio, Sandra Kentish, Raymond Mawson, Lloyd Simons, Kamaljit Vilkhu and Cornelis (Kees) Versteeg

To my family,

who are always behind me

no matter what
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1.1 INTRODUCTION

The term *ultrasound* refers to sound waves with frequencies above human hearing, typically between 18 kHz to 10 MHz [1]. When ultrasonic waves are passed through a liquid, a phenomenon known as *acoustic cavitation* can occur. Acoustic cavitation encompasses the formation, growth and violent implosive collapse of bubbles in a medium under the influence of an acoustic field [2].

In practice, applications involving acoustic cavitation can consist of a single bubble levitated in a liquid irradiated where a precise standing wave is established (i.e., a single bubble system), or more commonly, many bubbles co-exist in the liquid medium (i.e., a multibubble system).

The violent collapse of an acoustic bubble is accompanied by the generation of extremely high temperatures and pressures inside the bubble. These extreme conditions can induce many high energy chemical reactions, making the cavitation bubbles ideal micro-reactors for various chemical processes. This branch of chemistry relating to utilising ultrasound to assist/induce chemical reactions is termed *sonochemistry*. Apart from the chemical effects, the collapse of acoustic bubbles also gives rise to various physical effects, including shear forces, microjetting, acoustic streaming, turbulence, as well as the emission of light (*sonoluminescence*) [2].
With the increasing use of ultrasound in recent times, common applications include water treatment [3], polymerisations [4-6], formation of nanoparticles [7-10] and protein microspheres [11,12], as well as other applications in the food industry (e.g., membrane cleaning [13], treatment of milk products [14]) and in the medical field (e.g., ultrasound contrast agents [15,16], sonodynamic therapy [17]). Most excitingly, the process of concentrating diffuse sound energy by acoustic cavitation is speculated to be able to generate temperatures required for nuclear fusion [18,19]. In 2002, Taleyarkhan et al.[20] claimed to have achieved this. However, a number of researchers have doubted this claim [21,22] and attempts to repeat the experiment [23] were unsuccessful, leaving this ultimate goal for sonochemists/sonophysicists to be further pursued.

1.2 SOUND WAVES AND ACOUSTIC CAVITATION

1.2.1 The sound wave

A sound wave is a sinusoidal cycle of positive and negative pressures passing through a medium. Sound waves travel in a longitudinal fashion, such that the molecules in the medium oscillate about their mean positions in a direction that is parallel to the propagation of the waves. The fluctuating wave causes compression and rarefaction of the medium at positive and negative pressures, respectively. A sound wave is characterised by its amplitude and frequency (or wavelength, according to \( c = \lambda f \), where \( c \) is the speed of sound in m \( s^{-1} \), \( \lambda \) is the wavelength in m and \( f \) is the frequency in Hz).

A travelling sound wave can be reflected by a boundary. When two identical waves, travelling in opposite directions, are superimposed, it results in the formation of a standing wave (Figure 1.1). This standing wave contains a series of alternating pressure nodes and pressure antinodes. A pressure node signifies a
region of zero pressure variation with time, whereas a pressure antinode is a region where pressure variation with time is at a maximum.

![Diagram of sound wave](image)

**Figure 1.1** The sinusoidal cycle of positive and negative pressures of a sound wave. The superimposition of two identical waves, travelling in opposite directions, forms a standing wave with alternating pressure nodes and pressure antinodes.

### 1.2.2 Acoustic cavitation

**1.2.2 (a) Cavitation inception**

Without any pre-existing nuclei, about 1000–1500 atm of negative pressure is required to overcome the tensile strength of water and create a cavity in the liquid [2]. In practice, however, acoustic cavitation is often observed at much lower applied acoustic pressures in the order of 1 atm to a few atm. This is because cavitation is generally a nucleated process, that is, it occurs at adventitious weak points in the liquid that greatly reduce the tensile strength of the liquid. One of the sources for these pre-existing nuclei is the presence of minute stabilised gas bubbles inherently present in the liquid. Another possibility is the gas trapped in the crevices of the container walls or on hydrophobic dust particles.
The idea of crevices in solids as possible nucleation sites was first proposed by Gernez [24], although it is often credited to Harvey et al. [25] Figure 1.2 illustrates how an air bubble can be nucleated from these crevices. Along with the medium around it, a gas pocket trapped in a crevice responds to the alternating positive and negative pressures of the applied sound waves by compressing and expanding, respectively. If the negative pressure is sufficiently large, this gas pocket expands considerably and eventually detaches itself from the crevice, forming a free bubble in the liquid. Dissolved gas in the liquid then subsequently fills the crevice and the cycle is repeated.

![Figure 1.2](image.png)

Figure 1.2 The crevice model of bubble nucleation. Gas pockets in the crevices of a solid surface expand during the rarefaction cycle of a sound wave, eventually forming a free bubble in liquid.

1.2.2 (b) Rectified diffusion

Free bubbles in a liquid tend to dissolve over time due to the higher pressure inside the bubbles compared to the surrounding medium. When the liquid is subjected to ultrasonic irradiation, however, these bubbles can grow as a result of unequal mass transfer across the air/water interface during bubble oscillation. This process is known as rectified diffusion [1,26,27]. There are two factors that contribute to this phenomenon: the “area effect” and the “shell effect”.

The area effect occurs by virtue of the proportionality between the extent of gas diffusion through an interface and the interfacial area. When bubble is compressed during the positive pressure cycle, the pressure inside the bubble increases and this leads to gas diffusion out of the bubble into the liquid. Conversely, when bubble is expanded during the negative pressure cycle, the pressure inside the bubble decreases and hence gas diffuses from the liquid into the bubble. Due to the greater surface area of the bubble in its expanded state, there is a net flow of mass into the bubble.

The second aspect of rectified diffusion, the shell effect, is usually explained by considering a hypothetical, arbitrary shell of liquid surrounding the bubble. The outer boundary of this shell is considered to be constant, such that as the bubble oscillates, the volume of this shell changes accordingly, hence changing the concentration of dissolved gas in this liquid shell as a result. Because the diffusion rate of gas in a liquid is proportional to the concentration gradient of the dissolved gas, the rate of gas diffusion from the liquid into the bubble during bubble expansion is higher than the rate of gas diffusing out of the bubble during bubble contraction. The net effect is a flow of mass into the bubble over time, resulting in bubble growth. This explanation, however, can be somewhat misleading. An alternative approach to explain the shell effect is as follows.

Consider a bubble with a spherical shell of liquid surrounding it (Figure 1.3a). The volume of this shell is defined as the volume of liquid in which the dissolved gas concentration can be affected by the transport of the gas molecules into and out of the oscillating bubble. According to Fick’s law of mass transfer, the thickness of this shell is then equal to the mass diffusion length, \( x = (4Dt)^{1/2} \), where \( D \) is the diffusion coefficient of the dissolved gas in the liquid and \( t \) is the diffusion time. In water, the value of \( D \) is in the order of \( 1 \times 10^{-5} \) \( \text{cm}^2 \text{s}^{-1} \) [28].
Figure 1.3 A schematic showing the shell effect of rectified diffusion: (a) Bubble with a spherical shell surrounding it, whose thickness is equal to the mass diffusion length of the dissolved gas; (b) Diffusion of gas from the liquid shell into the bubble during bubble expansion – gas concentration in the shell is approximately the same as the bulk liquid; (c) Diffusion of gas out of the bubble into the liquid shell during bubble contraction – the time span of bubble contraction is shorter than bubble expansion, resulting in a thinner shell with a gas concentration higher than the bulk liquid; (d) As bubble expands again, essentially all of the gas molecules expelled from the bubble during the previous contraction phase diffuse into the bubble again, as well as other gas molecules existing in the thicker liquid shell. Over many repeated cycles, the net effect is diffusion of gas into the bubble, leading to bubble growth.
The diffusion time, $t$, corresponds to the time available for gas diffusion into and out of the bubble during bubble expansion and contraction phases, respectively.

As the bubble expands from equilibrium size, vacuum is created inside the bubble, resulting in the diffusion of gas from the liquid into the bubble. This expansion phase can be expected to last for at least half the period of bubble oscillation. For argument’s sake, consider the calculated radius-time profile for a bubble under irradiation at an acoustic frequency of 300 kHz (3 bar) found in Figure 1 in ref. [29]. The bubble expansion period is around 2 $\mu$s under these conditions, hence the thickness of the liquid shell surrounding the bubble in which dissolved gas molecules have enough time to diffuse into the bubble can be calculated to be approximately 90 nm. Any dissolved gas existing in the liquid within this distance from the bubble wall can be expected to have diffused into the bubble within the finite time of bubble expansion. Since transport of gas molecules in the shell is into a vacuum, there is a constant replenishing of dissolved gas from the bulk liquid towards the shell, such that there is no appreciable concentration gradient in the shell (Figure 1.3b).

As the bubble then contracts, gas molecules diffuse out of the bubble into the surrounding liquid. However, the time span of this contraction phase is shorter than the expansion phase (around 1 $\mu$s for the example considered previously [29]). Gas molecules expelled from the bubble can only diffuse up to a distance of approximately 60 nm within this shorter time period, resulting in a shell of liquid with a higher gas concentration just outside the bubble wall compared to the gas concentration in the bulk liquid (Figure 1.3c).

Then as the bubble expands again, there is enough time within the bubble expansion period for essentially all of the material expelled in the previous contraction phase to diffuse into the bubble again, in addition to other dissolved
gas molecules in the comparatively thicker liquid shell surrounding the bubble during its expanded state (Figure 1.3d). Over time, after many repeated cycles, the net effect is a greater diffusion of gas molecules into the bubble, leading to an overall bubble growth.

1.2.2 (c) Bubble collapse and hot spot formation

In the absence of other processes (e.g., coalescence, §1.4), a bubble in an ultrasonic field continues to oscillate and grow via rectified diffusion until it reaches a critical (resonance) size. At this resonance size ($R_{\text{res}}$), the bubble’s natural oscillation frequency matches the frequency of the applied field, such that optimum coupling occurs. The bubble then grows rapidly within the negative pressure cycle until it is unable to sustain itself against the weight of the liquid around it and undergoes an inertial collapse. This violent, near adiabatic collapse heats up the interior of the bubble, reaching very high temperatures and pressures within the bubble core.

This so-called hot spot model was first proposed by Noltingk and Neppiras [30,31], and has been shown to agree with experimental observations [32-36]. The maximum temperature ($T_{\text{max}}$) and pressure ($P_{\text{max}}$) attainable inside a collapsing bubble can be approximated as Equations 1.1 and 1.2, assuming an adiabatic collapse [30,31].

\[
T_{\text{max}} = T_0 \left\{ \frac{P_m (\gamma - 1)}{P_v} \right\} \quad \text{(Equation 1.1)}
\]

\[
P_{\text{max}} = P_v \left\{ \frac{P_m (\gamma - 1)}{P_v} \right\}^{(\gamma - 1)/\gamma} \quad \text{(Equation 1.2)}
\]
Chapter 1: Introduction, theory and literature review

Here $T_0$ is the ambient temperature of the liquid, $P_m$ is the pressure of the liquid at bubble collapse ($P_m$ is the sum of the hydrostatic and acoustic pressures), $P_v$ is the pressure inside the bubble at its maximum size (which is usually assumed to be the vapour pressure of the liquid) and $\gamma$ is the ratio of the heat capacities ($\gamma = C_p/C_v$, where $C_p$ and $C_v$ are the heat capacity of the gas at constant pressure and constant volume, respectively).

Due to the transient nature of the cavitation event, direct measurements of cavitation conditions at collapse are generally not possible by conventional methods. Using a comparative-rate chemical thermometry [32] and spectral studies of sonoluminescence [33,34,37], the cavitation temperature in a multibubble system has been approximated to be of the order of 5000 K, while for the more symmetric single bubble collapse, a temperature as high as 15000 K has been reported [38]. Suslick et al. [32] proposed that the extremely high temperatures inside the bubble cause a shell of liquid directly adjacent to the bubble wall to be considerably heated up to 2000 K. This hot shell extends only $\approx 200$ nm from the bubble wall and only lasts for $< 2 \mu$s after collapse. The pressure reached inside a cavitation bubble in a multibubble system has been estimated to be around 300 atm [35].

1.2.2 (d) Bjerknes forces

The applied acoustic waves can exert forces on the bubbles. These forces are known as the Bjerknes forces, named after C.A. Bjerknes and his son, V.F.K. Bjerknes, who extensively studied these hydrodynamic forces in the early 1900’s [39]. There are two general classes of Bjerknes forces. The primary Bjerknes force concerns the interaction between the applied sound field and the individual bubbles. The secondary Bjerknes force is related to the interaction
between two bubbles, as the secondary sound field radiated by an oscillating bubble affects the other bubble [1].

**Figure 1.4** illustrates the origin of the primary Bjerknes force [40,41]. Due to the continuous nature of the acoustic field and the finite size of the bubbles, there is a pressure gradient across the bubbles. Bubbles tend to move towards the region of low pressure. Hence, during the compression phase, the force is directed towards the node, and conversely, it is directed towards the antinode during the rarefaction phase. Bubbles smaller than \( R_{\text{res}} \) oscillate in-phase with the applied acoustic field (i.e., bubble volume is minimum when acoustic pressure is maximum, and vice versa), whereas those larger than \( R_{\text{res}} \) oscillate out of phase with the applied field (i.e., bubble volume is maximum when acoustic pressure is maximum, and vice versa). Therefore, a bubble smaller than \( R_{\text{res}} \) is pushed towards the node during the compression phase when it is at its minimum size, but it is pushed towards the antinode during the rarefaction phase when the bubble is at its maximum size. Since the displacement of the bubble is proportional to the bubble volume, the bubble displacement when it is at its maximum size dominates, and hence the net effect is the movement of bubbles smaller than \( R_{\text{res}} \) towards the antinode. The opposite occurs for bubbles larger than \( R_{\text{res}} \), resulting in the primary Bjerknes force directing them towards the node.

The principles of the secondary Bjerknes force are depicted in **Figure 1.5**. Consider a pair of bubbles, A and B, oscillating in-phase with each other. When bubble A is at its minimum size, it starts to expand, forcing the surrounding liquid to accelerate away from it. If bubble B is in the vicinity, then it will also accelerate along with the liquid, away from bubble A (**Figure 1.5a**). When bubble A is now at its maximum size, it starts to contract, forcing the surrounding liquid as well as bubble B to accelerate towards it (**Figure 1.5b**).
Bubbles tend to move towards the region of low pressure. For bubbles with $R < R_{\text{res}}$, the primary Bjerknes force is directed towards the pressure node when the bubble is compressed and towards the pressure antinode when the bubble is expanded. Due to the larger bubble volume in its expanded state, the force towards the pressure antinode dominates. The opposite is true for bubbles with $R > R_{\text{res}}$.

The radiation force exerted by bubble A on bubble B is proportional to the volume (or mass) of bubble B. Since the acceleration of bubble B towards bubble A occurs when it is at a larger size, the net effect is an attraction between the two bubbles.

On the other hand, when a pair of bubbles are oscillating out of phase with each other (e.g., bubbles A and C), the opposite takes place, and the net effect is a repulsion between the two bubbles. Therefore, the theory for secondary Bjerknes force predicts the attraction or repulsion between a pair of bubbles in an acoustic field depending on whether the bubble sizes are on the same side or the opposite sides of $R_{\text{res}}$, respectively.
The magnitude of secondary Bjerknes force is proportional to the square of the pressure amplitude of the incident acoustic field [42].

![Diagram of secondary Bjerknes force between pairs of bubbles in an acoustic field. Depending on whether the bubbles are oscillating in-phase or out of phase with each other, the net force is attraction or repulsion, respectively.]

**Figure 1.5** The secondary Bjerknes force between pairs of bubbles in an acoustic field. Depending on whether the bubbles are oscillating in-phase or out of phase with each other, the net force is attraction or repulsion, respectively.

Young [43] stated that the sign and magnitude of Bjerknes forces depend on whether the bubbles are oscillating harmonically or strongly non-linearly. The above explanation is true for relatively low applied acoustic amplitudes. Matula et al. [41] showed that at large applied acoustic amplitudes, it is possible to reverse the direction of the primary Bjerknes force, while Doinikov and Zavtrak [44] explained how the attraction between two bubbles due to the secondary Bjerknes force can become repulsion as the bubbles approach each other.
1.3 ADSORPTION OF SURFACE ACTIVE SOLUTES AT INTERFACES

1.3.1 Surface active solutes

The use of surface active solutes is ubiquitous in many practical applications. In general, a surface active solute is defined as a substance that has a tendency to preferentially partition at an interface, hence reducing the interfacial tension of that interface [45]. The term surfactants usually denotes those surface active solutes which are able to form micelles at relatively low concentrations. In fact, one of the most prominent characteristics of surfactants is the existence of the critical micelle concentration (cmc), at which abrupt changes occur in some physical properties of the solution [46].

All surface active solutes exhibit an amphiphilic structure, that is, they possess a hydrophobic part (usually a long hydrocarbon chain) as well as a hydrophilic part (often referred to as the head group), as shown in Figure 1.6.

![Figure 1.6 General structure of a surface active molecule.](image)

Depending on the nature of the head group, surface active solutes can be classified as anionic (negatively charged head group), cationic (positively charged head group), zwitterionic (both negatively and positively charged...
functional groups on the head group) or non-ionic (no charge on the head group).

This amphiphilic nature of surface active molecules is precisely the driving force for their preferential adsorption at a gas/solution interface. Water molecules at the air/water interface have a higher potential energy than those in the bulk solution. Therefore, work has to be done on the system to bring a water molecule from the bulk liquid to the interface (i.e., to create an interface). The interfacial tension (or surface tension) of a liquid is defined as the minimum amount of work required to create a unit area of interface [45].

When surface active solutes are present in the solution, the hydrophobic part of these molecules disrupts the water structure in the bulk, resulting in an increase in the free energy of the systems. Therefore, it is thermodynamically much more favourable to bring these molecules to the air/water interface, where they partition such that the hydrophilic group stays in the solution, while the hydrophobic part is oriented away from it. In fact, the work required to bring a surface active molecule to the interface is lower than that required to do so with a water molecule, which is why the addition of surface active solutes reduces the surface tension of the solution.

1.3.2 Gibbs surface excess

The amount of surface active molecules that partition at the gas/solution interface is quantified as the (Gibbs) surface excess concentration, \( \Gamma \). The

\[ \xi \]

For surfactants with a single hydrophilic group (regardless of charge), the area occupied by a surfactant molecule at the interface appears to be determined by the hydrated head group, not the hydrophobic tail [45]. For example, the area occupied by a sodium dodecylsulfate (SDS) molecule at surface saturation (at 25 °C) is 53 Å², as compared to \(~20\) Å² for an aliphatic hydrocarbon chain partitioning at a right angle to the interface.
simplest way to illustrate the concept of surface excess is by considering two portions of solution containing identical number of moles of solvent: one at the interface region, the other in the bulk solution (Figure 1.7) [47]. The difference between the amount of solute molecules at the interface (\(n_{\text{int}}\)) and the amount of solute molecules in the bulk solution (\(n_b\)), divided by the area of the interface (\(A\)), yields the surface excess concentration (Equation 1.3) [46].

\[
\Gamma = \frac{n_{\text{XS}}}{A} \quad \text{(Equation 1.3)}
\]

It is arduous to measure surface excess directly due to difficulties in isolating the interfacial region from the bulk solution. Therefore, it is usually calculated indirectly from surface tension data using the Gibbs adsorption equation. Equation 1.4 shows the most general form of the Gibbs adsorption equation [45], where \(d\sigma\) is the change in the surface tension of the air/water interface, \(\Gamma_i\) and \(d\mu_i\) are the surface excess concentration and the change in chemical potential of component \(i\) in the solution, respectively.

\[
d\sigma = -\sum_i \Gamma_i d\mu_i \quad \text{(Equation 1.4)}
\]
However, the form of the equation that is most commonly used is as shown in Equation 1.5 [46], since it enables surface excess concentration to be estimated directly from the slope of a plot of surface tension of the air/water interface ($\sigma$) versus the natural log of the bulk concentration of solution (C).

$$\Gamma = -\frac{1}{n \mathcal{R} T} \frac{d\sigma}{d(\ln C)} \quad \text{(Equation 1.5)}$$

Here $\mathcal{R}$ denotes the universal gas constant and $T$ is the solution temperature. The value of $n = 1$ for solutions containing solutes with no net charge (i.e., non-ionic, zwitterionic, or ionic surfactants in the presence of excess electrolyte), and $n = 2$ for 1:1 ionic surfactants in the absence of any added electrolytes.

### 1.3.3 Adsorption dynamics

The adsorption of surface active solutes at the gas/solution interface is not instantaneous. When a new interface is created, a finite time is required to reach an equilibrium between the interfacial and bulk concentrations [48]. This is because the adsorption process takes place in two consecutive steps: transfer of solute molecules from bulk phase to the subsurface by diffusion, followed by adsorption of the solutes in the subsurface at the interface (Figure 1.8) [49].

The region between the interface and the subsurface is sometimes referred to as the adsorption layer, with a thickness of only a few molecular diameters [50], as opposed to the much larger diffusion region. As it is a dynamic process, adsorption of solute molecules at the interface is always accompanied by some desorption of the molecules back into the subsurface (or bulk), even under equilibrium conditions. This is a result of a balance between the tendency
towards adsorption and the tendency towards complete mixing in the bulk due to thermal (Brownian) motion [46].

In general, there are two main models that have been proposed to account for experimentally observed rates of surfactants adsorption: the diffusion controlled model and the mixed diffusion-kinetic controlled model. In the diffusion controlled model, surfactant monomers diffuse from the bulk phase to the subsurface, and once they are in the subsurface, adsorption at the interface is virtually instantaneous. This model was initially proposed by Ward and Tordai [51]. The other alternative, the mixed diffusion-kinetic controlled model, assumes the same diffusion process from the bulk phase to the subsurface. However, once in the subsurface, the surfactant monomers have to overcome some adsorption barriers in order to adsorb at the interface (i.e., the adsorption step is now the rate limiting step). These barriers include increased surface pressure, less vacant sites available for adsorption (especially approaching saturation) and having to adopt the correct orientation to adsorb [48]. If the surfactant monomers are unable to overcome these barriers, it results in them back-diffusing into the bulk solution and not adsorbing.
The existence of these adsorption barriers have been observed experimentally by a number of researchers [52-55]. Chang [52] studied the adsorption kinetics of a non-ionic surfactant, octaethylene glycol mono n-decyl ether (C\textsubscript{10}E\textsubscript{8}), and calculated the effective diffusion coefficient (D\textsubscript{eff}) values as a function of surfactant bulk concentration. They found that D\textsubscript{eff} decreases with increasing concentration, and attributed this to a shift in the adsorption mechanism, from purely diffusion controlled at lower concentrations to mixed diffusion-kinetic controlled as the concentration was progressively increased. For ionic surfactants, electrostatic interactions pose as an additional barrier for adsorption [50,53]. Furthermore, due to the existence of these various barriers, Ferri and Stebe [56] found that surfactants with high surface activities (i.e., those with low equilibrium surface tension) require longer times to equilibrate with the interface, compared to those which are less surface active.

1.3.4 Adsorption dynamics at cavitation bubbles

As discussed in §1.3.3, adsorption is a time-dependent process, with a typical time required to reach equilibrium in the order of milliseconds. Non-volatile surfactants have been shown to readily accumulate in the hot shell surrounding collapsing bubbles [57,58]. Moreover, Fyrillas and Szeri [59] proposed that the accumulation is influenced by the oscillations of cavitation bubbles. Considering bubbles oscillate on a microsecond time scale, it is expected that equilibrium adsorption may not be achieved on bubbles under ultrasonic irradiation. In fact, this has been shown experimentally by Sostaric and Riesz, both through EPR (electron paramagnetic resonance) spin trapping [60] and sonoluminescence [61] experiments. Knowledge regarding the extent of adsorption of surface active solutes on cavitation bubbles is of prime importance because it dictates the effectiveness of some ultrasound-assisted processes. For example, it has been
shown that the effectiveness of sonodynamic therapy depends on the ability of the sonosensitiser molecules to accumulate at the bubble surface [62].

In their EPR spin trapping study of homologous $n$-alkyl surfactants, Sostaric and Riesz [60] observed the radical scavenging activity to increase with decreasing $n$-alkyl chain length of the surfactants, indicating that the less surface active surfactants accumulate more readily at the interface. This is in line with the conclusion of Ferri and Stebe [56] with “static” bubbles. Similar inferences were also derived from the results of investigating the intensity of excited sodium atom emission from these surfactant solutions [61].

Sostaric and Riesz then extended their previous study [60] to examine the effect of ultrasonic power and frequency [63]. The relative ability of the surfactants to scavenge radicals at the interface was found to depend on the frequency, but was independent of the ultrasonic intensity under the experimental conditions employed. They further conclude that adsorption is further away from equilibrium value as the ultrasonic frequency decreases.\footnote{Our results on bubble coalescence in \textbf{Chapter 3} appear to contradict this finding.}

The effect of pulsed ultrasound on the adsorption of surfactants at cavitation bubbles has also been recently investigated [64-66]. Pulsed ultrasound was found to strongly affect the relative adsorption ability of the surfactants at certain frequencies, but not at other frequencies [64]. The reasons behind this remain unclear, although hypotheses based on the frequency dependence of the resonance bubble size have been proposed.
1.4 BUBBLE COALESCENCE

1.4.1 The coalescence process

The process of bubble coalescence can be summarised in three main steps [67,68]. First, bubbles must come into contact with each other. Flattening of the bubble surfaces occurs as a result, and a thin liquid film with a thickness of around 1-10 µm forms in between the bubbles. Secondly, this liquid film thins further to approximately 10 nm before the last step, rupture of the film, takes place very rapidly via an instability mechanism to finally coalesce the bubbles. The rate limiting step of this whole process is the film thinning step. Hence, if the bubble contact time is shorter than the time taken for the film to sufficiently thin for rupture to occur, coalescence will not take place.

1.4.2 Coalescence inhibition

Adsorption of surface active solutes at bubble/solution interface can inhibit coalescence primarily via two different means: steric hindrance and electrostatic repulsion, if the surface active solutes are charged.

1.4.2 (a) Steric hindrance

Steric effect is only effective in inhibiting bubble coalescence when the bubbles are in very close vicinity of each other since it arises from the physical presence of the adsorbed solutes at the interface. It is the principal mechanism operating when the solutes are uncharged, such as with alcohols. Oolman and Blanch [67] and Zahradnik [69] reported that bubble coalescence in aqueous alcohol solutions is significantly hindered, and that longer chain alcohols inhibit bubble coalescence more effectively.
1.4.2 (b) Electrostatic repulsion

Surfaces in contact with aqueous media are often negatively charged. This is because cations are generally more hydrated than anions, and hence have a greater tendency to remain in the bulk solution. On the other hand, the smaller, less hydrated anions tend to adsorb at the interface [46]. Therefore, air bubbles in water are also negatively charged. However, when charged surface active solutes (such as ionic surfactants) are present, their adsorption will usually determine the overall charge on the bubble/solution interface.

The charges on the bubble surface influence the distribution of ions in the liquid surrounding it, where counter-ions are attracted and co-ions are repelled. This gives rise to an unequal distribution of electrical charges across the interface, where one side is positively charged while the other is negatively charged, hence forming the electrical double layer (EDL). The Stern model, which is a modification of the Gouy–Chapman model, is often employed to describe the EDL [45-47]. In this model, the solution side of the double layer consists of two regions: an inner region of strongly held counter-ions (the Stern layer) and a diffuse region where ions (both counter-ions and co-ions) are distributed according to electrical potential and Brownian motion (the diffuse layer), as illustrated in Figure 1.9.

The Stern plane is located one hydrated ion radius away from the charged surface. Mathematical treatment of the diffuse region of the EDL yields the term $1/K$, which is better known as the Debye length (Equation 1.6) [46]. It signifies the distance from the charged surface that defines the extent of the electrical double layer into the bulk solution.
Figure 1.9 Schematic representation of the electrical double layer. The potential changes from $\Psi_0$ (the surface potential) to $\Psi_\delta$ (the Stern potential) in the Stern layer, and decays exponentially from $\Psi_\delta$ to zero in the diffuse layer. $\delta$ is the thickness of the Stern layer, and the Debye length ($1/\kappa$) is defined as the distance over which the potential in the diffuse layer decreases by an exponential factor.
Here \( \varepsilon \) is the permittivity of the liquid, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( e \) is the elementary charge, \( N_A \) is the Avogadro’s number, \( C \) is the bulk concentration of the electrolyte (in mol m\(^{-3} \)) and \( z \) is the valency of the counter-ions.

For an aqueous solution of 1:1 electrolyte (e.g., NaCl, SDS) at 25 °C, where \( \varepsilon = 78.4 \times \varepsilon_0 \) (\( \varepsilon_0 \) is the permittivity of a vacuum) and \( T = 298 \) K, Equation 1.6 can be written as:

\[
\frac{1}{\kappa} = \left( \frac{\varepsilon k T}{2e^2 N_A C z^2} \right)^{1/2} \quad \text{(Equation 1.6)}
\]

where \( C \) is now in mol L\(^{-1} \) and \( 1/\kappa \) is in nm. Some examples of Debye length values calculated using Equation 1.7 are presented in Table 1.1, where it is evident that as the electrolyte concentration is increased, the Debye length decreases.

Table 1.1 Debye length calculated for a 1:1 electrolyte in an aqueous solution at 25 °C.

<table>
<thead>
<tr>
<th>Electrolyte concentration (M)</th>
<th>Debye length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-6} )</td>
<td>304.0</td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>9.6</td>
</tr>
<tr>
<td>( 10^{-1} )</td>
<td>1.0</td>
</tr>
</tbody>
</table>
1.5 BUBBLE FATE IN AN ACOUSTIC FIELD

A summary of the possible fates of bubbles in a liquid under ultrasonic irradiation is illustrated in Figure 1.10. As ultrasonic waves pass through a liquid medium, bubble nuclei present in the liquid can grow at the antinodes via rectified diffusion (§1.2.2 (b)) or coalesce with one another to form a larger bubble. Upon coalescence (§1.4), if the resulting bubble is larger than the resonance size, it will be pushed towards the nodes by the primary Bjerknes force (§1.2.2 (d)), hence becoming “inactive” (i.e., no longer oscillates with the applied acoustic field). These bubbles may eventually float out of the liquid due to buoyancy once the acoustic field is turned off. On the other hand, if the resulting bubble is still smaller than the resonance size, it can continue to grow via rectified diffusion to reach the resonance size and then collapse violently (§1.2.2 (c)) and emit sonoluminescence (§1.6).

Figure 1.10 Possible fates of individual bubbles in liquid under ultrasonic irradiation. (Note that “resonance size” here is not necessarily the linear resonance size, but simply the size where bubbles are able to collapse violently and emit SL [70].)
There are two possible pathways that a bubble can undergo after collapse. It can continue to grow further by rectified diffusion following exposure to more acoustic cycles, reaching a size larger than the resonance size and then be forced to the node and become “inactive”. Alternatively, it can fragment to smaller daughter bubbles that will then either dissolve away or act as further nuclei. For multibubble systems, most of the bubbles exist in clusters, which generally lead to asymmetric collapse of the bubbles. This is more likely to make fragmentation the dominant pathway after bubble collapse.

1.6 SONOLUMINESCENCE (SL)

1.6.1 Origin of SL emission

SL is often used as a means to probe the nature of cavitation in liquid media. Interpreting SL intensities under different experimental conditions allows inferences to be drawn regarding the behaviour of bubbles in the cavitation field, including the number of “active” bubbles and any pyrolysis processes inside the bubbles.

SL was first detected in the 1930’s when Marinesco and Trillat [71] observed a “fogging” on photographic plates immersed in a liquid under ultrasonic irradiation. However, at the time it was thought that the observation was thermally-induced, and it was not until later that Frenzel and Schultes [72] realised it was due to light emission from cavitation bubbles. Since then, various theories have been proposed on the mechanism of this light emission when bubbles collapse violently under the influence of an ultrasonic field. Some of these theories have been discounted over the last few decades, while others are still actively under debate [43]. In general, all the theories fall into two broad categories: electrical or thermal origin.
The theory proposing an electrical origin of SL suggests that light emission is generated by electrical discharge due to the electrical potential attained at the bubble interface in liquid [73]. However, this theory has its downfalls. Addition of salt (e.g., NaCl) to aqueous solutions increases the ionic strength of the liquid, and hence reduces the potential at the bubble interface [46]. If the electrical theory was correct, this is expected to decrease the SL intensity. Experiments showed that SL intensity increases upon the addition of salt [74-76], thereby discounting this theory. Moreover, Flint and Suslick [77] observed emission lines from excited radical species on the SL spectra, but not lines that would have been expected from charged particles.

The first thermal theory of SL was put forward by Noltingk and Neppiras [30,31]. They proposed that a bubble grows isothermally during the rarefaction phase of the bubble oscillation until it reaches a maximum radius, at which a fast adiabatic collapse of the bubble then follows, causing a “hot spot” to form at the centre of the bubble. The interior of the bubble gets heated so much such that light is emitted as a result of the incandescence of the bubble contents (i.e., a blackbody emission). This thermal theory agrees well with the observation from spectral studies, in which a SL flash is observed towards the end of bubble collapse, when the bubble’s core temperature is the hottest [74,78]. Nonetheless, emission lines from excited chemical species are often observed on SL spectra, indicating that SL emission must be at least partly chemiluminescent in origin [75]. Sehgal et al. [79] and Flint and Suslick [77] suggested that chemiluminescence is the main mechanism responsible for SL emission.

1.6.2 MBSL v SBSL

Most of the earlier work involving SL has been related to light emission from a population of bubbles in a cavitation field (i.e., multibubble SL, or MBSL). In
the early 1990’s, Gaitan et al. [78] successfully suspended a stable single bubble in solution, which sonoluminesces in a periodic manner, emitting short light pulses once every acoustic period. This phenomenon, termed single bubble SL (SBSL), opened up new avenues for theoretical modelling and investigation of the effect of various parameters on bubble dynamics. This has not been possible previously with MBSL since the large number of bubbles co-existing interact with each other, and hence may affect the acoustic field experienced by other bubbles. MBSL, however, is more useful from a practical point of view, if the SL intensity is to be correlated with the yield of sonochemical processes.

Yasui [81] explained that the difference between MBSL and SBSL lies in the maximum temperature and pressure attainable in the bubble core upon collapse, both of which are much higher in the SB case due to the sphericity of collapse. Nevertheless, even in a multibubble field, it is possible for some of the bubbles to behave like a single bubble [81,82]. The following sections will focus entirely on aqueous MBSL since this is the system studied in this thesis.

1.6.3 Dependence of aqueous MBSL on various factors

Since a multibubble system comprises an ensemble of bubbles, the MBSL intensity is determined by the number of sonoluminescing (i.e., “active”) bubbles, as well as the intensity of SL emitted by the individual bubbles. The latter is dictated by the maximum temperature reached inside the bubbles ($T_{\text{max}}$). In aqueous media, $T_{\text{max}}$ is very much governed by the amount of water vapour and the saturating gas inside the bubbles.

---

Yosioka and Omura [80] were the first to produce SBSL. However, the discovery of SBSL as a reproducible well understood phenomenon is attributed to Gaitan et al. [78]
Chapter 1: Introduction, theory and literature review

The effect of liquid temperature on MBSL intensity has been investigated by some researchers [83-86]. In general, MBSL intensity was found to decrease as liquid temperature increased since more water vapour evaporated into the bubble at the higher temperatures. This leads to more energy consumption through the endothermic bond breaking reactions of the water molecules, hence giving rise to less SL emission. Didenko et al. [86] found that this temperature dependence was different for high and low acoustic frequencies, while Dezhkunov [83] reported a dependence on the applied ultrasonic intensity.

The type of saturating gas also influences the MBSL intensity. The higher is the thermal conductivity of the saturating gas, the lower is the MBSL intensity due to relatively cooler bubbles [87,88].

Tuziuti et al. [89] found that for the same gas saturation, the MBSL intensity increased as the ambient pressure was decreased. Didenko [90] varied the applied acoustic pressure whilst monitoring the MBSL intensity. The MBSL intensity was observed to increase with increasing acoustic pressure, which was attributed to an increase in the number of “active” bubbles. Hatanaka et al. [91,92], however, reported that at excessively high applied acoustic pressure, MBSL intensity was suppressed due to the transformation of “active” bubbles into bubble clusters, which did not contribute to MBSL emission.

The frequency dependence of MBSL has also been studied. Early studies showed that SL intensity decreased with increasing frequency [93,94]. Nevertheless, frequency effect is a complex matter since it is impossible to vary the acoustic frequency without inducing changes in other parameters as a consequence. From his theoretical studies, Yasui [70] explained that the range of ambient bubble radius for SL narrowed with increasing frequency. Moreover, as the acoustic frequency increases, the amount of water vapour trapped inside the
bubble during collapse decreases. Thus, Yasui [70] concluded that while the mechanism for light emission at 20 kHz is due to both \( ^\cdot \text{OH} \) chemiluminescence and plasma emission, only the latter is dominant at 1 MHz.

### 1.6.4 Effect of solutes on MBSL intensity

Many studies investigating the effect of adding various solutes on MBSL intensity have been undertaken [76,95-101] because solute molecules affect the physical behaviour of bubbles, and hence the interactions between bubbles. Thus, it may assist us to gain a better understanding of the processes taking place in the cavitation bubble field.

MBSL intensity is governed by both the “active” bubble population and the cavitation bubble temperature. The number of “active” bubbles, which refers to those bubbles that can collapse violently and emit SL#, is greatly dependent upon the spatial arrangement of the bubbles in the cavitation field [91,92,102]. More specifically, factors such as bubble coalescence, bubble clustering, acoustic shielding and the rates of bubble dissolution and rectified diffusion can influence the population of “active” bubbles in a multibubble field. The cavitation bubble temperature, which is the maximum temperature that can be attained in the bubble core upon collapse, determines the intensity of SL emitted from the individual bubbles [1]. This temperature depends on the severity of the bubble collapse, which in turn is a function of a number of factors, including the symmetry of collapse, the change of bubble volume upon collapse and the presence and type of gaseous materials within the bubble.

---

# According to the theoretical calculations by Yasui [70], these sonoluminescing bubbles are generally much smaller than the (linear) resonance size.
When a sufficient amount of solute is present in a solution, the MBSL intensity is, generally, either quenched or enhanced as a result.

1.6.4 (a) SL quenching by the addition of alcohols

Volatile solutes, such as short chain aliphatic alcohols, have been found to quench the intensity of MBSL [97]. Figure 1.11 summarises the possible factors responsible for this phenomenon. One of the occurrences that would lead to a decrease in the SL intensity is a decrease in the “active” bubble population. The degree of bubble coalescence in the solution affects the bubble population. The study by Oolman and Blanch [67] found that alcohols retard the rate of bubble coalescence in stagnant liquids – a result which was later corroborated by the ultrasonic study of Lee et al. [103] This inhibition of bubble coalescence results in an increase in the number of available nuclei in the solution, thereby increasing the “active” bubble population and hence the SL intensity, rather than decreasing it.

The possibility of an increase in the degree of bubble clustering and/or acoustic shielding leading to the lowering of MBSL intensity is unlikely since there is no obvious physico-chemical reason for the addition of alcohols at relatively low concentrations to increase bubble clustering. The absence of any changes in the MBSL intensity of short chain alcohol solutions sonicated at 20 kHz [98] suggested that the solutes do not lower MBSL intensity by altering the “active” bubble population. However, under the conditions employed in the 20 kHz experiments [98], most of the bubbles in the cavitation field are transient bubbles, which only live for a few acoustic cycles. For stable bubbles at the higher frequencies employed in this study, it is not clear whether the structure of the bubble clusters is affected by the addition of alcohols.
Figure 1.11 Summary of possible factors responsible for SL quenching by the addition of alcohols.
Based on the 20 kHz results [98], any changes in the rates of rectified diffusion in the presence of alcohols are not likely to cause a decrease in the MBSL intensity by affecting the “active” bubble population.

Ashokkumar et al. [97] proposed that the accumulation of hydrocarbon products inside the bubble over many acoustic cycles is primarily responsible for the observed MBSL quenching in the presence of alcohols. One might argue that this accumulation leads to an increase in the pressure inside the bubble, and as a result, the average bubble size distribution might be shifted to a larger size and out of the SL “active” range. This possibility can be discounted based on the SBSL studies carried out by Guan and Matula [104] and Ashokkumar et al. [105], which showed that complete SL quenching can be achieved without a significant change in the maximum bubble size (R_{max}).

The observation that SL quenching by alcohols also occurs in single bubble experiments [104,105] strongly suggests that it is primarily an intrabubble event. Consumption of thermal energy by endothermic reactions of decomposing alcohol molecules inside the heated gaseous core of the bubble into hydrocarbon products has been proposed to be the main mechanism leading to SL quenching [106]. Results of the measurement of cavitation bubble temperatures by the methyl radical recombination (MRR) method conducted by Rae et al. [107] and Ciawi et al. [108] show that the temperature decreases with increasing yield of hydrocarbon products, hence supporting this proposition.

The presence of alcohol molecules is not expected to affect the symmetry of bubble collapse since it is unlikely that the spatial arrangement of bubbles is significantly altered. Changes in the ratio of bubble volume upon collapse and

\footnote{Yasui [70] showed that there is a range of bubble radii for SL bubbles rather than a single resonance size.}
cushioning of collapse are also unlikely to be the cause of SL quenching in the presence of alcohols, based on the observation that SBSL quenching is achieved without a significant change in the radius–time profile of the bubble [105,109].

1.6.4 (b) SL enhancement by the addition of SDS

The effect of SDS on MBSL intensity has been previously investigated [97]. Whilst it is generally agreed that the origin of the SDS effect is related to the interbubble electrostatic interactions between the charged SDS molecules adsorbed at the bubble/solution interface, precisely how these interactions affect the cavitation bubble field is not quite as widely agreed upon. Following a similar approach of reasoning as for the case for alcohols (§1.6.4 (a)), the possible factors giving rise to SL enhancement in the presence of SDS is summarised in Figure 1.12.

Bubble coalescence in aqueous solutions is inhibited in the presence of SDS [103,110]. Therefore, this will lead to a smaller average bubble size distribution, as well as an increase in the number of available nuclei, hence increasing the SL intensity. As will be discussed further in Chapter 4 (§4.2.1), however, bubble coalescence alone cannot fully describe the SL enhancement observed under different experimental conditions.

Another factor that has been suggested to play a role is the extent of bubble clustering leading to impedance shielding [97,111]. It is proposed that in addition to inhibiting bubble coalescence, the electrostatic repulsions between bubbles also result in more open (i.e., less dense) bubble clusters. The impedance shielding hypothesis [1] argues that if there is a cluster of bubbles, only those bubbles around the perimeter of the cluster will experience a sufficient local acoustic pressure required for SL. The bubbles in the centre of the cluster are shielded from the applied acoustic waves and therefore do not
Figure 1.12 Summary of possible factors responsible for SL enhancement by the addition of SDS.
collapse violently enough to emit SL. A more open bubble cluster structure will then result in a greater number of sonoluminescing bubbles.

The rate of bubble dissolution is a function of the surface tension of the solution [112]. SDS lowers the surface tension of the solution, hence can be expected to lower the rate of bubble dissolution accordingly [113]. Nevertheless, SL intensity in 1 mM SDS + 0.1 M NaCl solution was found to be similar to that of water [97,114], despite the marked difference in the surface tension of the two liquids. This indicates that any changes in the rate of bubble dissolution is not an important factor in determining MBSL intensity.

The rate of rectified diffusion has been shown to increase in the presence of SDS [115]. However, the investigation into the initial SL growth conducted by Lee et al. [114] shows that in 1 mM SDS + 0.1 M NaCl solution, although the SL growth rate increased in the presence of the surfactant, the steady-state SL intensity achieved was similar to that of water under identical experimental conditions. This strongly suggests that with regard to steady-state SL intensity, the change in the rate of rectified diffusion due to the presence of SDS does not significantly affect the “active” bubble population.

Another possible pathway for increasing the “active” bubble population is by decreasing the cavitation threshold. The cavitation threshold is proportional to the surface tension of the bubble/solution interface, since the higher is the surface tension, the harder it is to induce cavitation (i.e., create a new surface). SDS lowers the surface tension of the air/water interface, and thus is expected to lower the cavitation threshold. However, based on a similar argument regarding the SL intensity in 1 mM SDS + 0.1 M NaCl solution discussed above, it can be concluded that any changes in the cavitation threshold does not play a major role in determining MBSL intensity.
The finding that low concentrations of SDS did not significantly affect the radial dynamics nor the SL intensity of a single bubble in water [109] implies that the SL enhancement observed in multibubble systems is primarily due to interbubble process. Nevertheless, Ashokkumar et al. [111] suggested that the relatively more open bubble cluster structure might also allow a more symmetrical collapse of the “active” bubbles, hence resulting in a greater $T_{\text{max}}$ and consequently a greater SL intensity emitted.

Unlike the case for alcohols (§1.6.4 (a)), no definite inferences can be deduced on the effect of changes in the ratio of bubble volume upon collapse on SL intensity. This is because in a previous SBSL study, although the radius–time profile of the bubble was shown to be relatively unchanged in the presence of 30 µM SDS [109], this low concentration of the surfactant also hardly increased the SBSL intensity (relative to water). Hence, these results do not offer any insights regarding SL enhancement in the presence of SDS.

Other possible factors affecting $T_{\text{max}}$ are the degrees of cushioning of bubble collapse and the endothermic reactions inside the bubble. Both of these factors are related to the amount of gaseous materials inside the bubble, which will increase with an increase in the rate of rectified diffusion. However, as it has been concluded earlier in this discussion that the change in rectified diffusion rate is not a significant factor in determining the MBSL intensity, these last two factors are also unlikely to be significant. It is noteworthy that at high applied acoustic amplitudes [116], or under argon saturated conditions [61,99], SL quenching in the presence of SDS is possible due to the pyrolysis of the alkyl chain of those SDS molecules adsorbed at the bubble/solution interface.

Ω It is worth noting, however, that the SDS concentration used in the single bubble experiments (30 µM) was much lower than the typical concentrations used in multibubble experiments (0.5 – 10 mM).
1.7 CAVITATION-INDUCED EMISSION FROM EXCITED ALKALI METAL ATOMS

Emission lines from excited state alkali metal atoms are often observed on top of MBSL spectra when solutions containing these metals are irradiated [61,75,117-123]. Nonetheless, despite the common occurrence of the phenomenon, questions remain regarding the origin and mechanism of this emission. It is generally agreed that the mechanism leading to emission is driven by the high temperatures and pressures generated inside the bubbles upon collapse. Whether this emission takes place in the gas phase in the core of the collapsing bubbles or in the liquid phase inside or outside of the bubbles, however, remains under debate. Moreover, the precise mechanisms of metal cation reduction and the subsequent excitation of the metal atom continue to be actively investigated.

Based on an examination of previously published studies on ultrasonically generated metal atom emission, mechanisms to account for the emission have been proposed to originate either in the gas phase or in the liquid phase. The proposition where emission is from the gas phase inside the vapour/gaseous core of the collapsing bubbles [75,117,119,121] suggests that as metal ions are not volatile, this would involve either the ablation of the liquid shell directly adjacent to the bubble or the injection of fluid (most likely interfacial material) into the bubble core. This is followed by subsequent evaporation of the water, leaving bare metal ions in the gas phase, in a fashion not dissimilar to what takes place in atomic absorption spectroscopy. These ions are then reduced and electronically excited in the gas phase, and eventually relax back to the ground state by emitting light. It has also been suggested that emission from excited metal atoms occurs from a liquid phase at the bubble/solution interface, where the volume of liquid directly adjacent to the collapsing bubble is heated.
sufficiently such that the metal ions existing in this hot liquid shell are reduced, excited, and then emit light [61,118].

Sehgal et al. [117], who studied the SL from aqueous alkali metal salt solutions, observed that the atomic spectral lines were shifted to longer wavelengths (i.e., red-shifted), significantly broadened with asymmetry towards the red, and with the presence of blue satellite bands. They interpreted the shift in the position of the emission lines as a pressure-induced shift, which is a result of the perturbation of the energy levels of the emitting species by neighbouring molecules or atoms. The presence of the blue satellite bands has been explained to originate from alkali metal – argon exciplexes, which occur when a mixture of alkali metal vapour and argon gas are rapidly compressed [124]. The broadening of the emission lines due to the high pressures is a consequence of the Heisenberg uncertainty principle, $\Delta E \times \Delta t = \frac{h}{2\pi}$. At high pressures, there are more collisions between the emitting species and the neighbouring molecules or atoms per unit time, hence resulting in a decrease in lifetime ($\Delta t$) and subsequently an increase in the energy distribution (line width) of the emission ($\Delta E$). These interpretations brought them to conclude that metal atom emission arises from a highly compressed gas phase environment in the bubble core, and then further used their data on the emission line width to estimate the pressure generated inside a collapse bubble.

The study conducted by Flint and Suslick [118] aimed to extend the work of Sehgal et al. [117] in using alkali metal SL to probe acoustic cavitation conditions by varying different parameters known to affect the cavitation bubble temperature, such as the solvent vapour pressure and the thermal conductivity of the saturating inert gas. While they observed similar results to that of the previous study in terms of the position of the emission lines and the line
broadening, they found that neither of these changed as a function of the solvent vapour pressure or the inert gas thermal conductivity. This strongly suggests that emission does not originate directly from the cavitation hot spot. Instead, they proposed a mechanism whereby high energy radicals produced from the solvent vapour inside the heated core of the cavitation bubble diffuse out of the hot spot and react with the alkali metal ions in the hot liquid shell surrounding the bubble, producing excited state metal atoms which subsequently emit light.

While the arguments presented by Flint and Suslick [118] seem convincing, Lepoint-Mullie et al. [119] still questioned the participation of the liquid phase immediately adjacent to the bubble/solution interface in producing metal atom emission. Their results corroborated the proposition of Sehgal et al. [117] that emission originates from the gas phase inside the bubble core. They also suggested a mechanism where metal atoms are generated via homolytic cleavage of metal-halide salts in the gas phase, such that it does not involve the reduction of metal cation (Scheme 1.1).

Scheme 1.1 Generation of neutral metal atoms by homolytic cleavage of metal-halide salts in the gas phase, as proposed by Lepoint-Mullie et al. [119]
Once the metal atom is produced in the gaseous state, it is then electronically excited by a three-body reaction involving the sonochemically generated H• and •OH radicals (Reactions 1.1 – 1.2, where M represents a third body).

\[
\begin{align*}
\text{H}^+ + \cdot \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M}^* \quad (1.1) \\
\text{H}^+ + \text{H}^+ + \text{M} & \rightarrow \text{H}_2 + \text{M}^* \quad (1.2)
\end{align*}
\]

These excited metal atoms then form complexes with the rare gas molecules in the bubble interior, which eventually relax back to the ground state accompanied by light emission.

In a more recent study of Choi et al. [125], where emission from argon saturated NaCl aqueous solutions doped with ethanol was monitored, it was found that with increasing ethanol concentration, the line width of the emission band increased while the overall emission intensity decreased. They rationalised the decrease in intensity by the lowering of the bubble temperature due to the volatility of ethanol leading to the formation of hydrocarbon products inside the bubble (§1.6.4 (a)). The increasing line width with increasing ethanol concentration is thought to be due to collisions of Na+ with the hydrocarbon products of ethanol decomposition in addition to collisions with argon gas, hence implying gas phase origin of Na+ emission. It is noteworthy, however, that in addition to being volatile, ethanol is also known to be surface active and hence will partition at the bubble/solution interface. Results obtained from the studies conducted by Taylor and Jarman [75] and Arakeri [121] also support emission occurring in the gas phase.

All of the studies discussed so far involve either the heated shell model or the injection droplet model (Figure 1.13) as a means of introducing non-volatile metal cations into the heated interior of collapsing bubbles. Matula et al. [122]
examined both SBSL and MBSL spectra obtained from aqueous NaCl solutions, and found that while the Na\(^+\) emission line was prominent in the MBSL spectrum, it was practically absent in the SBSL spectrum. Since the primary difference between the two systems is the sphericity of bubble collapse, this observation led them to conclude that mechanism of emission must involve the injection of droplets from the interfacial liquid into the heated core of the bubble, via surface wave action or microjetting. For the stable and highly symmetric collapse of a SB, injection of liquid droplets is very unlikely to occur, hence the absence of Na\(^+\) emission.

![Figure 1.13](image)

**Figure 1.13** (a) The heated shell model and (b) the injected droplet model leading to excited metal atom emission from cavitation bubbles (adapted from ref. [126]).

Flannigan and Suslick [126] examined the variation in SL emitted from a moving SB in solutions of sulfuric acid containing alkali metal salts. They observed that as the acoustic pressure was increased, the bubble motion became more erratic and bubble collapse more asymmetric. This was paralleled by a decrease in the intensity of the continuum in the SL spectrum, while the Na\(^+\) emission line intensity increased, hence further corroborating the hypothesis presented by Matula et al. [122]
It is worth mentioning the ingenious experiments conducted by Ohl [127], where the luminescence from a laser initiated single cavitation bubble was monitored as the degree of asphericity of the bubble collapse was varied. The degree of asphericity was controlled with an adjustable rigid boundary near the bubble. In water, it was observed that the luminescing regions were larger for the non-spherical cases. More specifically, for those cases a halo was observed around the central luminescing area. The area of this halo extended nearly 14 times that of the central part. The implication of this is that part of the luminescence comes from the liquid surrounding the cavitation bubble. In other words, it was hypothesised that there are two distinct source of light emission for non-spherically collapsing bubbles: from the bubble interior and from the liquid around it. For 1 M NaCl aqueous solution, a weak Na$^+$ emission was observed. Interestingly, with increasing asphericity of bubble collapse, the ratio of the intensity of the Na$^+$ emission line to the continuum was found to decrease first, before increasing strongly. This finding suggests the existence of two different mechanisms leading to Na$^+$ emission: from the bubble interior by heating Na trapped in the bubble, and from the liquid surrounding the bubble.

In summary, it can be said that the site from where metal atom emission lines originate remain under conjecture.

The precise mechanism of the generation of metal atoms from metal-halide salt solutions also remains an open question. Lepoint-Mullie et al. [119] suggested homolytic cleavage of metal-halide salts in the gas phase (Scheme 1.1), while Flint and Suslick [118] proposed a reaction between metal cations and high energy radicals produced during bubble collapse (Reaction 1.3), where $P'$ signifies a high energy radical (e.g., RO' from the decomposition of primary alcohols) and M$^+$ is the metal cation.
\[ P^- + M^+ \rightarrow M + P^+ \quad (1.3) \]

Vu [128] suggested that the reduction of metal cation to neutral metal atom (Reaction 1.4) takes place in the heated liquid shell near the bubble/solution interface. One possible source of the electron required for the reduction process is from the counter-ions. However, this possibility was discounted based on the observation that the Na\(^+\) emission intensity remained relatively constant when the counter-ion was varied (Cl\(^-\), Br\(^-\) and I\(^-\)).

\[ M^+ + e^- \rightarrow M \quad (1.4) \]

Another possibility is where the electron comes from water molecules in the heated shell. The temperature of this heated shell has been approximated to be around 2000 K [32]. Under this condition, the dielectric constant of water decreases significantly to almost 1, and hence making it virtually impossible for the water molecules to retain their polarity. It is speculated that the electrons released by these water molecules can then reduce the metal cations to form metal atoms [128].

\* Arakeri [121] made a similar observation with KCl and KI solutions, where the K\(^+\) emission intensity from the two salt solutions did not vary significantly. However, they interpreted this result was an indication that dissociation of the salt into its ionic constituents may not be involved. Instead, they suggested the possibility of the metal salt solution aerosol being heated above a critical temperature in the bubble core, resulting in the availability of the atomic constituents directly.
1.8 SONOCHEMILUMINESCENCE OF LUMINOL

In contrast to SL (§1.6), when light emission is a result of reaction between an added chemical and sonochemically generated radicals, the emission is called sonochemiluminescence (SCL) [129]. The chemical that is generally added for SCL studies is luminol (I), whose structure is shown in Scheme 1.2. Luminol SCL is usually utilised to visualise the “active” regions in sonoreactors [130,131] and also as an indicator of sonochemical activity [132].

The mechanism of luminol SCL has been proposed by McMurray [129] and is depicted in Scheme 1.2. Due to the amphoteric nature of luminol, it can act as a base, resulting in the amino group being protonated at low pH. Under the experimental conditions employed in this study, however, the extent of this protonation is negligible [133]. At higher pH, luminol is a weak diprotic acid with the first and second pKa values (pKa₁ and pKa₂, corresponding to the hydrazide hydrogens) of ~6.3 and ~13–15, respectively [133-135].* Thus, it exists predominantly as the monoanion species (II) at the pH range employed in our experiments (pH ~10.5). The luminol monoanion is then oxidised by the sonochemically generated •OH to produce the diazaquinone radical anion (III). This oxidation is in competition with reactions between •OH and H₂O₂ / HO₂⁻ generated during sonication of aqueous solutions. Species III then react further with O₂⁻ to form the hydroperoxide addition product (IV), which decomposes and eventually relaxes to give the ground state of the aminophthalate monoanion (V) accompanied by the emission of a characteristic blue fluorescence around 430 nm.

* The pKa values of luminol vary with the ionic strength of the liquid [133-135]. However, this variation has been shown to be minimal for pKa₁ (≤ 0.2 pKa units) in the range of ionic strength between 0.004 to 0.5 [133]. The ionic strength under the experimental conditions employed in this study is 0.003. The values for pKa₂ reported in the literature vary from 13.0 [134] to 15.1 [135]. Differences in the measurement methods used were suggested to give rise to the discrepancy.
Scheme 1.2  Mechanism of SCL emission from luminol solution at pH ~10.5 (adapted from ref. [129]). Oxidation of luminol monoanion by the sonochemically generated •OH results in a bright blue light emission at 430 nm.

1.9 SONOCHEMISTRY (SC)

The field of sonochemistry (SC) encompasses any chemical reactions that are altered, enhanced or assisted by the application of ultrasonic waves. The sonochemical effects, however, do not arise from direct interactions of the sound waves with molecular species [136]. Considering the acoustic wavelength in typical liquids in most applications ranges from millimetres to a few
centimetres, the acoustic field cannot couple directly with the molecular energy levels. Rather, SC occurs primarily as a consequence of acoustic cavitation (§1.2).

SC mainly concerns reactions with free radicals. While these radical reactions are extremely useful in many cases, in particular applications such as in medical treatment and diagnosis [137] and some food industry applications [138], the generation of these free radicals might not be desirable. Hence, it is important to study the fundamental aspects of SC, in addition to the potential applications of the technology.

Sonochemical reactions utilise both the physical and chemical effects of acoustic cavitation. Shear forces arising from cavitation can give rise to mechanical degradation of macrostructures (e.g., polymer strands) in solution [139]. Radicals generated from the pyrolysis of vapour in the heated core of cavitation bubbles can react in the hot gas phase inside the bubbles (e.g., with volatile solutes), at the interfacial region or in the bulk liquid (e.g., with non-volatile solutes), as depicted in Figure 1.14.

![Figure 1.14](image)

**Figure 1.14** Three possible sites of sonochemical reaction. Volatile solutes react in the hot gas phase in the bubble interior (1), while non-volatile solutes react either at the interfacial region (2), or in the bulk liquid (3).
1.9.1 Aqueous SC

1.9.1 (a) Radical reactions
SC in aqueous solutions are dominated by reactions involving H’ and ’OH since the main reaction occurring is the homolytic cleavage of water vapour molecules inside cavitation bubbles (Reaction 1.5).

\[
\text{H}_2\text{O} \rightarrow \text{H’} + \text{’OH} \quad (1.5)
\]

The existence of this reaction was first proposed by Weiss [140], followed by the first experimental evidence from the work of Parke [141]. More evidence for H’ and ’OH formation during sonication of aqueous solutions has been obtained since, including indirect evidence by the detection of H₂O₂ (Reaction 1.6) [142-144] and direct evidence from electron spin resonance spectra of trapped species [145-147].

Most of these primary radicals recombine inside the bubble (Reactions 1.6 – 1.9) and it has been estimated that only about 10% of the H’ and ’OH generated in cavitation bubbles reach the liquid phase [57,139,148].

\[
\text{H’} + \text{’OH} \rightarrow \text{H}_2\text{O} \quad (1.6)
\]
\[
\text{H’} + \text{H’} \rightarrow \text{H}_2 \quad (1.7)
\]
\[
\text{’OH} + \text{’OH} \rightarrow \text{H}_2\text{O}_2 \quad (1.8)
\]
\[
\text{’OH} + \text{’OH} \rightarrow \text{O} + \text{H}_2\text{O} \quad (1.9)
\]

When O₂ is present in the bubble, additional reactions are possible (Reactions 1.10 – 1.16) [144,148-150].
Chapter 1: Introduction, theory and literature review

\begin{align*}
O_2 & \rightarrow O + O \quad (1.10) \\
H^\bullet + O_2 & \rightarrow HO_2^\bullet \quad (1.11) \\
HO_2^\bullet + HO_2^\bullet & \rightarrow H_2O_2 + O_2 \quad (1.12) \\
H^\bullet + O_2 & \rightarrow \cdot OH + O \quad (1.13) \\
H^\bullet + H_2O_2 & \rightarrow \cdot OH + H_2O \quad (1.14) \\
H^\bullet + H_2O & \rightarrow \cdot OH + H_2 \quad (1.15) \\
H_2O + O & \rightarrow \cdot OH + \cdot OH \quad (1.16)
\end{align*}

Fischer et al. [148] noted that Reaction 1.7 does not occur to a significant extent in liquids under air-saturated condition. Petrier et al. [151] only detected the existence of \( \cdot OH \) and not \( H^\bullet \) or \( HO_2^\bullet \) during the sonication of water under air-saturated condition. \( HO_2^\bullet \) was not detected even when the water was saturated with oxygen. It is noteworthy, however, that in other studies, the presence of \( HO_2^\bullet \) has been detected by its ability to bring about specific reactions [12,152].

Yasui [153] proposed that for an air bubble, there exists an optimum bubble temperature for the production of oxidants (such as \( \cdot OH \), \( O^\bullet \), \( H_2O_2 \), \( O_3 \)) from pyrolysis of water vapour inside a heated bubble. This optimum temperature, which was estimated to be around 5500 K, occurs because at higher bubble temperatures, these oxidants are thought to be strongly consumed by reaction with nitrogen (Reaction 1.17, where \( M \) represents a third body).

\begin{equation}
\cdot OH + NO + M \rightarrow HNO_2 + M \quad (1.17)
\end{equation}

When solutes are present in the solution, the primary radicals generated may also react with volatile solute molecules inside the bubble, or alternatively, they
may diffuse away and react with dissolved solutes at the bubble/solution interface or in the bulk solution.\textsuperscript{\Delta}

1.9.1 (b) Dosimetry for \textsuperscript{•}OH yield

Since the chemical effects of ultrasound in aqueous solutions are largely associated with the formation of radicals (particularly \textsuperscript{•}OH), it is necessary to be able to quantify the yield of these radicals in order to determine sonochemical efficiency. There are three common methods to quantify the amount of \textsuperscript{•}OH produced during sonication of aqueous solutions: Fricke, iodide and terephthalate dosimetries [155].

Fricke dosimetry is a photometry-based analysis utilising the oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+} in solution [156]. The amount of Fe\textsuperscript{3+} is determined by monitoring its absorbance at 304 nm. This method is simple and reproducible, however the downside is that oxidation of Fe\textsuperscript{2+} can be brought about by reaction with \textsuperscript{•}OH, H\textsubscript{2}O\textsubscript{2}, H\textsuperscript{•} and HO\textsubscript{2}\textsuperscript{•}, and thus is not specific for \textsuperscript{•}OH [157].

The second method, iodide dosimetry, is similar to Fricke dosimetry. Analysis is based on the oxidation of I\textsuperscript{−} by \textsuperscript{•}OH and H\textsubscript{2}O\textsubscript{2} to form I\textsubscript{2}, which then react further with another I\textsuperscript{−} moiety to form I\textsubscript{3}−. The amount of I\textsubscript{3}− generated is calculated from its absorbance at 353 nm, and the concentration of \textsuperscript{•}OH / H\textsubscript{2}O\textsubscript{2} is subsequently determined by stoichiometric ratio [58].

Unlike the other two dosimetries, the terephthalate dosimetry involves measuring the fluorescence intensity of the oxidation product instead of its absorbance. Terephthalate anion reacts with \textsuperscript{•}OH to generate the highly

\textsuperscript{\Delta} In particular the \textsuperscript{•}OH radicals since they are known to penetrate deeper into the solution compared to H\textsuperscript{−} [152]. H\textsuperscript{•} almost exclusively recombine inside the bubble, and hence are not readily available to reduce solutes in solution [154].
fluorescent 2–hydroxyterephthalate ion, which can be excited at 315 nm and emits fluorescence at 425 nm [157-159]. This method is specific for ’OH and has a high sensitivity up to $1.2 \times 10^{11}$ molecules/mL. This excellent sensitivity of the terephthalate dosimetry enabled ’OH yield from a single bubble to be measured [22].

There is another method to specifically determine the amount of ’OH generated, which is by using ESR spin trapping measurements. However, this technique is not widely available in most laboratories [157].

1.9.2 Applications in food processing

The application of ultrasound in food processing has been reviewed by McClements [160] and Knorr et al. [161] Extraction of food materials sees an enhanced extraction rate upon the application of ultrasound [162,163]. This enhancement have been proposed to be due to the microjetting causing a greater penetration of solvent into the food material, as well as enhanced mass transfer due to microstreaming. Emulsification processes [164] also benefit from the shear forces generated by the intense collapse of acoustic bubbles in solution. A reduction in the size of fat globules after the ultrasonic treatment of milk has been reported by Villamiel and de Jong [14]. Several examples of more novel applications include controlling crystallisation of pharmaceutical products [165], tenderisation of meat [166], enhancing agglomeration of soybean protein [167] and alteration of enzyme activity [168].

1.9.3 Antioxidants

Chapter 6 discusses the possibility of modifying the structure of food compounds in order to enhance their antioxidant activity. An antioxidant is a
substance which slows or prevents the oxidation of other substances. It works by “de-activating” free radicals, and in doing so, the antioxidant itself becomes oxidised (Scheme 1.3).

Scheme 1.3  Schematic of how an antioxidant works. Antioxidants become oxidised upon capturing free radicals. Hence, the potency of an antioxidant depends on the stability of the oxidised species.

The extent of the reaction shown in Scheme 1.3 depends on the stability of the “oxidised antioxidant”: the more stable it is, the better (i.e., more potent) is the antioxidant. Some of the most common antioxidants are carotenoids (e.g., β-carotene) [169] and polyphenolic compounds [170]. Of the polyphenols, flavonoids represent the most common and widely distributed group of plant phenolics [170-174].

1.10 SCOPE OF THIS THESIS

The use of ultrasound is becoming increasingly widespread in many applications. The efficiency of these applications, many of which involve the presence of surface-active solutes, very much depends on the cavitation bubble field. The objective of this present study was to investigate the behaviour of a multibubble field under different acoustic powers and frequencies in the presence of various surface active solutes, which are typical conditions for sonochemical processes.
A greater understanding of how the cavitation field is affected by different parameters would enable a better prediction of the outcome of sonochemical processes. Several different experimental techniques involving investigation into the phenomena of bubble coalescence, SL and SCL are employed to study the multibubble field.

Bubble coalescence affects sonochemical activity by altering the number of “active” bubbles in the system. As discussed in §1.4.2, surface active solutes interfere with the process of bubble coalescence. Chapter 3 looks into the extent of bubble coalescence under various experimental conditions.

As there are other processes occurring during sonication, knowing the extent of bubble coalescence alone is not enough to describe the bubble field. In Chapter 4, SL is utilised to further probe cavitation conditions as acoustic power and frequency are varied in the presence of surface active solutes.

Emission lines from excited metal atoms are often observed in SL spectra of aqueous metal-halide solutions. However, as elaborated in §1.7, the origin and mechanism of this interesting phenomenon is still under conjecture. Spectral and photographic techniques have been employed in attempt to provide further insight and these are covered in Chapter 5.

Chapter 6 explores the applied aspect of sonochemistry. Methods to control the free radicals production during sonication of aqueous solutions are discussed. Preliminary results on the feasibility of sonochemistry in the hydroxylation of food materials are also presented.

Finally, an overview of the insights gained from this study, as well as possible future investigations, are presented in Chapter 7.
CHAPTER TWO

Experimental Details

2.1 MATERIALS

2.1.1 Alcohols, diols and triol

All alcohols used in this study were of analytical reagent grade. Ethanol, n-propanol and n-butanol were obtained from BDH. n-Pentanol was obtained from Rhône Poulenc. Ethylene glycol (99+%, extra pure) was purchased from Acros Organics. 1,3-Propanediol (puriss., ≥99%) was purchased from Fluka. 1,4-Butanediol (99.5%) was supplied by Riedel-de Haën. Glycerol (≥99.5%), a triol, was obtained from Merck. All reagents were used as supplied. Some of the physical properties of these solutes are listed in Table 2.1.

2.1.2 Surfactants

The anionic surfactant sodium dodecylsulfate (SDS) was a special purity grade supplied by BDH. n-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (Zwittergent® 3–12 detergent), a zwitterionic surfactant, was obtained from Calbiochem. Both surfactants were used as received. Table 2.2 shows the structures and the critical micelle concentrations (CMC) for these two surfactants.
Table 2.1 Some physical properties of the –OH containing solutes used in this study
(n = the number of carbon atoms in the molecule).

<table>
<thead>
<tr>
<th>n</th>
<th>Solute</th>
<th>Structure</th>
<th>$P_{\text{vap}}$ at 25 °C (mmHg)$^a$</th>
<th>$\eta$ at 25 °C (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ethanol</td>
<td></td>
<td>59.3</td>
<td>1.074$^b$</td>
</tr>
<tr>
<td>3</td>
<td>n-propanol</td>
<td></td>
<td>21.0</td>
<td>1.945$^b$</td>
</tr>
<tr>
<td>4</td>
<td>n-butanol</td>
<td></td>
<td>6.7</td>
<td>2.54$^b$</td>
</tr>
<tr>
<td>2</td>
<td>ethylene glycol</td>
<td></td>
<td>0.0920</td>
<td>15.82$^c$</td>
</tr>
<tr>
<td>3</td>
<td>1,3-propanediol</td>
<td></td>
<td>0.0441</td>
<td>39.41$^c$</td>
</tr>
<tr>
<td>4</td>
<td>1,4-butanediol</td>
<td></td>
<td>0.0105</td>
<td>67.03$^c$</td>
</tr>
<tr>
<td>3</td>
<td>glycerol</td>
<td></td>
<td>0.000168</td>
<td>934$^b$</td>
</tr>
</tbody>
</table>

$^a$ Values obtained from ref. [175].
$^b$ Values obtained from ref. [28].
$^c$ Values obtained from ref. [176]

Table 2.2 Surfactants used in this study.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$<em>{12}$H$</em>{25}$SO$_4$Na</td>
<td>C$<em>{17}$H$</em>{37}$NO$_3$S</td>
</tr>
<tr>
<td>Structure</td>
<td>CH$_3$(CH$_2$)$_9$CH$_2$O–S–O’Na$^+$</td>
<td>CH$_3$(CH$_2$)$_9$CH$_2$–N$^+$–(CH$_2$)$_3$SO$_3$–</td>
</tr>
<tr>
<td>Class</td>
<td>anionic</td>
<td>zwitterionic</td>
</tr>
<tr>
<td>CMC (mM)$^*$</td>
<td>8</td>
<td>2 – 4</td>
</tr>
</tbody>
</table>

$^*$ Values obtained from manufacturers.
2.1.3 Electrolytes

Sodium chloride (NaCl, 99.9%) was purchased from BDH, and was used for the experiments conducted at The University of Melbourne (UoM). For the experiments carried out at The National Institute of Advanced Industrial Science and Technology (AIST), NaCl (min. 99.5%), potassium chloride (KCl, min. 99.5%) and sodium carbonate (Na₂CO₃) were purchased from Wako Chemicals Japan.

2.1.4 Reagents for applied food science studies

All chemicals were used as received without further purification. Phenol was of analytical reagent grade and was obtained from BDH. L-ascorbic acid (>99.7%) was purchased from Chem-Supply. Betatene® 30% Soy was purchased from Cognis. Betatene® 30% Soy is a suspension of natural mixed carotenoids in soybean oil. It consists of primarily β-carotene (94.5%), with α-carotene (3.5%) and other carotenoids (cryptoxanthin, zeaxanthin, lutein, 2.0%) making up the rest of the composition. Morin, in powder form, was obtained from Sigma. Cyanidin 3-glucoside samples used in this study was in the form of black carrot juice concentrate supplied by Food Science Australia. The concentration of crude cyanidin in the sample was 19.6 µg cyanidin 3-glucoside equivalent / mg fluid weight. The structures of these chemicals, along with some of their physical properties, are outlined in Table 2.3.

Various solvents were used as eluents in the high performance liquid chromatography (HPLC) analyses. Acetonitrile (HPLC grade, ≥99.9%) was purchased from BDH. Methanol (HPLC grade, ≥99.8%) was purchased from
Merck, while tetrahydrofuran (THF, ≥99.5%) and formic acid (99% w/w) were obtained from Chem-Supply.

Table 2.3  Some physical properties of the chemicals used in the applied food science studies.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Structure</th>
<th>Molecular formula</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td><img src="image" alt="Phenol Structure" /></td>
<td>C₆H₅OH</td>
<td>94.1</td>
<td>8.3 g / 100 mL at 20 °C</td>
</tr>
<tr>
<td>L-ascorbic acid</td>
<td><img src="image" alt="L-ascorbic Acid Structure" /></td>
<td>C₆H₈O₆</td>
<td>176.1</td>
<td>soluble</td>
</tr>
<tr>
<td>Morin</td>
<td><img src="image" alt="Morin Structure" /></td>
<td>C₁₆H₁₀O₇</td>
<td>302.2</td>
<td>soluble in aqueous basic solution</td>
</tr>
<tr>
<td>Cyanidin 3-glucoside</td>
<td><img src="image" alt="Cyanidin 3-glucoside Structure" /></td>
<td>C₂₁H₂₁O₁₁</td>
<td>449.4</td>
<td>soluble</td>
</tr>
<tr>
<td>β-carotene</td>
<td><img src="image" alt="β-carotene Structure" /></td>
<td>C₄₀H₅₆</td>
<td>536.9</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

For hydroxide peroxide measurements, all chemicals used were of analytical reagent grade. Sodium hydroxide (NaOH), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄.⁴H₂O) and potassium hydrogen phthalate (KC₈H₆O₄) were obtained from Ajax Chemicals (Univar). Potassium iodide (KI) was obtained from Chem-Supply.

For the antioxidant activity measurements, tris(hydroxymethyl) aminomethane (Trizma® base, reagent grade) and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma.
2.1.5 Other reagents

Luminol (3-aminophthalhydrazide) was purchased from Wako Chemicals Japan and was used as supplied. All the solutions were made up using Milli-Q water, with a conductivity of \(<10^{-6} \text{ S cm}^{-1}\) at 20 °C, unless specified otherwise.

2.2 METHODS AND EQUIPMENTS

2.2.1 Multibubble sonoluminescence (MBSL) at UoM

2.2.1 (a) Solution preparation

For the surfactants, aqueous stock solutions were prepared. These stock solutions were then subsequently diluted with Milli–Q water to the appropriate concentrations. All the other solutions were prepared simply by adding the required amount of reagent to Milli–Q water. All solutions were left overnight to allow full air saturation before use.

2.2.1 (b) Experimental setup

Two different ultrasound generators were used: an ELAC Nautic RF generator type LVG 60 A operating at 358 kHz and 1062 kHz as well as an ELAC Nautic RF generator type LVG 60–10 operating at 213 kHz and 647 kHz. Both units were operated in a continuous mode. The sonication cell holding the solution was a quartz cylinder equipped with a Pyrex cooling jacket, mounted over a flat plate transducer (\(d = 5.45 \text{ cm}\)). The cell, together with an end–on photomultiplier tube (PMT, Hamamatsu, model no. E849–34, detection range 350–600 nm), was kept in a light-proof enclosure to minimise the detection of stray light. The integrated SL emission signal from the PMT was amplified (\(\times 800 \text{ V}\)) by a high voltage power supply (Canberra Industries Inc.,
Chapter 2: Experimental details

Model 3002). It was then displayed on a digital oscilloscope (Tektronix TDS 320), after passing through an in-house built high voltage protection device, and recorded for further analysis (Figure 2.1).

Figure 2.1 Schematic and photograph of the MBSL experimental setup at UoM.

2.2.1 (c) SL intensity measurements

All experiments were conducted at room temperature (~20 °C). The temperature of the solutions was not controlled, but monitored to ensure that any heating during sonication was limited to a few degrees. The volume of the solutions sonicated was 200 mL, which corresponds to about 70 mm liquid height in the cell. The power absorbed by the liquid was determined
calorimetrically. In a typical experiment, the SL intensity was obtained by first sonicating the solution for 2 minutes and allowing it to stand undisturbed for another 2 minutes before the sonicator was turned on again and the average SL intensity recorded. This procedure was found to give reproducible results.

2.2.1 (d) SL spectra measurements

The SL spectra were recorded on a Hitachi fluorescence spectrophotometer (Model F–4500). The slit width was set at maximum (20 nm resolution) to detect as much signal as possible, and the PMT voltage was set at 950 V. In order to be able to directly correlate the SL spectra to the integrated SL intensities, the solutions were subjected to identical sonication conditions: 2 minutes sonication followed by allowing the solution to stand undisturbed for another 2 minutes, before sonication was started again and the spectrum recorded. A spectrum from 200–800 nm took about 2.5 minutes to complete. The temperature of the solutions was kept around 19–21 °C with the aid of cooling water passing through the water jacket surrounding the cell. To remove any background effects, a reference spectrum was recorded prior to each run and was later subtracted from the SL spectrum of the sample.

2.2.1 (e) Gas chromatography measurements

The yield of hydrocarbon products generated at different acoustic powers and frequencies was measured on a Shimadzu GC–17A gas chromatograph employing a flame ionisation detector. 10 mL aliquots of 100 mM ethanol solution were contained in 15-mL vials fitted with septum. These vials were then placed vertically in a sonication cell (the same one used for SL/SC experiments) filled with ~200 mL Milli-Q water through holes in a fitted rubber lid, and were held in place by rubber O-rings. The height of the vials in the water was adjusted such that the water surface was in line with the top of the liquid meniscus inside the vials (Figure 2.2). Duplicate vials were sonicated
each time to ensure reproducibility. Cooling water was passed through the water jacket surrounding the cell to maintain moderate (<30 °C) solution temperature throughout the 30 minutes sonication. At the end of sonication, 50 µL aliquots were obtained from the headspace in each vial and injected into the GC. The resulting chromatograms were then analysed and the peak areas were converted into concentrations using calibration curves.

![Figure 2.2 Schematic of the sonication setup for GC measurements.](image)

### 2.2.2 Multibubble sonoluminescence (MBSL) at AIST

#### 2.2.2 (a) Solution preparation

Unlike the procedure followed at UoM, each solution was made fresh on the day of experiment using distilled water (Yamato, Autostill WG 200). It was sparged thoroughly with either air or argon as necessary for at least 30 minutes prior to experiment to ensure full gas saturation. During the sparging period, the solution was kept in a thermostatted bath at 20 °C. For the luminol-doped solutions, an appropriate amount of a basic luminol stock solution was added to
the sample solution to obtain a final concentration of 0.01 mM luminol (in 1 mM Na₂CO₃).

2.2.2 (b) Experimental setup

Most of the experiments described in this section were undertaken using a continuous wave ultrasound generated by a function generator (NF Wavefactory 1942) that was further amplified by a 55–dB power amplifier (EIN, Model 1140 LA). The amplified wave was then fed to a Langevin-type transducer (Honda Electronics, d = 45 mm, thickness = 55 mm) driven at a frequency of 38, 71.4 or 139 kHz. The transducer was fixed to the centre of a circular stainless steel plate (d = 100 mm, thickness = 1 mm), upon which a rectangular quartz cell (60 mm × 60 mm × 79 mm external dimensions, thickness = 2 mm) was mounted. The volume of liquid sonicated for each run was 200 mL, which corresponds to about 65 mm liquid height in the cell. The setup was kept inside a light-proof enclosure to minimise the detection of stray light (Figure 2.3).

Figure 2.3 Schematic for the setup for MBSL experiments at AIST.
2.2.2 (c) SL intensity measurements

All experiments were conducted at room temperature (~20 °C) and a temperature probe was placed in the middle of the solution to monitor the temperature in-situ. For the experiments investigating the effect of varying the applied acoustic amplitude, the applied amplitude was automatically increased in 5 mV\textsubscript{p–p} steps from 0 to 500 mV\textsubscript{p–p}. Each run took approximately 1 minute, during which any increase in the solution temperature was less than 2 °C. A converging lens was placed between the cell and the PMT (Hamamatsu Photonics R928, detection range 200–900 nm) to ensure that as much light as possible emitted from the whole solution was detected. The integrated intensity was then displayed on the oscilloscope and used for further analysis.

2.2.2 (d) Bubble cloud and SL/SCL imaging

Imaging of the bubble clouds was carried out by recording video clips of the sonicated solutions using a video camera. Snapshots were then obtained from these video clips using the AVI to MPEG Converter 1.5 for Windows software (FlyDragon Software Inc.). The sonication conditions were as stated in the relevant figure captions in Chapter 4.

SL and SCL photographs were captured under pitch black conditions using a Nikon D70 digital camera, with 5 minutes exposure time for SL and 2 minutes for SCL images. Cooling was assisted by air circulation around the cell such that the temperature of the solutions after 5 minutes sonication did not exceed 26 °C. In all photographs, the transducer driving frequency was set at 139 kHz and the output voltage of the function generator was 360 mV\textsubscript{p–p}, equivalent to ~0.1 W cm\textsuperscript{–3} as determined by calorimetry.
2.2.2 (e) SL spectra measurements

Due to equipment availability, the measurement of uncalibrated SL spectra was performed using a different function generator (NF Wavefactory 1946A) and under slightly different conditions (159 kHz, 0.06 W cm$^{-3}$). The monochromator used was a Jasco M25–T and an ICCD camera (ANDOR 501–18F) was employed as the detection system.

2.2.3 Bubble coalescence

The ultrasound generators used were the same as those described in Section 2.2.1. The sonication cell used was similar to that employed by Lee et al. [103], modified to suit the appropriate transducers. The Pyrex capillary cell used in this work consisted of two detachable parts: the base of the cell which had a volume of approximately 250 mL and a long capillary neck with the capacity of around 19 µL cm$^{-1}$ attached on top (Figure 2.4). The base of the cell was mounted on the flat plate transducer and filled with the test solution until almost full, taking care to avoid creating any visible bubbles adhering to the walls of the cell. The capillary neck was then attached on top and a syringe with a 19-gauge needle was used to carefully fill the capillary to about 1 cm from the base. Each solution was then sonicated for 10 seconds, during which the liquid interface was seen to rise up the capillary. The distance covered by the liquid interface after sonication was then measured, and this is termed $\Delta V_T$, the ‘total volume change’ (Figure 2.5). Unlike what was observed by Lee et al. [103], however, no appreciable drop in the liquid interface level was observed once the ultrasound was switched off. The height of the liquid interface remained approximately constant for at least a couple of minutes. A typical volume measured for the $\Delta V_T$ was between 20–120 µL. Each experiment was conducted multiple times to ensure reproducibility. All the data points
presented are averages of at least four runs. The solution temperature was not controlled, but was monitored to be around 21–22 °C and any temperature rise was limited to ~0.3 °C after 10 seconds of sonication.

**Figure 2.4** Photograph of the capillary cell used in the bubble coalescence studies.

**Figure 2.5** Schematic showing the measurement of the volume change of the liquid following sonication.
2.2.4 Surface tension measurements

Surface tension measurements were carried out using the Wilhelmy plate technique with a McVan Analite Tensiometer (Model 2141) and the supplied glass plates. The petridish and plates were rinsed in methanol, followed by copious rinsing in Milli–Q water prior to use.

2.2.5 Power calibration (calorimetry)

For each experiment, the applied ultrasound power was estimated using a calorimetric method. A volume of water was sonicated for a given time, and the rise in the solution temperature was recorded. Assuming that almost all of the ultrasound energy absorbed by the water is converted to heat, the ultrasound power can then be approximated, either in terms of $W \text{ cm}^{-2}$ (taking into account the area of the transducer plate) or $W \text{ cm}^{-3}$ (taking into account the volume of the solution).

2.2.6 Applied food science studies

2.2.6 (a) Sonication method

The ultrasound generators used for sonication were the same as the ones used in SL experiments. In a typical experiment, 200 mL of liquid was sonicated for up to 4 hours. A steady stream of cooling water was passed through the water jacket surrounding the cell to keep the solution temperature moderate ($<30 ^\circ\text{C}$) during the sonication period. Small aliquots of the liquid (2–3 mL) were taken out at regular intervals throughout the reaction for analysis.
2.2.6 (b) *OH radical yield measurements

The *OH radical yield was quantitatively measured using a modified version of the colorimetric method described by Alegria et al. [58] *OH radicals produced by the cleavage of water molecules inside the bubble upon cavitation (Reaction 2.1) can recombine to form H$_2$O$_2$ (Reaction 2.2). The H$_2$O$_2$ produced can then oxidise iodide ions (present in the solution as an added reagent), with the aid of an ammonium molybdate catalyst, to form molecular iodine (Reaction 2.3). The molecular iodine then further reacts with a free iodide to form a triiodide ion, I$_3^-$ (Reaction 2.4). The concentration of I$_3^-$ is subsequently determined spectrophotometrically by monitoring its absorbance at 353 nm and applying the Beer–Lambert law with the experimentally determined molar absorptivity of $\varepsilon = 26,400$ M$^{-1}$ cm$^{-1}$ [177]. It follows then that the amount of *OH radicals generated during sonication can be determined from this I$_3^-$ concentration by simple stoichiometric ratio.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \cdot\text{OH} & (2.1) \\
\cdot\text{OH} + \cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2 & (2.2) \\
\text{H}_2\text{O}_2 + 2\Gamma & \rightarrow \text{I}_2 + 2\text{OH}^- & (2.3) \\
\text{I}_2 + \Gamma & \rightarrow \text{I}_3^- & (2.4)
\end{align*}
\]

This was carried out by mixing a freshly prepared iodide reagent (1 mL of solution A (0.4 M KI, 0.05 M NaOH, 1.6 x 10$^{-4}$ M (NH$_4$)$_6$Mo$_7$O$_{24}.4\text{H}_2\text{O}$) and 1 mL of solution B (0.1 M KHC$_8$H$_4$O$_4$)) with 1 mL of the sample solution. The absorbance spectrum was immediately taken spectrophotometrically using a Varian Cary Bio 50 UV–Visible spectrophotometer in a 1–cm quartz cuvette.
Chapter 2: Experimental details

2.2.6 (c) HPLC analyses

For all the food compounds studied, any changes in the concentration were monitored using both the UV–Visible spectrophotometer and a Shimadzu reverse-phase HPLC, with an octadecyl column (Econosphere C18 5µm, 4.6 x 150 mm (Alltech)) and a single wavelength UV–Visible detector. All runs were carried out at ambient temperature. Table 2.4 outlines the HPLC parameters used for each compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mobile phase Composition</th>
<th>Mobile phase flow rate (mL / min)</th>
<th>Detection wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>water – methanol 70 : 30 (v/v)</td>
<td>0.5</td>
<td>270</td>
</tr>
<tr>
<td>Morin</td>
<td>acetonitrile – water – formic acid 50 : 50 : 5 (v/v/v)</td>
<td>1.0</td>
<td>274</td>
</tr>
<tr>
<td>Cyanidin 3–glucoside</td>
<td>acetonitrile – water – formic acid 50 : 50 : 5 (v/v/v)</td>
<td>0.5</td>
<td>323 380 528</td>
</tr>
<tr>
<td>β–carotene</td>
<td>acetonitrile – methanol – THF 50 : 35 : 15 (v/v/v)</td>
<td>1.5</td>
<td>450</td>
</tr>
</tbody>
</table>

2.2.6 (d) Radical-scavenging activity evaluation

Evaluation of the radical-scavenging activity of some of the compounds was achieved by employing the HPLC method described by Yamaguchi et al. [178] An aliquot of the sample (0.200 mL) was added to a mixture of 100 mM Tris–HCl buffer (pH 7.4, 0.800 mL) and 500 µM DPPH in ethanol (1.00 mL). The resulting solution was shaken vigorously and left undisturbed in the dark for 30 min at ambient temperature, after which it was injected into the HPLC. The HPLC analyses were performed using an octyl column (Inertsil C8–3 5µm, 4.6 x 150 mm (GL Sciences Inc.)) at ambient temperature, with
methanol/water (70:30, v/v) mobile phase flowing at 1.0 mL min\(^{-1}\). The DPPH radical was detected by the absorbance at 517 nm (**Figure 2.6**).

![DPPH radical (purple) DPPH – H (yellow)](image)

**Figure 2.6** Scavenging of the DPPH radical by an antioxidant, RH.

The radical-scavenging activity is evaluated by the decrease in area of the DPPH radical peak according to **Equation 2.1**:

\[
\text{Radical – scavenging activity} = \frac{A_w - A_s}{A_w} \times 100 \% \quad (\text{Equation 2.1})
\]

where \(A_w\) and \(A_s\) are the areas of the DPPH peak in the presence of water (i.e., “blank”) and the sample, respectively.

### 2.2.6 (e) Mass spectrometry

A Micromass QUATTRO II electrospray ionisation (ESI) mass spectrometer coupled with the Masslynx Version 4 software was used to analyse phenol and morin samples. Analyses were carried out in negative ESI mode, with 1% ammonia solution added to the samples to assist spraying and increase sensitivity. The injection volume was 20 \(\mu\)L each time and the samples were injected at a temperature of 70 °C. A cone voltage for 30 or 50 V was employed. The mobile phase consisted of water–methanol 50:50 (v/v) for phenol and water–acetonitrile 50:50 (v/v) for morin. Flow rate of solvent was fixed at 0.03 mL min\(^{-1}\) for all samples.
3.1 INTRODUCTION

The presence of surface active solutes in solution can alter the bubble population as well as bubble sizes in a liquid exposed to ultrasound. Both of these factors are important for sonochemical reactions since they affect the interfacial area available for mass transfer, hence dictating the overall sonochemical yield.

The “active” bubble population is mainly governed by the degree of bubble clustering leading to impedance shielding [1,97] and bubble coalescence. It is well-known that the extent of bubble coalescence in solution is very much affected by the presence of surface active solutes [67,69,103,116]. The adsorption of these solutes at the bubble/solution interface generally retards the process of bubble coalescence. In addition, the work of Sostaric and Riesz [60,63] concludes that, unlike the case for “static” bubbles in a liquid, equilibrium adsorption of some surfactants at the surface of bubbles exposed to ultrasound is not achieved.

In this chapter, the extent of bubble coalescence in aqueous solutions containing surface active solutes under different sonication conditions is investigated. The obtained results also illustrate the sheer novelty of employing ultrasound as a method for probing the dynamics of surfactant adsorption at the acoustic bubble/solution interface.
3.2 RESULTS AND DISCUSSION

3.2.1 Bubble coalescence and $\Delta V_T$

Referring back to Figure 1.10 in Chapter 1 (§1.5), when bubbles in a liquid under ultrasonic irradiation coalesce, there are two possible scenarios that can occur. If the resulting bubble is smaller than the resonance size, it will continue to grow via rectified diffusion to reach the resonance size before undergoing violent collapse. On the other hand, if the coalesced bubble is larger than the resonance size, it will be pushed towards the nodes by primary Bjerknes forces, and thus no longer oscillates since the net pressure change is zero at the nodes. Consequently, the influence of the applied ultrasound on the bubble is only to keep it at the nodal region. It is this population of the larger bubbles in the nodes that persists for a relatively long time that is measured by the $\Delta V_T$ values in these experiments. The smaller bubbles below the resonance size dissolve within seconds of turning the applied ultrasound off (see Appendix 3), and therefore do not contribute to the experimentally measured $\Delta V_T$.

The $\Delta V_T$ values discussed in this chapter are considered to be directly related to the amount of bubble coalescence in the liquid [103]. The greater the extent of bubble coalescence, the greater the number of larger bubbles produced and hence the higher the value of $\Delta V_T$ measured. In order to see the effect of added solutes on bubble coalescence, $\Delta V_T$ values in the following sections are normalised with respect to the $\Delta V_T$ for pure water under identical experimental conditions. Therefore, a smaller $\Delta V_T$ value indicates a lower level of bubble coalescence in the liquid.
3.2.2 Bubble coalescence in the presence of surface active solutes

Figures 3.1 and 3.2 show the typical volume changes observed following sonication of aqueous solutions containing a range of alcohols and SDS, respectively. The concentrations are plotted on a log scale to show the features of the data points more clearly. Consistent with the findings from previous studies [67,69,103], it is evident that the extent of bubble coalescence is affected by the presence of the surface active solutes, as indicated by the significant decrease in the $\Delta V_T$. As the concentration of the solutes increases, $\Delta V_T$ decreases until it reaches a minimum and then slightly increases again at higher concentrations. Moreover, for the alcohols, the longer the alkyl chain length of the alcohol, the lower is the concentration required to achieve the same amount of decrease in $\Delta V_T$. All of these behaviours have been previously explained as a consequence of the adsorption of surface active solutes at the surface of cavitation bubbles [103].

![Figure 3.1](image_url)  
**Figure 3.1** Average change in total bubble volume relative to pure water as a function of alcohol concentration in aqueous solutions sonicated at 358 kHz, 0.9 W/cm$^2$.
As discussed in Chapter 1 (§1.4.2), adsorption of surface active solutes at the bubble/solution interface can inhibit coalescence via two different means: steric repulsion (or other short-range repulsive forces), as well as electrostatic repulsion if the surface active solutes are charged. Steric repulsion (or other short-range repulsive forces) only takes effect when the adsorbed solutes are in very close vicinity to each other, whereas electrostatic repulsions can act at both long-range and short-range, depending on the nature of the solutes present. All of these repulsive forces act to keep the bubbles sufficiently far apart such that the liquid film between them does not become thin enough to allow rupture, thus preventing coalescence.

For the alcohols under investigation (Figure 3.1), only the steric effect (or other short-range repulsive effects) is important. As the alcohol concentration is increased, more alcohol molecules adsorb on the bubble/solution interface, thereby increasing the steric hindrance to coalescence and consequently reducing the normalised $\Delta V_T$ value. The slight increase in $\Delta V_T$ at higher alcohol
concentrations has been attributed to the increasing level of dissolved air in the solution [114] rather than an interfacial phenomenon.

On the other hand, for the anionic surfactant SDS, both steric hindrance and electrostatic repulsion forces contribute to the results observed in Figure 3.2. It has been proposed that at higher SDS concentrations, the excess surfactant molecules act as an electrolyte, which reduces the strength of the electrostatic repulsion between interacting surfaces and hence also the inhibition of bubble coalescence [97]. This is probably the reason behind the slight increase in $\Delta V_T$ at higher SDS concentrations because unlike with the alcohols case, the level of dissolved air in the solution remains approximately constant in the range of SDS concentrations investigated [179].

3.2.3 Effect of applied acoustic power and frequency

Applied acoustic power and frequency can have a marked effect on sonoluminescence intensity [98, 116]. It was argued that this arises from their effect on the bubble population, which is largely controlled by the degree of bubble clustering leading to impedance shielding, and bubble coalescence. To further probe this latter aspect, experiments were conducted at various acoustic powers and frequencies, and the results are presented in Figures 3.3–3.5.

Figures 3.3a–3.5a show that absolute $\Delta V_T$ values are greater for the higher applied acoustic powers. This is most probably due to a greater number of bubbles being created at higher power [116]. However, it is clearly shown in Figures 3.3b–3.5b that once these values are normalised to the $\Delta V_T$ for water, they lie on the same curve (within the experimental error of this technique), indicating that there is no significant power dependence on the processes
Chapter 3: Coalescence of acoustic bubbles

Figure 3.3 Average change in total bubble volume as a function of ethanol concentration in aqueous solutions sonicated at various applied acoustic frequencies and powers expressed as: (a) absolute $\Delta V_T$, (b) $\Delta V_T$ relative to that of pure water under the same conditions.

Responsibility for $\Delta V_T$ values. Based on Figure 1.10 ($\S$1.5), it should be possible to qualitatively correlate $\Delta V_T$ to the SL intensity. For SDS solutions in the presence of 0.1 M NaCl, whereas the $\Delta V_T$ data (inset in Figure 3.5b) show no power dependence, the corresponding multibubble sonoluminescence (MBSL) data (Figure 4.3b) suggests some dependence on the applied acoustic power.
It has been speculated in previous MBSL studies \([97,114,116]\) that the adsorption of charged surfactants at the bubble/solution interface leads to the “declustering” of cavitation bubbles, which is responsible for the enhanced MBSL (under the conditions where surfactant decomposition does not play a significant role in quenching the SL intensity). In a recent acoustic emission spectral study \([111]\), it was demonstrated that the presence of SDS in the
Figure 3.5 Average change in total bubble volume as a function of SDS concentration in aqueous 0.1 M NaCl solutions sonicated at various applied acoustic frequencies and powers expressed as: (a) absolute $\Delta V_T$, (b) $\Delta V_T$ relative to that of pure water under the same conditions. (The inset shows the power comparison for 358 kHz, $\bullet$ 0.8 W/cm$^2$ and $\bigcirc$ 1.1 W/cm$^2$. All the data points for the different frequencies in (b) are averages of runs at different powers, with the error bars showing the variation.)

solution not only affects bubble coalescence, but also the structure of the bubble clusters produced. The coalescence results presented here also provide further evidence for the hypothesis that the effect of charged surfactants on
MBSL is primarily related to bubble clustering. It has been observed in a previous MBSL study in the presence of small amounts of SDS ($\sim$ 1–2 mM), that the normalised MBSL signal returns to that of pure water at higher power levels ($1.13 \text{ W/cm}^2 - 1.61 \text{ W/cm}^2$) [116], once the electrostatic repulsion between bubbles is eliminated by the addition of excess electrolyte. However, the normalised bubble coalescence in SDS solutions in the presence of 0.1 M NaCl does not revert back completely to the level observed in pure water, irrespective of the acoustic power used (Figure 3.5b). This observation supports the hypothesis that the changes to bubble clustering, caused by the adsorption of charged surfactants at the bubble/solution interface, is primarily responsible for the SL enhancement reported in the next chapter (Figure 4.1).

The increase in $\Delta V_T$ at higher SDS concentrations (Figure 3.4) is not a consequence of a change in the gas concentration in the liquid, as in the case of the alcohols. Rather, this is due to the excess surfactant molecules acting as an electrolyte, hence reducing the electrostatic repulsions between bubbles to some extent.

In addition to varying the applied acoustic powers, experiments were also conducted at a few different acoustic frequencies using an identical cell design. Minimal frequency dependence was observed for ethanol (Figure 3.3b) and for lower concentrations of SDS ($< 2$ mM) (Figure 3.4b). However, dependence on the applied acoustic frequency is apparent at higher SDS concentrations and SDS in the presence of 0.1 M NaCl (Figures 3.4b – 3.5b). The implications of this will be discussed in more detail in the following sections.
3.2.4 The effect of nonequilibrium adsorption of surface active solutes on cavitation bubbles

The data discussed so far in this chapter also offer valuable information on the dynamics of surfactant adsorption on cavitation bubbles. It has been shown that the addition of an electrolyte may partly counteract the effect of surface active solutes on bubble coalescence [103]. Figure 3.6 shows the change in $\Delta V_T$ when increasing amounts of NaCl were added to ethanol or SDS solutions. The addition of up to 0.4 M NaCl to 100 mM ethanol solution has no significant effect on the $\Delta V_T$. This is expected because ethanol molecules, although polar, have no formal charge. In contrast, for SDS solutions $\Delta V_T$ increases with increasing NaCl concentration until it reaches a plateau value. This increase in $\Delta V_T$ is consistent with the proposition that the addition of salt reduces the strength of the electrostatic repulsion between the charged surfactant head groups on the bubbles, leading to a lessening of coalescence inhibition.

Another noteworthy feature from Figure 3.6 is that the limiting $\Delta V_T$ plateau values reached for the various SDS concentrations investigated are not the same: it is lower for higher SDS concentrations. It should also be noted that for all three cases, these values still fall below that of water (i.e., $\Delta V_T = 1.0$). This confirms that even when the long-range electrostatic repulsion between bubbles is turned off, there is still some residual coalescence inhibition due to steric repulsion and probably also a very short-range electrostatic repulsion†, which occur to a greater extent at a higher SDS concentration.

† For example, the Debye length in solutions with an electrolyte concentration of 0.1 M is calculated to be around 1 nm [46].
Figure 3.6 Average change in total bubble volume relative to pure water for selected solutions as a function of added NaCl concentration. The aqueous solutions were sonicated at 358 kHz, 0.8 W/cm$^2$ (closed symbols) or 1.6 W/cm$^2$ (open symbols). No appreciable variation is observed in the normalised $\Delta V_T$ for the two different power levels. For the SDS solutions, the normalised $\Delta V_T$ increases then reaches a plateau as the concentration of NaCl added increases. (See text for boxed data points)

The strength of the steric repulsion (or other short-range repulsive forces) between bubbles can be expected to depend on the number of surfactant molecules on the surface, which can be directly related to the surface excess of the surfactant. The higher is the surface excess, the greater is the strength of the steric repulsion (or other short-range repulsive forces) between bubbles and hence the greater is the extent of inhibition of bubble coalescence. This statement brings us to an interesting observation. Consider the data points for 2 mM SDS + 0.1 M NaCl and 100 mM ethanol solutions (see boxed points on
Steric repulsion (or other short-range repulsive forces) is the principal factor contributing to coalescence inhibition in these two cases. The equilibrium surface excess ($\Gamma_{eq}$) for 2 mM SDS + 0.1 M NaCl is $2.6 \times 10^{14}$ molecules/cm$^2$ [180], while $\Gamma_{eq}$ for 100 mM ethanol is $0.55 \times 10^{14}$ molecules/cm$^2$ [97]. It is evident that even though $\Gamma_{eq}$ for 100 mM ethanol is only about one-fifth of that for 2 mM SDS + 0.1 M NaCl, it has a lower $\Delta V_T$ which means it inhibits bubble coalescence to a greater extent! This strongly suggests that, within the lifetime of the bubble, there are more ethanol molecules adsorbed at the bubble/solution interface than SDS. In other words, the thermodynamic equilibrium surface excess in the SDS system is not reached. This interpretation supports the work of Sostaric and Reisz [60,63] who came to the same conclusion based on EPR and spin-trapping studies on some sonicated surfactant solutions.

Figure 3.5b indicates that not only is the equilibrium surface excess not reached in systems containing SDS, but just how far the system is from equilibrium very much depends on the applied acoustic frequency. It is apparent that as the applied acoustic frequency is increased, the bubble coalescence is inhibited to a lesser extent. This indicates that a lower number of SDS molecules adsorb at the bubble/solution interface at higher frequencies.

The nonequilibrium surface excess is generally difficult to quantify due to the dynamic nature of the adsorption process. The work by Eastoe and Dalton [48] concluded that surface active solutes need a finite time to equilibrate with the interface. Solutes of low surface-activity (such as short chain molecules) were found to equilibrate extremely rapidly. In contrast, surfactants that have a relatively higher $\Gamma_{eq}$ at a particular bulk concentration, and reduce the surface

---

‡ Those two points were chosen because the long-range electrostatic repulsion does not play a significant role in these cases, hence allowing the steric effect to be compared.
tension more significantly than short alkyl chain alcohols, require longer times to equilibrate with the interface [56].

Previous studies with surface active solutes in sonicated systems [8,97,99,181] found that a quantitative relationship exists between $\Gamma_{eq}$ of a homologous series of alcohols and a number of sonochemical processes (such as the dissolution of MnO$_2$ particles [181] and the reduction of gold chloride [8,99]) and the quenching of sonoluminescence [97]. This strongly suggests that equilibrium adsorption is achieved for these aliphatic alcohols under the sonication conditions used. On the basis of these studies, a method utilising the $\Delta V_T$ data obtained to estimate the nonequilibrium surface excess values for some systems can be proposed.

When the $\Delta V_T$ data for aliphatic alcohol solutions are plotted as a function of the Gibbs surface excess, they all lie on a “master curve”, as shown in Figure 3.7. This curve directly relates the amount of surface active solutes adsorbed on the bubble/solution interface to the extent of coalescence inhibition they impart due to steric repulsion (or other short-range repulsive forces). This direct relationship, however, is not valid in systems where long-range electrostatic repulsions come into play (such as in SDS solutions without the addition of excess electrolyte). Hence, provided steric repulsion (or other short-range repulsive forces) is the dominant factor controlling the extent of coalescence inhibition, one can experimentally obtain the $\Delta V_T$ value for any given system and subsequently use this to estimate the surface excess value from the master curve (Figure 3.7). Consider the 2 mM SDS + 0.1 M NaCl solution, where the electrolyte is present in excess, thereby eliminating any long-range electrostatic interactions. The normalised $\Delta V_T$ value for this system was found to be around 0.36 for 358 kHz (see Figure 3.5b or Figure 3.6). Relating this
value to the master curve in Figure 3.7 gives a nonequilibrium surface excess value of $\sim 0.5 \times 10^{14}$ molecules/cm$^2$ (compared with $2.6 \times 10^{14}$ molecules/cm$^2$, if true equilibrium had been achieved [180]).

![Figure 3.7](image)

**Figure 3.7** Average change in total bubble volume relative to pure water as a function of Gibbs surface excess of aliphatic alcohols in aqueous solutions sonicated at 358 kHz, 0.9 W/cm$^2$.

### 3.2.5 Estimation of acoustic bubble lifetimes

Once the nonequilibrium surface excess value is estimated, it can be used further to gain some insight into the lifetime of acoustic bubbles in the antinodes in a multibubble field. It has been proposed that at relatively high frequencies such as the ones used in this work, bubbles exposed to ultrasonic irradiation undergo a large number of oscillations during their active life span [98]. However, the actual number of oscillations is unknown. Tajima’s work on SDS solutions in the presence of excess NaCl provides data on both surface tension and surface excess as a function of SDS concentration [180]. These two sets of data were combined and the result is shown in Figure 3.8. These data can then be used to convert the dynamic surface tension data for 2 mM SDS +
0.1 M NaCl obtained by Fainerman and Lylyk [182] into the surface excess of SDS as a function of time (Figure 3.9). It follows then that the time required for a given surface excess value to be achieved in a particular system can be estimated from Figure 3.9.

Figure 3.8 Combining literature data on surface tension and surface excess as a function of SDS concentration (adapted from ref. [180]) yields a plot showing the dependence of surface excess on surface tension for SDS solutions in the presence of excess NaCl.

It has to be pointed out here that there are limitations associated with adopting this approach. First, the data in the literature is for unstirred systems, whereas constant stirring exists in our systems due to the acoustic microstreaming brought about by cavitation [1]. This will largely affect the transport rate of
Combining dynamic surface tension data (adapted from ref. [182]) and surface excess data from Figure 3.8 to obtain a plot of surface excess as a function of time for 2 mM SDS in the presence of 0.1 M NaCl. The inset shows the region of very short times, which is assumed to be linear.

Surfactant molecules towards the bubble/solution interface. Previous studies found that SDS adsorption at the air/aqueous solution interface is mainly diffusion controlled at low bulk concentrations, but the governing mechanism is shifted to mixed diffusion-kinetic controlled at higher bulk concentrations [53,183,184]. More specifically, Chang and Franses [183] reported that SDS follows a mixed diffusion-kinetic mechanism at SDS concentrations of 1.7 – 8.1 mM at 25 °C. Since the maximum SDS molecule (monomer) concentration
Chapter 3: Coalescence of acoustic bubbles

is fixed by the cmc, the estimations of the bubble lifetime are based on the data for 2 mM SDS + 0.1 M NaCl. Using this data, the time estimated from Figure 3.9 would be an upper limit to the bubble lifetime. As explained earlier in this discussion, however, not all of the bubbles in the antinodes would be active if bubble clustering takes place. In other words, it is likely that the bubbles in the antinodes, whose maximum lifetimes are estimated here, consist of both active and inactive bubbles. Therefore, even though strictly speaking what is being estimated here is the maximum time a bubble can live in the antinodes, it can be inferred that this time is also the upper limit of the active bubble population.

The limited amount of data points available to construct Figure 3.9 do not cover the range of surface excess values that are of interest here. Nevertheless, it is reasonable to assume linearity of the surface excess as a function of time for very short times between 0–2 ms (see inset). This gives the time required for \(0.5 \times 10^{14}\) molecules/cm\(^2\) of SDS to adsorb at the interface as \(\sim 0.30\) ms, which equates to around 110 oscillations for the applied frequency of 358 kHz. Note that it is assumed that the rate of surfactant adsorption and desorption during the active life span of an oscillating bubble is the same as that of a “static” bubble. This is a reasonable assumption because the rate-determining step of surfactant adsorption at an interface involves molecular transformations (e.g., the reorientation of the surfactant molecules and the dehydration of the hydrophobic tail) rather than bulk diffusion.

In addition, it has been found from sonovoltammetric measurements that in an aqueous solution where vigorous stirring by ultrasound is present, the thickness

---

\(\xi\): The cmc for SDS in the presence of excess NaCl is around 1.62 mM [180].

At lower surfactant concentrations, the lifetime of the bubbles will be shorter due to a lesser number of surfactant molecules adsorbed on the interface protecting the bubbles from coalescing, as reflected in the higher \(\Delta V_T\) values.
of the “stagnant” diffusion layer around an electrode is in the order of 1 µm [185]. Based on the lifetime of bubbles estimated in this study, the mass diffusion length of SDS molecules can be calculated using Fick’s law of mass transfer, \( x = (4Dt)^{1/2} \), where \( D \) is the diffusion coefficient of SDS in water \((\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1} [186])\) and \( t \) is the diffusion time, which in this case is the bubble lifetime. For the estimated bubble lifetime of 0.30 ms at 358 kHz, this diffusion length is also around 1 µm.\(^\#\) Because this value is approximately the same as the “stagnant” diffusion layer, the approach of applying “static” diffusion data to estimate the lifetime of acoustic bubbles outlined here is valid.

Referring back to Figure 3.5b, a similar approach can be followed for all the other frequencies, and the results are summarised in Table 3.1. From the table, it is evident that the maximum lifetime of the bubbles decreases with increasing applied frequency. Furthermore, for the range of frequencies investigated, these lifetimes equate to the bubbles undergoing an upper limit of 50–200 oscillations in their active lifetime.

This result is highly significant, in that it indicates that active bubbles exposed to an acoustic field have a finite lifetime in a multibubble system, which is not necessarily the case for a single bubble [70,104]. It has been previously estimated that bubbles at a frequency of 515 kHz have an upper limit of 5000 oscillations [95]. However, the present method provides a much better estimate of the persistence time of an acoustic bubble in a multibubble field. It also demonstrates the dependence of the bubble lifetime on the applied frequency.

\(^\#\) For the other frequencies investigated in this study, the diffusion length of SDS molecules in water within the estimated bubble lifetimes ranges from \( \sim 1.2 \text{ µm} \) at 213 kHz to \( \sim 0.6 \text{ µm} \) at 1062 kHz.
Table 3.1 Summary of the estimated maximum bubble lifetimes for the various applied frequencies investigated.

<table>
<thead>
<tr>
<th>applied frequency (kHz)</th>
<th>period (µs)</th>
<th>estimated max bubble lifetime (ms)</th>
<th>estimated max number of oscillations</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>4.7</td>
<td>0.35 ± 0.05</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>358</td>
<td>2.8</td>
<td>0.30 ± 0.05</td>
<td>110 ± 20</td>
</tr>
<tr>
<td>647</td>
<td>1.6</td>
<td>0.15 ± 0.05</td>
<td>100 ± 30</td>
</tr>
<tr>
<td>1062</td>
<td>0.9</td>
<td>0.10 ± 0.05</td>
<td>110 ± 50</td>
</tr>
</tbody>
</table>

3.3 CONCLUSIONS

Adsorption of surface active solutes at the bubble/solution interface in liquids under sonication is a dynamic and complex process. It affects the phenomenon of bubble coalescence, which can in turn influence the efficiency of the whole sonochemical process. Within the limitations of the measurement method and the systems studied, bubble coalescence does not seem to depend on the applied acoustic power. Dependence on the applied acoustic frequency, however, is apparent in some systems. The method used also provides important insight into the dynamics of surface active solutes adsorbing at the bubble/solution interface and can be used to estimate the nonequilibrium surface excess values of some surfactants in liquids exposed to ultrasound. An acoustic bubble in a multibubble field has a finite lifetime, as a consequence of bubble–bubble coalescence processes and rectified growth, which is shorter for higher applied acoustic frequency. It is estimated that these bubbles undergo no more than 50–200 oscillations in their lifetime for applied frequencies in the range of 200 kHz to 1 MHz.
APPENDIX 3: Bubble dissolution time

Bubbles below resonance size gradually dissolve once the applied ultrasound is turned off. Assuming the bubbles dissolve as individual stationary bubbles in saturated solutions, the equation derived from the study by Epstein and Plesset [112] below can be used to estimate the dissolution time.

\[
t = \left( \frac{2 (1 + \delta)}{3 \delta} \right) \left( \frac{\rho_g R^2}{2 D C_s} \right)
\]

where

\[
\delta = \frac{2 M \sigma}{R \rho_g R_o}
\]

\( t \) is the bubble dissolution time (s).

\( M \) is the molecular weight of the gas in the bubble (0.029 kg mol\(^{-1}\) for air).

\( \sigma \) is the surface tension of the liquid (72 × 10\(^{-3}\) N m\(^{-1}\) for water).

\( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)).

\( T \) is the temperature of the liquid (294.65 K).

\( \rho_g \) is the density of gas in the bubble (1.29 kg m\(^{-3}\) for air).

\( R_o \) is the initial bubble radius (8 × 10\(^{-6}\) m for 358 kHz).\(^5\)

\( D \) is the diffusion coefficient of the gas (2.42 × 10\(^{-9}\) m\(^2\) s\(^{-1}\) for air).

\( C_s \) is the saturation concentration of dissolved gas in solution (0.023 kg m\(^{-3}\) for air).

Using these values, the maximum dissolution time for bubbles below resonance size at 358 kHz is calculated to be approximately 3.5 seconds. Thus, this population of bubbles do not contribute to the experimentally measured \( \Delta V_T \).

\(^5\) Linear resonance radius is taken as the initial bubble radius in order to obtain the maximum dissolution time.
4.1 INTRODUCTION

It has been shown in Chapter 3 how the presence of surface active solutes in solution affects the cavitation bubble field by altering the bubble–bubble coalescence process. Looking at the extent of bubble coalescence alone, however, only offers insight into interbubble phenomena taking place in the bubble field; it does not reveal anything about processes happening inside the cavitation bubble itself or how interbubble events (such as bubble coalescence) affect the cavitation activity.

SL intensity is determined by both the interbubble interactions and the temperature attained inside cavitation bubbles upon collapse, and thus can give an indication to any intrabubble processes occurring. In fact, SL is often employed as a means of probing cavitation conditions in a system since it is relatively straightforward to carry out experimentally. Many previous studies investigated the effect of varying different parameters on the SL intensity emitted from aqueous solutions [70,76,83,84,95-98,105,109,187-192]. Some of the findings from these studies have been discussed in detail in Chapter 1 (§1.5.3). In this chapter, two of the parameters, namely the acoustic power and frequency, are explored further.

In order to gain a better understanding of the behaviour of the cavitation bubble field in solutions, much of the work undertaken by the UoM research group has
focused on investigating the effect of adding various surface active solutes on the SL intensity generated in aqueous solutions [76,95-97,105,109,190-192]. To this end, however, all of the earlier studies have always been carried out over a small range of acoustic power. The work presented in this chapter attempts to extend the previous studies by examining the significance of varying applied acoustic power on the extent to which the presence of surface active solutes affects bubble behaviour in solution, and consequently the SL emission intensity.

Furthermore, this study also aims to contribute to the current understanding of the effect of acoustic frequency on a multibubble system by investigating the SL from aqueous alcohol solutions. The effect of acoustic frequency is probably one of the hardest parameters to elucidate because it is impossible to change the ultrasonic frequency without inducing changes in other parameters (e.g., cavitation threshold, number of bubbles) as a consequence. This makes it difficult to isolate this factor and to compare results from different experiments. The effect of acoustic frequency on a given process will depend on the reactor geometry. Since part of the results presented in this chapter were obtained from experiments carried out at UoM while the rest were undertaken at AIST, employing a very different reactor geometry, results from the two different setups will be discussed separately.

4.2 RESULTS AND DISCUSSION

4.2.1 Effect of acoustic power on MBSL from aqueous SDS solutions

The SL intensity emitted from aqueous solutions containing various concentrations of the anionic surfactant SDS sonicated at different acoustic powers (358 kHz) is presented in Figure 4.1. In agreement with results from
previous studies [95,97,98], for all applied acoustic powers investigated, the signal is seen to increase up to about 1 mM, after which a further increase in the SDS concentration results in a decrease in the intensity of the SL emission.

![Graph](image)

**Figure 4.1** (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a function of SDS concentration in aqueous solutions sonicated at 358 kHz at various applied acoustic powers. Higher relative SL enhancement is observed at lower powers. (The lines joining the data points are only intended to guide the eyes and are not theoretical fits.)

The various factors giving rise to this behaviour have been explained in detail in Chapter 1 (§1.6.4 (b)). It was concluded that apart from changing the rate of
bubble dissolution, the effect of SDS on SL intensity is mainly related to the electrostatic interactions between the head groups of the adsorbed surfactants leading to an inhibition of both bubble–bubble coalescence and bubble clustering. The decrease in the extent of bubble coalescence due to SDS is evidenced in the photograph presented in Figure 4.2, where the presence of large bubbles seen in pure water is clearly eliminated upon the addition of 1 mM SDS into the solution.

Figure 4.2 Photographs of pure water and 1 mM SDS solution sonicated at 139 kHz (0.1 W/cm$^3$). The presence of large bubbles (produced as a result of bubble coalescence) seen in pure water is eliminated in 1 mM SDS.

Figure 4.1a shows that the absolute SL intensity increases with increasing applied acoustic power. This is most probably due to the greater number of bubbles being created at higher powers. However, when normalised to the SL intensity emitted from pure water under identical experimental conditions, it is clearly seen in Figure 4.1b that the extent of SL enhancement increases as the acoustic power decreases.
In order to explain this power dependence of the SL enhancement, the two main factors that govern MBSL intensity, the “active” bubble population and the cavitation bubble temperature, should be considered. When the applied acoustic power is varied, it can cause a change in one or both of these factors. Two possible reasons for a greater relative enhancement of MBSL intensity upon the addition of SDS at lower powers are: a greater increase in the “active” bubble population, or a greater increase in the bubble temperature, relative to pure water at the same power.

Charged surfactants are known to affect the processes of bubble dissolution [114], growth [115], coalescence [67,69,103,193] and clustering [97,111]. It has been reported that the adsorption of surfactants at the bubble/solution interface decreases the rate of bubble dissolution [113,114], which may increase the number of bubble nuclei available in the solution. However, this cannot explain the power dependence of SL enhancement since the change in the rate of bubble dissolution is a result of a change in the surface tension of the solution [113], and hence has no relation to the ultrasonic parameters.

The rate of rectified diffusion leading to bubble growth is known to increase in the presence of surfactants such as SDS, and this increase is greater at higher acoustic powers [26,115]. However, as explained in §1.6.4 (b), while it affects the SL growth rate, any changes in the rate of rectified diffusion in the presence of surfactants does not alter the steady-state SL intensity.

The coalescence of acoustic bubbles is examined in Chapter 3. Figure 3.4 illustrates the extent of bubble coalescence as the applied acoustic power is varied at 358 kHz. As can be seen from Figure 3.4b, there is no significant power dependence apparent, which strongly suggests that bubble coalescence cannot explain the behaviour seen in Figure 4.1b.
This leaves bubble clustering as the likely process responsible for the effect. It has been suggested that electrostatic interactions between bubbles brought about by the adsorption of charged surfactants at the bubble/solutions interface result in more open (i.e., less dense) bubble clusters [97,111]. The possibility that this decrease in the degree of bubble clustering occurs to a greater extent at lower applied acoustic powers can be rationalised by taking into account that the magnitude of the secondary Bjerknes forces is proportional to the square of the sound pressure [42]. At higher applied acoustic powers, one would expect the secondary Bjerknes forces to be stronger. This would bring the bubbles in a cluster closer together, hence resulting in more compact bubble clusters. The impedance shielding hypothesis [1] argues that if there is a cluster of bubbles, only those bubbles around the perimeter of the cluster will emit SL, as the ones in the centre of the cluster will be shielded from the applied acoustic waves, and therefore will not experience a sufficient local acoustic pressure that is required for SL. This then leads to a decrease in the number of “active” bubbles, hence causing less relative enhancement of the SL emission intensity. The relatively more open bubble clusters structure might also allow a more symmetrical collapse of the “active” bubbles, as suggested by Ashokkumar et al. [111] This can be expected to increase the cavitation bubble temperature and consequently the SL intensity emitted from the individual bubbles.

The addition of 0.1 M NaCl into SDS solutions is known to eliminate the SL enhancement because the electrolyte screens any electrostatic interactions between bubbles [97]. Figure 4.3 shows the SL intensity obtained when the SDS experiments at various applied acoustic powers were repeated in the presence of 0.1 M NaCl. There are two main features that are evident from these results. First, for all powers, the overall SL enhancement (Figure 4.3b) is much less compared to the case of SDS alone (Figure 4.1b). This is due to both
the lower powers, and this enhancement still seems to be power dependent.

Towards that of pure water, once the long-range electrostatic repulsion forces
the extent of bubble coalescence and bubble clustering starting to revert back
(b)
(a) Absolute SL intensity and (b) SL intensity relative to pure water, as a
Absolute SL intensity (mV)
Absolute SL intensity (mV)
Absolute SL intensity (mV)
Absolute SL intensity (mV)
Absolute SL intensity (mV)
Relative SL intensity
Relative SL intensity
Relative SL intensity
Relative SL intensity
Relative SL intensity
[SDS] (mM)
[SDS] (mM)
[SDS] (mM)
[SDS] (mM)
[SDS] (mM)

Figure 4.3 (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a
function of SDS concentration in aqueous solutions sonicated at 358 kHz at various applied
acoustic powers in the presence of 0.1 M NaCl. Relative SL enhancement is significantly
lower than in the absence of background electrolyte (Figure 4.1). Power dependence of
the extent of SL enhancement is still apparent. (The lines joining the data points are only
intended to guide the eyes and are not theoretical fits.)

the extent of bubble coalescence and bubble clustering starting to revert back
towards that of pure water, once the long-range electrostatic repulsion forces
are turned off. Secondly, there is still some residual enhancement observed at
the lower powers, and this enhancement still seems to be power dependent.
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The inset in Figure 3.5b (Chapter 3) shows the lack of power dependence in the extent of bubble coalescence at this frequency. Hence, it can be inferred that any steric hindrances or other short-range repulsive forces due to the adsorption of SDS molecules on cavitation bubbles, that are still present even after the addition of salt, must lead to a modification of the structure of bubble clusters. The photograph in Figure 4.4 supports this notion, where more dense bubble clusters are clearly observed in the presence of the electrolyte. Furthermore, similar to the case of SDS alone, the magnitude of secondary Bjerknes forces dictates the extent of which this phenomenon is occurring.

**Figure 4.4** High magnification photographs of the bubble field in aqueous solutions of 1 mM SDS and 1 mM SDS + 0.1 M NaCl, sonicated at 139 kHz (0.1 W/cm$^3$). More dense bubble clusters are observed in the solution containing the excess electrolyte.

To further confirm that the effect of electrolyte addition to the system is primarily electrostatics based, experiments were conducted with a zwitterionic surfactant, Zwittergent® 3–12. The surface activity of this surfactant is comparable to SDS, however adsorption to the bubble/solution interface will lead to no net charge on the bubble. Therefore, the behaviour of the SL
emission from this solution is expected to be similar to that of SDS in the presence of excess electrolyte. The results presented in Figure 4.5 show that this is indeed the case, where the relative SL enhancement shown in Figure 4.5b closely resembles that in Figure 4.3b.

Figure 4.5 (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a function of Zwittergent® 3–12 concentration in aqueous solutions sonicated at 358 kHz at various applied acoustic powers. Since there is no net charge on the bubbles upon the adsorption of the zwitterionic surfactant molecules, addition of electrolyte does not affect SL intensity. Higher relative SL enhancement is observed at the lower applied power.
4.2.2 Effect of acoustic power on MBSL from aqueous aliphatic alcohol solutions

The presence of volatile solutes, such as aliphatic alcohols, has been found to quench MBSL intensity in aqueous solutions [97,105,109]. The results presented in Figure 4.6 for ethanol are consistent with this. An interesting observation from Figure 4.6b, which has not been reported in the previous studies, is the effect of applied acoustic power on the extent of SL quenching. As the applied power increases, the extent of SL quenching also increases. This behaviour is also observed with longer chain alcohols, as shown in Figure 4.7 for \(n\)-propanol and Figure 4.8 for \(n\)-butanol.

For all three alcohols, it is noteworthy that at the lower powers used, some enhancement of the SL intensity is observed. Figure 4.9, in which the relative SL intensity as a function of alcohol concentration is shown for all three alcohols at 0.8 W/cm\(^2\) applied power, shows this more clearly. A greater relative enhancement is observed with ethanol compared to \(n\)-propanol, although a higher concentration of ethanol is needed to achieve this effect. Similarly for \(n\)-butanol, its relative enhancement is lower than the other two alcohols, but this enhancement occurs at a significantly lower \(n\)-butanol concentration. Furthermore, comparing the data in Figures 4.6–4.8, for a given alcohol concentration, more quenching is observed the longer the alkyl chain of the alcohol. This is in agreement with previous work of Ashokkumar et al. [97]

To explain the power dependence of the SL quenching seen in Figures 4.6–4.8, following a similar approach of reasoning as in the SDS case (§4.2.1), a greater relative quenching of MBSL upon the addition of alcohols at higher acoustic powers can be achieved by having a greater decrease in the “active”
bubble population or a greater decrease in the bubble temperature, relative to pure water at the same power.

**Figure 4.6** (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a function of ethanol concentration in aqueous solutions sonicated at 358 kHz at various applied acoustic powers. Greater relative SL quenching is observed at higher powers, while some SL enhancement is apparent at lower powers. (The lines joining the data points are only intended to guide the eyes and are not theoretical fits.)
Figure 4.7  (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a function of $n$-propanol concentration in aqueous solutions sonicated at 358 kHz at various applied acoustic powers. Greater relative SL quenching is observed at higher powers, while some SL enhancement is apparent at lower powers. The insets show enlargements of the results at low concentrations. (The lines joining the data points are only intended to guide the eyes and are not theoretical fits.)
Figure 4.8  (a) Absolute SL intensity and (b) SL intensity relative to pure water, as a function of n-butanol concentration in aqueous solutions sonicated at 358 kHz at various applied acoustic powers. Greater relative SL quenching is observed at higher powers, while some SL enhancement is apparent at lower powers. The insets show enlargements of the results at low concentrations. (The lines joining the data points are only intended to guide the eyes and are not theoretical fits.)
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Figure 4.9 SL intensity relative to pure water as a function of alcohol concentration in aqueous solutions sonicated at 358 kHz (0.8 W/cm$^2$). An initial SL enhancement is observed for all three alcohols, followed by a subsequent SL quenching. (The lines joining the data points are only intended to guide the eyes and are not theoretical fits.)

The quenching by alcohols is mainly due to the evaporation of these volatile solutes from the bubble/solution interface during bubble expansion, followed by endothermic chemical reactions within the bubble on bubble collapse [97,104,109,190,192]. At 358 kHz the bubbles are considered to be “stable”, i.e., they live long enough (estimated to be in the order of a hundred oscillations [193]) to allow the hydrocarbon products produced by these thermally initiated decomposition reactions to accumulate within the bubble over a number of acoustic cycles. The presence of these products and their thermal decomposition results in a lowering of the bubble temperature, leading to a lower SL intensity. A decrease in the “active” bubble population is unlikely to have a significant contribution to the observed SL quenching, as detailed in §1.6.4 (a).

To see if varying the applied acoustic power affects the extent of decrease in bubble temperature, the amount of hydrocarbon products produced at different
acoustic powers was measured. **Table 4.1** shows that the amount of hydrocarbon products produced is greater at higher applied acoustic powers. It can be proposed that, at higher powers, as bubbles can be expanded to a relatively larger size during their expansion cycle, more volatile material would evaporate into the bubble before collapse. This, combined with the greater volume change of the bubble upon collapse, would result in more hydrocarbon products being produced and therefore a greater level of accumulation of these products inside the bubble. The overall increase in complex gaseous chemical products inside the bubble would lead to a lowering of the bubble temperature and hence a decrease in the SL emission intensity (**Figure 4.10**). This proposition is in agreement with previous results on single bubble SL [194], where the maximum radius of the bubble ($R_{\text{max}}$) was found to vary proportionally with the magnitude of the driving pressure (i.e., $R_{\text{max}}$ increases when the driving acoustic pressure is increased).

**Table 4.1** Amount of hydrocarbon products produced upon the sonication of 100 mM ethanol solutions at 358 kHz for 30 minutes$^a$.

<table>
<thead>
<tr>
<th>applied acoustic power ($W/cm^2$)</th>
<th>ethylene concentration (mM)</th>
<th>acetylene concentration (mM)</th>
<th>ethane concentration (mM)</th>
<th>$T_{\text{max}}^b$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.58</td>
<td>1.23</td>
<td>0.06</td>
<td>5500</td>
</tr>
<tr>
<td>1.1</td>
<td>1.54</td>
<td>2.49</td>
<td>0.20</td>
<td>4900</td>
</tr>
<tr>
<td>1.6</td>
<td>3.91</td>
<td>2.76</td>
<td>0.78</td>
<td>3800</td>
</tr>
</tbody>
</table>

$^a$ The amount produced at 0.8 W/cm$^2$ was too low to allow $T_{\text{max}}$ determination, and hence was not included in the table.

$^b$ $T_{\text{max}}$ was calculated according to the method used in previous studies [107,149,195].
Figure 4.10 Diagrammatic representation of a bubble being expanded to a relatively larger size during the expansion cycle at higher applied acoustic powers. This leads to a greater level of hydrocarbon product (P) accumulation inside the bubble, lowering the bubble temperature, and hence quenching the SL intensity to a greater extent.

To further investigate the nature of SL quenching by alcohols, uncalibrated SL spectra from pure water and 100 mM ethanol solutions were measured and compared. Figure 4.11 shows that upon normalisation, it appears that the SL quenching is uniform throughout the wavelength range investigated (i.e., no preferential quenching over certain wavelength ranges). The continuum in MBSL spectra mainly arises due to emission from excited state species as well as from processes associated with the plasma that may form inside the bubble [196]. The extent to which all of these processes take place depends on the cavitation bubble temperature. Hence, when this cavitation bubble temperature decreases, it can be expected that the continuum in the SL spectrum will decrease uniformly, which is in agreement with the results in Figure 4.11.
Inhibition of bubble coalescence leads to an increase in the number of bubble nuclei in the solution, and hence the number of “active” bubbles that would be expected to lead to a relative enhancement of SL intensity. Considering the observation that alcohols inhibit bubble coalescence in solution, both SL

**Figure 4.11** Uncalibrated SL spectra of pure water and 100 mM ethanol solution sonicated at 358 kHz at two different applied acoustic powers. Upon normalisation, there is little, if any, difference between the spectra of the two solutions, indicating that SL emission is quenched uniformly over the wavelength range in the presence of the alcohol in solution.
quenching (due to material evaporation) and SL enhancement (due to inhibition of bubble coalescence) can take place upon the addition of alcohols to aqueous solutions. The overall outcome with respect to the effect on the SL intensity is determined by the relative importance of these two processes. At low applied acoustic powers, it is possible that the SL enhancement dominates over the SL quenching, which accounts for the results presented in Figure 4.9. Furthermore, examining the data presented in Figures 4.6–4.8, this balance between SL quenching and enhancement in alcohol solutions is also observed at higher powers, albeit less markedly. As suggested earlier, the extent of SL quenching increases as the power is increased, thus at higher powers this enhancement is not as prominent as at low powers. It should also be noted that the alcohol concentrations at which the inhibition of bubble coalescence starts to be significant, usually termed the transition concentration, differ slightly from the values obtained by previous studies [67,69]. A possible reason for the apparent discrepancy is that the previous studies were undertaken under steady-state equilibrium conditions, whereas the bubble oscillations and clustering in our case can be expected to give rise to somewhat different interaction conditions, thereby leading to different transition concentrations for the alcohols. The concentrations observed in this work agree very well with those obtained in the more recent acoustic study of Lee et al. [103] (Table 4.2).

It is worthwhile to compare the data presented in Figure 4.9 with that of Price et al. [96] They have shown that at 20 kHz, where SL quenching is negligible due to the transient nature of the cavitation bubbles at this frequency, longer alkyl chain alcohols show marked enhancement in SL intensity compared to their shorter chain counterparts. In the present work, however, SL enhancement is more pronounced for shorter chain alcohols. This is because at the frequency used in this work (358 kHz), SL quenching is an important competing process to the SL enhancement (due to the cavitation being “stable”),
and that longer chain alcohols will cause more quenching. As a result, the combined effect of these two competing processes leads to an overall weaker enhancement for longer chain alcohols.

Previous reports [96,97] have also shown that the amount of material that evaporates into a bubble, hence the extent of SL quenching by alcohols, depends on the amount of alcohol adsorbed at the bubble/solution interface and not the type or bulk concentration of the alcohol in solution. Using the method outlined by Ashokkumar et al. [97], the relative SL intensity is plotted against the air/water Gibbs surface excess for all the alcohols at the different acoustic powers used, as shown in Figure 4.12. As expected, at higher acoustic powers (Figure 4.12c and 4.12d) there is a good correlation between the relative SL intensity and the Gibbs surface excess, since under these conditions SL quenching is the dominant process. However, at lower powers (Figure 4.12a and 4.12b), a poor correlation is observed. This can be ascribed to the significant contribution of the inhibition of bubble coalescence by the interfacially adsorbed alcohol molecules on the overall SL emission intensity.

Table 4.2 Comparison between transition concentrations of aliphatic alcohols observed in this work and those obtained in previous studies.

<table>
<thead>
<tr>
<th>solute</th>
<th>transition concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work\textsuperscript{a}</td>
</tr>
<tr>
<td>ethanol</td>
<td>0.040</td>
</tr>
<tr>
<td>n-propanol</td>
<td>0.015</td>
</tr>
<tr>
<td>n-butanol</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The transition concentration value denotes the concentration at which the relative SL intensity starts to increase after the initial decrease (see Figure 4.9).

\textsuperscript{b} Ref. [103]

\textsuperscript{c} Ref. [67]
4.2.3 Effect of acoustic frequency on MBSL from aqueous aliphatic alcohol solutions

4.2.3 (a) UoM setup

SL intensity, relative to pure water, emitted from aqueous solutions containing various concentrations of ethanol or \( n \)-butanol sonicated at two different frequencies is shown in Figure 4.13. It is evident from Figure 4.13a that for ethanol solutions, there is less SL quenching occurring at 358 kHz than at 1062 kHz. As SL quenching in the presence of alcohols is proposed to be primarily a results of the accumulation of hydrocarbon products inside the
bubble over many acoustic cycles (§1.6.4 (a)), the yield of these hydrocarbon products generated at both frequencies were measured and tabulated in Table 4.3.

![Graph](image)

**Figure 4.13** (a) SL intensity, relative to pure water, as a function of alcohol concentration in aqueous solutions sonicated at two different frequencies at 0.8 W/cm². Less SL quenching observed at 358 kHz for ethanol. (b) Enlargement of the results for n-butanol at low concentrations. SL intensity from 5 mM n-butanol solution is slightly less quenched at 358 kHz due to the contribution of SL enhancement via coalescence inhibition.
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Table 4.3 Yield of hydrocarbon products generated upon the sonication of 100 mM ethanol solutions at the different frequencies for 30 minutes, as measured by gas chromatography (details in §2.2.1 (e)).

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Concentration (mM)</th>
<th>Concentration (mM)</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ethane</td>
<td>ethylene</td>
<td>acetylene</td>
</tr>
<tr>
<td>358</td>
<td>0.03</td>
<td>0.23</td>
<td>0.49</td>
</tr>
<tr>
<td>1062</td>
<td>– (^a)</td>
<td>– (^a)</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(^a\) Concentration was too low to be detected.

The observation that more hydrocarbon products were generated at 358 kHz compared to 1062 kHz intuitively leads us to expect more SL quenching at the lower frequency. However, this is clearly not the case, as seen in Figure 4.13a. The rationale for this comes back to the balance between SL quenching due to products accumulation and SL enhancement due to inhibition of coalescence discussed in Section 4.2.2. Inhibition of coalescence is caused by the adsorption of surface active solutes on the bubble/solution interface (§1.4.2). As concluded in Chapter 3, this adsorption process is a dynamic one and the extent to which it occurs in a cavitating system depends on the acoustic frequency since it is limited by how long the bubble exists in solution. Since the bubble lifetime increases as acoustic frequency decreases [193], it is possible that alcohol adsorption on the interface and hence coalescence inhibition occurs to a greater extent at 358 kHz.\(^\ddagger\) This brings about some SL enhancement that partly counteracts the SL quenching, which results in an overall lessening of the degree of SL quenching at 358 kHz than what would otherwise be expected based on the accumulation of hydrocarbon products alone.

\(^\ddagger\) The assumption made in Chapter 3 (to construct Figure 3.7) is that equilibrium adsorption is achieved for short-chain alcohols under sonication at 20, 358 or 515 kHz. However, this may not be the case for the considerably higher frequency of 1062 kHz.
The results with \( n \)-butanol (Figure 4.13) further support this reasoning. Under identical conditions, the presence of \( n \)-butanol in solution gives rise to more SL quenching compared to ethanol because of the longer alkyl chain length [97]. Hence, it is expected that the difference in SL quenching behaviour between the two frequencies to be less significant when \( n \)-butanol is present instead of ethanol, since the quenching factor will be more dominant over the enhancement. This is indeed the case, as illustrated in Figure 4.13. In Figure 4.13b, where the data points at low \( n \)-butanol concentrations are shown more clearly, the SL intensity from 5 mM \( n \)-butanol solution sonicated at 358 kHz is slightly less quenched. This feature highlights the SL enhancement due to inhibition of coalescence, and has been discussed in §4.2.2.

When the applied acoustic power is increased, the extent of SL quenching increases while any SL enhancement is minimised (§4.2.2). Figure 4.14 shows the results obtained when the experiments describing Figure 4.13 were repeated at a higher acoustic power. As expected, the difference in the SL quenching between 358 kHz and 1062 kHz in ethanol is less significant at this higher acoustic power, while in \( n \)-butanol there is practically no difference between the two frequencies.

4.2.3 (b) AIST setup

The experimental setup employed at AIST allows the applied acoustic amplitude to be increased gradually while the emitted SL intensity is continuously monitored. Figure 4.15 shows the MBSL intensity emitted from pure water sonicated at different frequencies. There are two features to be noted from these results. First, as the acoustic frequency increases, higher acoustic amplitudes are required before SL emission can be detected. This is a result of an increase in the cavitation threshold with increasing acoustic frequency [2]. Secondly, and more interestingly, for all three frequencies investigated, the SL
Figure 4.14  (a) SL intensity, relative to pure water, as a function of alcohol concentration in aqueous solutions sonicated at two different frequencies at 1.1 W/cm². The difference in the SL quenching for ethanol between the two frequencies is less significant at this higher acoustic power. (b) Enlargement of the results for n-butanol at low concentrations. The extent of SL quenching is practically identical in both frequencies.

intensity increases with acoustic amplitude until it reaches a maximum value before it starts to decrease. This behaviour of SL suppression at high amplitudes has been observed previously by Hatanaka et al. [91,92] under similar
experimental conditions. They explained that it arises from a change in the bubble structures brought about at higher acoustic amplitudes. Bubble structures in the form of dendritic branches of filaments change into clusters by virtue of the secondary Bjerknes forces. These clusters are then expelled from the pressure antinodes, hence the overall SL emission is suppressed.

![Graph showing SL intensity as a function of applied acoustic amplitude in water sonicated at different frequencies. SL increases with acoustic amplitude until it reaches a maximum value before starting to decrease.](image)

**Figure 4.15** SL intensity as a function of applied acoustic amplitude in water sonicated at different frequencies. SL increases with acoustic amplitude until it reaches a maximum value before starting to decrease.

What has not been observed previously is the dependence of this SL suppression behaviour, due to high applied acoustic amplitudes, on the acoustic frequency. The decrease in the SL intensity after the maximum value occurs at lower amplitudes for lower frequencies (**Figure 4.15**). For example, at 139 kHz, the SL signal does not start to decrease until close to 500 mV$_{p-p}$ is applied, whereas it starts diminishing at around 150 mV$_{p-p}$ and 100 mV$_{p-p}$ for 71.4 kHz and 38 kHz, respectively. A plausible explanation for this stems from the fact that the bubbles are larger at lower frequencies. Since the magnitude of the radiation forces are proportional to the bubble volume (§1.2.2 (d)), it is expected that
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the secondary Bjerknes forces are stronger at lower frequencies, thus causing bubble clustering to occur at lower applied amplitudes.

The addition of aliphatic alcohols inhibits bubble coalescence [103,193], and hence is expected to lead to a smaller bubble size distribution. The effect of adding 200 mM \( n \)-propanol on SL intensity at 71.4 kHz is depicted in Figure 4.16. The overall SL intensity is reduced in the presence of the alcohol. Moreover, the maximum SL intensity is reached at a slightly higher applied acoustic amplitude compared to water. In a way, the effect of the smaller bubble size in the alcohol solution at this frequency on the observed SL behaviour is not dissimilar to what takes place in water in the 139 or 38 kHz case discussed earlier. Hence, similar reasoning regarding the dependence of the secondary Bjerknes force on the bubble size applies here as well.

Figure 4.16 SL intensity as a function of applied acoustic amplitude in water and 200 mM \( n \)-propanol sonicated at 71.4 kHz. SL is quenched in the presence of the alcohol, and maximum SL is reached at a slightly higher acoustic amplitude compared to water. The full width at half-maximum (FWHM) of the two plots does not differ significantly.
4.2.4 MBSL from aqueous glycols and glycerol solutions

From the previous sections, we have seen that evaporation of interfacial solute molecules into the bubble and the subsequent accumulation of hydrocarbon products generated upon the pyrolysis of these solutes are responsible for the observed SL quenching in aqueous solutions containing aliphatic alcohols. This is also supported by the observation that this phenomenon is not detected at a lower applied frequency of 20 kHz, where a majority of the cavitation occurring are transient in nature (i.e., bubbles only exist for a few cycles before they collapse violently), hence not allowing accumulation to take place.

Price et al.’s study [96] on MBSL from aqueous solutions containing simple ketones and alkyl acetates sonicated at 20 kHz, however, found that unlike the aliphatic alcohols, MBSL quenching does occur, albeit to a lesser extent, even at this low ultrasonic frequency. Upon examining the differences in the structures of the solutes, they proposed that the extent of hydrogen bonding existing between the solute molecules and the surrounding water molecules play an important role in determining whether a particular solute will quench MBSL. While the work of Price et al. was carried out at 20 kHz, the importance of the intermolecular forces between solvent and solute molecules has not been investigated at high frequencies, where the type of cavitation is significantly different to that observed at 20 kHz. Therefore, the investigation discussed in the previous section was extended by exploring the MBSL behaviour at 358 kHz, where “stable” cavitation dominates, in aqueous solutions containing solutes of varying hydrogen bonding characteristics.

Previous results for aliphatic alcohols ($< C_4$) at 358 kHz showed some SL quenching for concentrations up to 200 mM (Figures 4.6–4.8). In general, the extent of this SL quenching increases with an increase in the alkyl chain length at
Figure 4.17 SL intensity relative to pure water as a function of solute concentration in aqueous solutions sonicated at 358 kHz (1.1 W/cm^2). For clarity, the solutes are grouped according to the number of carbon atoms in the molecule, n, with: (a) n = 2, (b) n = 3, (c) n = 4.
a particular alcohol concentration, and also with increasing applied acoustic power. Figure 4.17 shows the normalised SL intensity emitted from aqueous solutions of the various diols and triol, corresponding to the aliphatic alcohols investigated previously, sonicated at 358 kHz (1.1 W/cm$^2$). All the SL intensity data presented has been normalised to that of pure water under the same conditions. The data has been plotted on a log scale in order to show the results at lower concentrations more clearly. The results obtained for alcohols as shown in Figures 4.6–4.8 are also included in grey (and dotted lines) for comparison.

There are two main features that can be clearly seen from these figures. First, SL enhancement is observed for some concentrations of the solutes, particularly with glycerol (Figure 4.17b) and 1,4–butanediol (Figure 4.17c). Secondly, for the range of concentrations investigated, the extent of SL quenching for the diols/triol is much less than their alcohol counterparts.

To elucidate the enhancement part further, the normalised SL intensity of aqueous solutions of glycerol and 1,4–butanediol sonicated at 358 kHz at two different acoustic powers is presented in Figure 4.18. SL enhancement is more pronounced at the lower applied acoustic power. As explained in the last section, the net effect of surface active solutes on MBSL intensity from aqueous solutions is a balance between quenching and enhancement. The latter has been attributed to the inhibition of bubble–bubble coalescence by the adsorption of solute molecules on the bubble/solution interface. This inhibition to coalescence has been shown to be more pronounced at lower acoustic powers because of the weaker secondary Bjerknes forces under such conditions [116], leading to a greater SL enhancement.

Diols are known to be less surface active than aliphatic alcohols [197-206]. This is illustrated in Figure 4.19, where in general, the aliphatic alcohols reduce surface tension to a greater extent. For example, the presence of 1 M ethanol
Figure 4.18 SL intensity relative to pure water as a function of (a) glycerol and (b) 1,4-butanediol concentration in aqueous solutions sonicated at 358 kHz (0.8 or 1.1 W/cm$^2$). SL enhancement is observed at some concentrations, and is more pronounced at the lower applied acoustic power.

reduces the surface tension of the solution to 57 mN/m, while a solution containing the same concentration of ethylene glycol has a higher surface tension of 70 mN/m. Recall that previous study [98] has concluded while the vapour pressure of the solutes controls the extent of SL quenching in transient cavitation generally found at lower frequencies (e.g., 20 kHz), this is not the case for higher frequencies. Rather, Ashokkumar et al. [97] proposed that for the stable cavitation at 515 kHz, the extent of SL quenching by aliphatic alcohols is governed by the amount of solute molecules adsorbed at the bubble/solution interface, which can then evaporate inside the bubble during expansion. They went on to show that SL intensity correlates well with the Gibbs surface excess.
Figure 4.19 Surface tension of solutes as a function of concentration (≈25 °C). In general, the alcohols reduce surface tension to a greater extent compared to their corresponding diols/triol, implying their higher surface activity. (The data points presented here are a combination of results obtained in this work and those found in refs. [46,198-206].)

Furthermore, for ethanol, n-propanol and n-butanol, all the data points lie on the same curve (within experimental error). This implies that regardless of the nature of the solutes (i.e., in this case, the alkyl chain length), so long as the surface excess is the same, the extent of SL quenching is the same. However, this is not necessarily the case for diols. Figure 4.20 compares the data for ethanol and ethylene glycol. The Gibbs surface excess is defined by Equation 1.5 in §1.3.2.

Combining the surface tension data in Figure 4.19 with this equation yields the surface excess as a function of concentration of the solute (Figure 4.20a). Ethylene glycol is less surface active than ethanol, hence it is expected that a higher bulk concentration of the former is needed to achieve a particular surface
Chapter 4: Effect of acoustic power and frequency on MBSL

excess value. As an example, Figure 4.20a shows that 0.46 M ethanol and 3.3 M ethylene glycol aqueous solutions both correspond to a surface excess value of approximately $1.6 \times 10^{14}$ molecules/cm$^2$. In spite of this, Figure 4.20b clearly illustrates that even though at these concentrations the same number of solute molecules partition on the bubble/solution interface, unlike in the case of aliphatic alcohols, the extent of SL quenching between the two is vastly different. In the ethylene glycol solution, only 10% of the SL intensity is quenched compared to the intensity in water. On the other hand, SL intensity is quenched by as much as 75% in the ethanol solution. This strongly indicates that compared to the aliphatic alcohols case, there is something else in play that affects the SL quenching mechanism.

Comparing the aliphatic alcohols and the diols investigated in this study (Table 3.1), there are two main differences that come to mind. First, in general, the viscosities of the neat diols (or triol) are much higher than the neat alcohols. However, having said this, the viscosities of the aqueous solutions in the concentration range investigated are essentially the same. The viscosity of 0.46 M ethanol solution [207] is close to 1.0 cP, whereas that of 3.3 M ethylene glycol [208] is around 1.5 cP. This difference in viscosity alone is unlikely to be the factor causing the considerable difference in the extent of SL quenching in the two solutions, as shown in Figure 4.20b. Moreover, an increase in the solution viscosity generally increases the cavitation threshold, which lowers the severity of bubble collapse when the same amount of acoustic power is applied. This will give rise to less SL emission. The fact that more SL emission was observed from the more viscous solution (i.e., 3.3 M ethylene glycol, Figure 4.20b) contradicts this, thus confirming that the difference in viscosity is not responsible for the contrast in SL quenching behaviour in this case.
Figure 4.20 (a) Surface excess of ethanol and ethylene glycol as a function of concentration; (b) SL intensity relative to pure water as a function of concentration of ethanol and ethylene glycol in aqueous solutions sonicated at 358 kHz (1.1 W/cm²). For a given surface excess value, SL is quenched to a lesser extent for ethylene glycol.

A more plausible explanation lies in the structural difference of the solutes, namely the presence of extra –OH group(s) in the diols and triol. McFeely and Somorjai [209] studied the vaporisation kinetics of hydrogen-bonded liquids and deduced that the breaking of the hydrogen bonds is the rate-limiting step in the mechanism of vaporisation of these liquids. The more hydrogen bonds that have to be broken in order for a molecule to evaporate into the gas phase, the longer
it will take to do so. The conclusion reached by Taylor and Garrett [210] from their molecular dynamics simulations also supports this. They found that the free energy of adsorption on the liquid/vapour interface of water is more negative for ethylene glycol than for ethanol. In other words, compared to ethanol, ethylene glycol molecules are more likely to be at the interface rather than in the gas phase. This is in line with the conclusion of McFeely and Somorjai, despite the fact that Taylor and Garrett studied the transport of molecules from the vapour phase into bulk water, which is essentially the opposite process of vaporisation. Therefore, relating this back to our results, in order to evaporate inside the bubble and consequently quench MBSL, the solute molecule must be able to overcome any hydrogen bonds (as well as dispersion forces) within the expansion cycle during bubble oscillation (at 358 kHz, this is approximately 1.4 µs). As such, it is reasonable to expect that it is easier for the alcohols, which only have one hydrogen bond to overcome, to evaporate from the aqueous solution into the bubble compared to the diols or triol with their multiple hydrogen bonds, and hence quench MBSL to a greater extent.

This result perfectly complements that of Price et al. [96], where the ketones and alkyl acetates are able to quench MBSL under the conditions where the alcohols are not, due to the lack of hydrogen bonds in the former. In addition, as a result of this additional factor controlling the extent of SL quenching, unlike the case of alcohols, when the SL intensity data is plotted against the Gibbs surface excess of the diols/triol, no clear correlation is observed (Figure 4.21). Further inspection of Figure 4.21 also supports the data shown in Figure 4.18, where any SL enhancement due to inhibition of coalescence dominates at the lower solute concentrations. As the concentration is increased, SL quenching becomes the main factor governing the overall SL intensity.
Figure 4.21  SL intensity relative to pure water as a function of Gibbs surface excess of solutes. No clear correlation is observed due to the additional factor of hydrogen bonding controlling the extent of SL quenching.

4.3 CONCLUSIONS

The presence of surface active solutes in aqueous solutions affects the MBSL intensity. The extent of these effects is strongly dependent on the applied acoustic power. With the anionic surfactant SDS, the greater relative MBSL enhancement observed at lower powers is argued to be due to the formation of relatively more open (i.e., less dense) bubble clusters, leading to a greater number of “active” bubbles by virtue of less impedance shielding. A higher cavitation bubble temperature due to a more symmetrical bubble collapse is also possible. The results observed in the presence of excess electrolyte in the SDS solutions suggest that the SDS effect is primarily related to the electrostatic interactions between bubbles.
With aliphatic alcohols as solutes, the greater relative MBSL quenching at higher powers is proposed to be due to the possibility of expanding the bubble to a relatively larger size during the expansion cycle throughout bubble oscillation. This allows more material to evaporate into the bubble core, and subsequently results in more hydrocarbon products accumulation inside the bubble over many acoustic cycles. This, in turn, leads to a lowering of bubble temperature, and hence a greater level of MBSL quenching. At lower powers, however, some enhancement of the MBSL emission intensity is observed as a result of the inhibition of bubble–bubble coalescence.

The effect of aliphatic alcohols on MBSL intensity does not depend solely on the applied acoustic power, but also on the acoustic frequency. The extent of SL quenching varies at different frequencies due to a difference in the dynamics of surfactant adsorption at the bubble/solution interface, as discussed in Chapter 3. Applied acoustic frequency was also found to affect the threshold of SL emission, as well as the bubble clustering due to secondary Bjerknes forces.

When diols/triol are present in the solution instead of aliphatic alcohols, MBSL quenching occurs to a much lesser extent compared to their alcohol counterparts. This is most probably due to the dependence of the vaporisation rate of the solutes, which governs SL quenching, on the breaking of hydrogen bonds present.
5.1 INTRODUCTION

As mentioned briefly in Chapter 4 (§4.2.2), MBSL spectra usually consist of a broad continuum encompassing the UV-Visible range. When metal ions are present in the solution being irradiated, emission lines from the excited-state metal atoms are observed in addition to the broad continuum – as reported by a number of researchers working with alkali metal salt solutions [61,75,117-123]. However, while this is a widely observed phenomenon, the mechanism for the formation of the excited metal atoms and the site where these emission lines originate from are still under conjecture. Several hypotheses regarding these issues have been proposed and have been discussed in detail in Chapter 1 (§1.7).

This chapter aims to provide further insight into the origin of alkali metal atom spectral line emissions, in particular from aqueous solutions containing Na\(^+\) ions. Evidence is presented that indicates Na\(^+\) emission is related to “chemically active” acoustic cavitation bubbles, but not necessarily from bubbles that also produce SL.
5.2 RESULTS AND DISCUSSION

5.2.1 Emission from aqueous solutions containing NaCl

Photographs of the SL and SCL from argon saturated water and its corresponding MBSL spectrum are shown in Figure 5.1. A faint blue SL emission can be seen predominantly in the centre of the cell (Figure 5.1a) towards the surface of the liquid. The dark area at the bottom of the cell near the transducer is consistent with the results obtained for the bubble distribution in the cell in a similar setup obtained by Tuziuti et al. [211] They explained that the area close to the ultrasound source is devoid of bubbles due to the damped standing wave field of ultrasound in this area. The spectrum of water in Figure 5.1b consists of a broad continuum emission stretching across the UV–Visible region, with a band around 300 nm which is generally accepted to be due to emission from electronically excited ‘OH radicals. The emission continuum has been attributed to a combination of various processes including emission from electronically excited molecules [212], emission from the decomposition of excimers [213], as well as from plasma inside the heated bubbles [214], and is a common feature of MBSL spectra of aqueous solutions.

When 0.1 M NaCl is added to the liquid, an emission band centred around 590 nm appears, on top of the continuum, in the MBSL spectrum from the salt solution† (Figure 5.2b). This emission band is well documented and is attributed to the emission from electronically excited sodium atoms (i.e., the sodium D line emission). In the SL photograph (Figure 5.2a) this emission is seen as a reddish tinge which appears in addition to the faint light blue SL. It is noteworthy that whereas the faint blue SL is from near the centre of the liquid

† Note that the small peak at around 670 nm (just after the main sodium peak) was an experimental artifact that could not be eliminated. However, this does not affect the qualitative treatment of the data, which is the focus here.
surface, analogous to that seen in water, the reddish \( \text{Na}^+ \) emission is predominantly from near the sides of the reaction cell.

![Figure 5.1](image)

**Figure 5.1** (a) SL photograph; (b) uncalibrated SL spectrum; (c) luminol SCL photograph of argon saturated water.

To explore this further, the SCL photograph of 0.1 M NaCl solution doped with luminol was taken, and is shown in **Figure 5.2c**. The mechanism of luminol SCL has been discussed in Chapter 1 (§1.8), which indicates that the strength (brightness) of luminol SCL is proportional to the amount of 'OH produced (i.e., the sonochemical activity).
The photographs seem to suggest that the SCL emission generally originates from larger volumes of the liquid compared to SL. This is probably a result of the lower threshold for SCL compared to SL [215]. (In other words, those bubbles which might not experience high enough acoustic pressures to emit SL can still emit SCL.) It is also possible that the lower spectral sensitivity of the digital camera in the UV region has some influence on the photographs (see §5.2.6). Nevertheless, the important feature to note from comparing Figures 5.2a and 5.2c is how the bright (dominant) regions emitting luminol SCL corresponds very well to the regions showing Na\(^+\) emission, where the SL
emission is relatively weak. This is a very interesting result because the photographs in Figure 5.2 indicate that Na$^+$ emission arise from a different population of bubbles than that of SL. The peak temperature inside a sonoluminescing bubble can be expected to be relatively high [196]. The observation that Na$^+$ emission seems to arise from those bubbles which are sonochemically active, but are not necessarily sonoluminescing, indicates Na$^+$ emission may originate from bubbles with relatively lower temperatures (i.e., the “chemically active” bubbles, or SC bubbles).

It is worth mentioning the study of Laborde et al. [216], where the regions in the reactor corresponding to luminol SCL emission, erosion of aluminium foil, as well as the pressure field as simulated using the computational fluid dynamics (CFD) code are compared. Employing a plate-type transducer operating at a frequency of 28 kHz, it was observed that the regions of high pressure amplitudes closely correspond to the erosion zones on the aluminium foil, while the regions of low pressure amplitudes correlate to luminol SCL emission. These observations are in line with our proposition.

The observation of luminol SCL emission from unstable “dancing” single bubble made by Hatanaka et al. [217], which led them to conclude that unstable bubble collapse is a key factor in SCL, also lends support to our hypothesis of linking luminol SCL emission to Na$^+$ emission (see §1.7 regarding proposed mechanisms of Na$^+$ emission).

5.2.2 Emission from aqueous solutions containing SDS

To confirm that what has been observed is not unique to NaCl solutions, the investigation was extended to solutions containing an anionic surfactant, SDS. Figure 5.3a shows the reddish Na$^+$ emission from 1 mM SDS solution is
Figure 5.3 (a) SL photograph; (b) uncalibrated SL spectrum; (c) luminol SCL photograph of argon saturated 1 mM SDS solution.

comparable to that arising from 0.1 M NaCl solution (see Figure 5.2a). Note, however, that the emission is still mainly from near the sides of the cell, and not at the centre of the cell close to the surface of the liquid where SL is the greatest. The corresponding MBSL spectrum in Figure 5.3b matches this closely. The intensity of the Na* emission peak in 1 mM SDS solution is similar to that in 0.1 M NaCl solution. This is quite intriguing considering the much larger bulk concentration of Na* ions in the latter case. The reason for this has been previously hypothesised [61,190] to be due to the strong dependence of
the Na peak emission intensity on the number of Na\(^+\) ions in close proximity to the bubble/solution interface of cavitating bubbles. SDS molecules are surface active, making them adsorb preferentially at the bubble/solution interface, with the hydrophobic tails inside the bubble and the hydrophilic negatively charged sulfate head groups in the aqueous phase. Consequently, upon the adsorption of these molecules at the bubble/solution interface, the bubble surface acquires an overall negative charge and thus attracts more Na\(^+\) closer to it. This results in a comparable concentration of Na\(^+\) near the interface in 1 mM SDS solution as in 0.1 M NaCl solution (despite the much lower bulk concentration), leading to an equally intense Na\(^+\) emission peak (Figure 5.4). From this data, the potential on the surface of the cavitation bubbles could be calculated using the Boltzmann equation, \([\text{Na}^+]_{\text{surface}} = [\text{Na}^+]_{\text{bulk}} \exp(-e\psi/kT)\). The calculated value of the surface potential (\(\psi\)), of approximately ~120 mV (see Appendix 5 for calculation), agrees well with the \(\psi\) value cited in a previous study [190].

Further examination of Figure 5.3b also reveals that upon the addition of 1 mM SDS, the intensity of the whole continuum also increases compared to that of water. This agrees well with the proposition that the number of “active” bubbles increases as a result of the adsorption of the SDS molecules onto the bubble/solution interface creating electrostatic repulsion forces between bubbles [97,110]. A more detailed discussion on this has been covered in Chapter 1 (§1.6.4 (b)).

The photograph of luminol SCL from 1 mM SDS solution is shown in Figure 5.3c. Comparing this to the water case (Figure 5.1c), there is a noticeable decrease in the overall SCL intensity (i.e., the emission appears much dimmer). A similar phenomenon was observed by Miyoshi et al. [218], in which the luminol SCL intensity was found to be 100 times lower than that in water, upon the addition of 3 mM SDS at an ultrasonic frequency of 140 kHz. This decrease in the luminol SCL intensity is a result of the scavenging of some of the
Chapter 5: Sodium atom emission from MBSL

Figure 5.4 Diagrammatic representation of the distribution of Na\(^+\) ions in the solution. The adsorbed surfactant molecules on the bubble/solution interface in the 1 mM SDS solution gives rise to an overall negative charge around the bubble, which attracts Na\(^+\) ions to the interface. Consequently, the concentration of Na\(^+\) ions in close proximity to the bubble/solution interface in 1 mM SDS is comparable to that in 0.1 M NaCl, despite the much lower bulk concentration.

\(^{1}\text{OH}\) radicals generated in the heated core of the bubble by the adsorbed SDS molecules [58], resulting in a lower amount of \(^{1}\text{OH}\) radicals remaining to oxidise the luminol monoanions, giving rise to less SCL emission. The hydrogen peroxide yield test using the iodometric method [58] carried out by Vu et al. [219], which shows that the \(\text{H}_2\text{O}_2\) yield (which is directly proportional to the \(^{1}\text{OH}\) yield) in argon saturated SDS solutions decreases substantially even at SDS concentration as low as 1 mM, also corroborates this interpretation. In addition, the negatively charged head groups of the adsorbed SDS molecules prevent luminol monoanions from approaching the bubbles, thus lowering the possibility of luminol reacting with \(^{1}\text{OH}\) radicals to generate SCL emission.
At higher SDS concentrations (10 mM), the Na\textsuperscript{*} emission is even more pronounced (Figure 5.5a) owing to the higher surface excess of SDS at the bubble/solution interface [220]. The much more intense Na\textsuperscript{*} emission peak in the MBSL spectrum (Figure 5.5b) supports this observation. The intensity of the continuum, however, is actually somewhat lower than that of water. This is a result of the partial quenching of SL intensity due to the decomposition of the adsorbed surfactant molecules in the high temperature environment in the bubble core upon collapse, leading to a lowering of the bubble temperature and hence a decrease of the emitted SL intensity [61,99]. The fact that SL and Na\textsuperscript{*} emission intensities are not affected in the same way suggests the existence of two different populations of bubbles: the SL bubbles giving rise to the continuum in the spectra and the SC bubbles which are responsible for the Na\textsuperscript{*} emission peak.

A similar idea was also proposed by Giri and Arakeri [221]. Their measurements reveal the pulse width of the sodium D emission to be in the range of tens of nanoseconds. This is longer than the usually estimated pulse width of SBSL/MBSL, which is in the sub-nanosecond or even picosecond regime [222,223]. This clearly indicates that these pulse widths are not a measure of the radiative lifetime of Na\textsuperscript{*}, which has been estimated to be less than 1 ps [118], but rather the time-span during which the conditions inside the collapsing bubble allow for SL or SCL emission. It strongly suggests that the conditions inside the bubble which are sufficient for inducing Na\textsuperscript{*} emission persists for a much longer time that what is required for SL emission. In other words, in line with the findings in this study, Na\textsuperscript{*} emission mainly originate from relatively “cooler” bubbles in the population of “active” bubbles in the system.
5.2.3 Emission from aqueous solutions containing SDS and NaCl

As mentioned in §5.2.2, the adsorption of SDS molecules creates a negative surface potential at the bubble/solution interface, which results in the attraction of Na\(^+\) ions from the bulk solution to the interface. Increasing the interfacial concentration of SDS increases the surface potential, which consequently increases the amount of Na\(^+\) ions attracted to the interface. As discussed in Chapter 4 (§4.2.1), the addition of 0.1 M NaCl to SDS solutions screens the repulsive electrostatic interactions between the negatively charged sulfate head
groups. This facilitates the adsorption of more SDS molecules on the bubble/solution interface, and hence as expected, the intensity of Na\(^*\) emission from an aqueous solution of 1 mM SDS in the presence of 0.1 M NaCl is much higher compared to that from a solution containing only 1 mM SDS (Figure 5.6). Similar measurements were carried out for 10 mM SDS, however as shown in Figure 5.7, any effects due to the addition of the electrolyte is minimal. This is because at 10 mM SDS, the amount of SDS molecules that can be accommodated at the bubble/solution interface is already at a maximum [61].

![Figure 5.6](image)

**Figure 5.6**  (a) SL photograph; (b) uncalibrated SL spectrum; (c) luminol SCL photograph of argon saturated 1 mM SDS in the presence of 0.1 M NaCl.
5.2.4 Emission from aqueous solutions containing SDS and KCl

Results obtained from an aqueous solution of 1 mM SDS + 5 mM KCl are shown in Figure 5.8. Comparing the photographs in Figure 5.8a to that in Figure 5.3a, it is evident that most of the reddish Na\(^+\) emission is diminished when KCl is present in the solution. It has been shown [224] that in the case of SDS, the binding ability of K\(^+\) counterion to the negatively charged sulfate head group is about the same as Na\(^+\). However, as the K\(^+\) bulk concentration exceeds
the Na\(^+\) bulk concentration, it is expected that when KCl is added to the SDS solution, the K\(^+\) ions will replace some of the Na\(^+\) bound to the head groups of the SDS molecules adsorbed at the interface. This leads to a lower number of Na\(^+\) ions near the bubble/solution interface of cavitating bubbles, which parallels the lower Na\(^*\) emission intensity observed. This result further confirms that it is not the concentration of Na\(^+\) ions in the bulk solution that governs the overall Na\(^*\) emission intensity, but rather the concentration of Na\(^+\) ions in close proximity to the bubble surface.

Figure 5.8  (a) SL photograph; (b) uncalibrated SL spectrum; (c) luminol SCL photograph of argon saturated 1 mM SDS in the presence of 5 mM KCl.
5.2.5 Effect of applied acoustic amplitude

A feature that is worth noting in the photographs is that the presence of acoustic nodes and antinodes is clearly seen as alternating dark and bright stripes throughout the liquid. Figure 5.9 shows a series of SL photographs taken from a 1 mM SDS solution sonicated at different acoustic amplitudes. At lower acoustic amplitudes, emission is seen to originate from small areas scattered throughout the liquid. Although the presence of standing waves is already visible, the bubble distribution is not uniform. As the applied acoustic amplitude is increased, the stripes of acoustic nodes and antinodes become progressively more apparent and the bubble distribution more developed and uniform. At the highest acoustic amplitude of 450 mV$_{p-p}$, the emission is slightly blurred due to the rapid upward movement of the bubble clouds and a significant disturbance of the liquid interface under these conditions. For this reason, an acoustic amplitude of 360 mV$_{p-p}$ was chosen as the “optimum” amplitude to use in order to achieve a high emission intensity whilst minimising the disturbance of the liquid interface to maintain well-defined nodal and antinodal regions in the bulk solution.

5.2.6 Limitation in interpreting emission photographs

It is worth mentioning that the spectral sensitivity of the digital camera used may have affected the photographs captured. Standard digital cameras, such as the one used here, use filters in acquiring light – typically a Bayer filter. The pixels in a Bayer filter are not evenly divided. The filter lets through more green light compared to red or blue light because the human eyes are most sensitive to green light (~530 nm). Considering the Na$^+$ emission is centred around 590 nm, one may expect more of this emission to be detected by the camera as compared to the blue SL / luminol SCL. In other words, Na$^+$ emission may be
Figure 5.9 SL photographs of argon saturated 1 mM SDS solution sonicated at different applied acoustic amplitudes (139 kHz).
more enhanced in the photographs compared to SL and luminol SCL. This may change the actual appearance of the images obtained. Nevertheless, it does not alter the conclusions drawn in this study. All of the photographs being compared were taken under the same experimental conditions. Moreover, since the basis of the investigation is the comparison between the dominant regions and differences in the relative intensity of emission, and not the absolute intensity, this limitation does not introduce a bias to the results and hence their interpretation.

5.3 CONCLUSIONS

The excited sodium atom emission from aqueous solutions containing NaCl or SDS under ultrasonic irradiation is a complex phenomenon. In agreement with a previous proposition, Na* emission is indeed highly dependent on the concentration of Na+ ions near the bubble/solution interface, for which this present study provides a direct visual support. Furthermore, the SL and luminol SCL photographs show that Na* emission correlates very well with the luminol SCL, which leads to the conclusion that Na* emission is primarily from those bubbles which are sonochemically active, but are not necessarily sonoluminescing. Further work is required to fully understand the processes that occur at the bubble/solution interface and within the bubble core, in order to explain how the neutral sodium atoms are produced.
APPENDIX 5: Calculation of bubble surface potential

When charged surfactants adsorb at the bubble/solution interface, they give rise to an overall charge on the bubble surface. The intensity of the Na\(^+\) peak emitted from 0.1 M NaCl solution (Figure 5.2b) is comparable to that from 1 mM SDS solution (Figure 5.3b), indicating a comparable Na\(^+\) concentration in close proximity to the bubble/solution interface in both solutions.

The potential on the surface of the cavitation bubbles in 1 mM SDS solution can be calculated using the Boltzmann equation [190]:

\[
[\text{Na}^+]_{\text{surface}} = [\text{Na}^+]_{\text{bulk}} \exp(-e\Psi / kT)
\]

[Na\(^+\)]\(_{\text{surface}}\) is the concentration of Na\(^+\) in close proximity to the surface of the surfactant-coated bubble (taken to be 0.1 M, based on the opening paragraph above).

[Na\(^+\)]\(_{\text{bulk}}\) is the concentration of Na\(^+\) in bulk solution (0.001 M).

\(e\) is the elementary charge (1.602 \times 10^{-19} \text{ C}).

\(\Psi\) is the bubble surface potential (V).

\(k\) is the Boltzmann’s constant (1.38 \times 10^{-23} \text{ J K}^{-1}).

\(T\) is the temperature of the solution (294.65 K).

Using these values, the surface potential of the bubbles is calculated to be -117 mV. It illustrates the significance of surfactant adsorption at the bubble/solution interface, giving rise to electrostatic interactions between bubbles.
6.1 INTRODUCTION

The previous chapters have dealt with the fundamental studies of ultrasound. This chapter aims to apply some of the understanding gained from fundamental studies to practical applications, particularly in the area of food processing.

In recent years, high energy ultrasound has found increasing use in the food industry [225, 226]. Whereas most applications are still limited to emulsification [227, 228] and cleaning [229, 230], the use of ultrasound is widening with more novel applications, such as in the aging of wines [231], extractions [163] and other food processing practices. One of the problems that can severely restrict the application of high power ultrasound as an innovative food processing technology is the generation of \(^{\cdot}\)OH radicals by cavitation upon the sonolysis of aqueous media. An example is the processing of lipid-containing foods using ultrasound, in which the radicals generated can react with the lipid and lead to the development of rancid and off flavours in the final product [138]. However, these sonochemically generated radicals also have the potential to be advantageous, such as to enhance the functionality of selected food ingredients.

Depending on the particular application, the generation of radicals during ultrasonic processing might or might not be desirable. It is therefore paramount to be able to control the amount of radicals generated by means of selecting the correct processing conditions. Some of the factors that influence this are
investigated further in this chapter. Results of preliminary work on the hydroxylation of food materials to increase antioxidant activity are also presented. While it is shown to be possible with the model compound, phenol, sonochemical hydroxylation attempts with a few actual food materials were not successful.

6.2 RESULTS AND DISCUSSION

6.2.1 Effect of applied acoustic frequency on the sonochemical generation of $\cdot$OH

Applied acoustic frequency is one of the significant parameters involved in determining the optimum reaction conditions. Since reactions with the sonochemically generated $\cdot$OH radicals is the main focus of this study, experiments were carried out for quantifying the amount of $\cdot$OH produced at different frequencies. As mentioned in Chapter 4 (§4.1), the effect of acoustic frequency on a given process will depend on the reactor geometry, among other factors. Noting this concern, experiments were conducted using identical reaction vessels, same reaction volumes, as well as the same calorimetric power for all the frequencies investigated (except for 20 kHz). The result shown for 20 kHz were adapted from a previous study [232], with a similar calorimetric power, however the reactor geometry was different. Therefore, the results for 20 kHz discussed here should only be regarded as a qualitative comparison.

The overall yield of $\cdot$OH radicals produced from the cleavage of water molecules inside a bubble in a multibubble system depends on the balance of several factors, including the amount of water vapour evaporating into the bubble, the temperature reached inside the bubble upon collapse, the number of cavitation bubbles in the system and the number of oscillations these bubbles
undergo. The extent of water evaporation into the bubble and the bubble temperature determine the amount of \( \cdot \)OH produced per bubble collapse, and subsequently multiplication of this by the number of cavitation bubbles in the whole system and the number of bubble oscillation gives the overall \( \cdot \)OH yield. Moreover, since the method of quantifying \( \cdot \)OH yield used in this study is based on the amount of H\(_2\)O\(_2\) formed in the bulk solution (§2.2.6 (b)), the extent of which \( \cdot \)OH radicals formed inside the bubble diffuse out into the bulk solution is also an important factor.

**Figure 6.1** shows the amount of \( \cdot \)OH radicals generated as a function of the number of bubble oscillations at the various acoustic frequencies. The gradients of these plots, which essentially gives the amount of \( \cdot \)OH produced per bubble oscillation, are tabulated and presented in **Table 6.1**. Except for 20 kHz, the yield of \( \cdot \)OH per bubble oscillation increases with decreasing frequency.† At low frequencies, the bubbles have longer expansion cycles, allowing more time for water molecules to evaporate into the bubble. Combined with the larger ratio of bubble volume upon collapse (i.e., bubble resonance size is larger at lower frequencies), this can be expected to produce a higher \( \cdot \)OH yield per bubble collapse, compared to the higher frequencies. The lower number of cavitation bubbles present at the lower frequencies, however, will also determine the overall amount of \( \cdot \)OH radicals generated in the solution. This is best illustrated by the 20 kHz results. Despite the much larger \( \cdot \)OH yield per bubble collapse that can be expected at this much lower frequency, the significantly lower number of bubbles present results in the amount of \( \cdot \)OH produced per bubble oscillation to be similar to that produced at 358 or 647 kHz.

† Note that since to date, the number of “active” bubbles in the system remains unknown, these values for \( \cdot \)OH yield take into account both the amount of \( \cdot \)OH generated per bubble as well as the number of “active” bubbles in the solution.
Figure 6.1 The amount of •OH generated as a function of the number of bubble oscillations at various acoustic frequencies (0.9 W/cm$^2$). The inset shows the data for 20 kHz.

Table 6.1 The amount of •OH generated per bubble oscillation, as obtained from the data in Figure 6.1. These •OH yields take into account the amount produced per bubble, as well as the number of bubbles present in the solution. Except for 20 kHz, the amount of •OH generated per bubble oscillation increases with decreasing acoustic frequency.

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>•OH generated per oscillation ($\times 10^{-9}$ µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>173 ± 11</td>
</tr>
<tr>
<td>358</td>
<td>86 ± 14</td>
</tr>
<tr>
<td>647</td>
<td>71 ± 12</td>
</tr>
<tr>
<td>1062</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>20</td>
<td>86 ± 28</td>
</tr>
</tbody>
</table>

It is evident from Table 6.1 that out of the frequencies investigated, 213 kHz is the optimum frequency to generate the most •OH radicals per bubble oscillation. Nevertheless, in typical sonochemistry applications, the efficiency of a reaction is usually based on the yield as a function of sonication time.
Figure 6.2 illustrates the data from Figure 6.1 plotted as a function of sonication time. Based on this, 647 kHz appears to be the optimum frequency where the production of •OH is maximum. This is due to a difference in the period of bubble oscillation at the various frequencies. For example, in order to generate 120 µM of •OH radicals, approximately $6 \times 10^8$ bubble oscillations are required at 213 kHz, compared to $1.5 \times 10^9$ oscillations at 647 kHz (Figure 6.1). However, since the period of bubble oscillation is longer at 213 kHz, the $6 \times 10^8$ oscillations required correspond to a sonication time of around 60 minutes, as compared to only 40 minutes required at 647 kHz.

The significantly lower number of bubbles present at 20 kHz is again highlighted in the minimal •OH production, as depicted in Figure 6.2. The comparatively low •OH yield at 1062 kHz is also expected, since the shorter period of bubble expansion cycle results in a comparatively lower amount of water molecules evaporating into the bubble [70].
The optimum frequency for •OH production, found to be around 650 kHz in this study, is in agreement with previous results obtained by Hung and Hoffmann [233]. Some other studies, however, concluded that around 300 kHz is the optimum frequency for sonochemistry [188,234,235].

6.2.2 Sonochemical hydroxylation of a model compound: phenol

To illustrate the hydroxylation of food materials by sonochemically generated •OH, phenol is chosen to be the model compound since phenolic compounds constitute one of the most widespread and diverse groups of secondary plant metabolites in the life of plants [170].

As discussed in Chapter 1 (§1.9.1), when sonication is carried out under airsaturated conditions, hydroperoxy radicals (HO_2•) may be present in the aqueous solution. However, these radicals have never been encountered during sonication of phenol solutions [151]. Moreover, the amounts of hydroxylated phenol intermediates formed upon the sonication of phenol solutions were found to quantitatively correlate to the amount of phenol reacted [232], hence strongly indicating the •OH radicals are essentially exclusively involved in the reaction with phenol. For these reasons, only reactions involving •OH radicals are considered in the following discussion.

It should also be noted that the pKa of phenol is 9.99 at 25 °C [28], which means that since the experiments discussed in this study were conducted at pH ~6, the presence of phenolate anion can be neglected.

6.2.2 (a) Effect of applied acoustic frequency

Figure 6.3 shows the yield of •OH radicals from aqueous solutions containing 1 mM phenol sonicated at different acoustic frequencies. Except for 20 kHz, the
•OH yield decreases for all frequencies in the presence of phenol in solution compared to that in pure water (Figure 6.2). The trend with respect to the varying frequencies, however, remains the same. It can be seen that there is practically no change in the amount of •OH radicals generated at 20 kHz upon the addition of 1 mM phenol. All these changes in the •OH yield closely correlate with the change in the phenol concentration as monitored by HPLC (Figure 6.4), which indicates that there is a direct link between the two. When phenol is present in the solution, the •OH produced can react with the phenol molecules, hence providing an alternative reaction pathway for the •OH radicals and lowering the \( \text{H}_2\text{O}_2 \) formation. Consequently, this also lowers the measured •OH yield. This reaction between the sonochemically generated •OH radicals and phenol molecules will be explored further in the following sections.

**Figure 6.3** Comparison of •OH radical yield generated in water (solid grey symbols) and in 1 mM phenol solutions (open symbols) upon sonication at different ultrasonic frequencies (0.9 W/cm²). Except for 20 kHz, the •OH yield decreases in the presence of phenol in solution.
6.2.2 (b) 1 mM phenol

Figure 6.5 shows the change in the UV-Visible absorption spectra as an aqueous solution of 1 mM phenol was sonicated at 647 kHz (1.1 W/cm²) for 3 hours. Phenol has a characteristic sharp absorption band centred around 270 nm. As sonication progresses, the shape of the UV-Visible spectrum of the solution becomes less and less defined, with a shoulder appearing on the red side of the phenol absorption band. This change is also reflected in the distinct colour change of the reaction solution, from initially colourless to orangey-brown at the end of the 3 hours sonication.

The change in phenol concentration as the reaction advances was also monitored in parallel using HPLC (Figure 6.6). The peak corresponding to phenol occurs at a retention time of around 5.4 minutes. Upon sonication, the intensity of this peak continually decreases, accompanied by the formation of two new peaks at 2 and 4 minutes. Previous studies [151,236] have shown that the main
Figure 6.5  Evolution of UV-Visible absorption spectra as 1 mM phenol solution is sonicated at 647 kHz (1.1 W/cm$^2$). A shoulder around 300 – 400 nm develops as sonication progresses.

Figure 6.6  Evolution of HPLC chromatograms as 1 mM phenol solution is sonicated at 647 kHz (1.1 W/cm$^2$). Phenol peak at 5.4 min decreases while new peaks at 2 and 4 min grow as sonication progresses.
reaction pathway when an aqueous solution containing phenol is sonicated involves a reaction with the sonochemically generated •OH radicals to form OH-added products (i.e., hydroxy- and dihydroxyphenols). These are depicted in Scheme 6.1. Upon further sonication, these entities can react further to produce organic acids.

UV-Visible spectra and HPLC chromatograms of the hydroxy- and dihydroxyphenols were measured (Figures 6.7 and 6.8) and compared to those of the sonicated phenol solution. Contrasting the HPLC results, it can be readily seen that the new peak at 4 minutes in Figure 6.6 corresponds to the formation of the hydroxylated phenols. The other peak at 2 minutes has been previously shown to be due to the organic acids [237]. The UV-Visible spectra, on the other hand, are not as easily interpreted. Figure 6.7 shows that the absorption profiles of all the hydroxylated phenols are quite similar. More importantly, none of them displays any absorption > 310 nm, which means that the shoulder
Figure 6.7 UV-Visible absorption spectra of phenol and its hydroxylated derivatives. All of the spectra are quite similar, and none displays any absorption >310 nm.

Figure 6.8 HPLC chromatograms of phenol and its hydroxylated derivatives. All of the hydroxylated phenols exhibit a peak around 4 min.
appearing in the absorption spectrum of the sonicated phenol solution cannot be explained based on the formation of these hydroxylated phenols alone. Some additional products must also be formed during sonication.

One possible process that may be taking place is the polymerisation of the phenol or hydroxylated phenol monomers to form polyphenolic compounds. Polyphenolic compounds typically exhibit absorption bands in the range of 220 – 600 nm [238] and their aqueous solutions generally appear brownish in colour [239]. In order to determine if this was the case, mass spectra of the phenol solutions before and after sonication were recorded, and these are presented in Figure 6.9. Before sonication, only the parent phenol peak (93.1 m/z) is present (Figure 6.9a). In Figure 6.9b, this peak has completely disappeared and is replaced by new peaks corresponding to the hydroxyphenols (109.1 m/z) and dihydroxyphenol (125.0 m/z) after 3 hours sonication. However, while the formation of hydroxylated phenols is further confirmed, no polyphenolic materials can be detected in the mass spectra. Having said this, the possibility of any polyphenolic materials that may have been formed during sonication undergoing degradation during mass spectra acquisition cannot be ruled out.

The main interest of this study was to utilise sonochemical hydroxylation to enhance the radical-scavenging activity (i.e., antioxidant activity) of food chemicals. Figure 6.10 illustrates the radical-scavenging activity of the sonicated phenol solutions, as well as that of hydroxylated phenols. It is found that the radical-scavenging activity increases dramatically with sonication, since

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‡ While the formation of organic acids is not the focus of this study and hence was not investigated further, the aqueous solutions of these acids are colourless and do not exhibit absorption >300 nm.

ξ The mass spectrometry measurement was carried out under –ve mode, which results in the m/z value being 1 a.m.u. less than the actual molecular mass of the compound.
phenol itself essentially does not possess any radical-scavenging activity at all. This result lends support to the notion that hydroxylation has the potential to increase the antioxidant activity of certain compounds.

![Figure 6.9](image)

**Figure 6.9** Mass spectra of 1 mM phenol solution (a) before sonication and (b) after 3 hours of sonication at 647 kHz (1.1 W/cm²). Phenol peak completely disappeared after sonication and is replaced by peaks corresponding to hydroxylated products.

### 6.2.2 (c) 10 mM phenol

In the last section, it was suggested that the sonication of aqueous solutions of phenol might lead to the formation of polyphenolic compounds. If this is indeed feasible, then a higher phenol concentration in the solution should facilitate the process. 10 mM aqueous solution of phenol was sonicated under identical conditions as previously used and the progress was monitored using UV-Visible spectroscopy and HPLC. These results are depicted in Figures 6.11 and 6.12. In contrast to the 1 mM phenol case, minimal change was observed even after 3 hours of sonication. The formation of the product peaks in the HPLC chromatograms is minimal, and there is hardly any shoulder forming around 300 – 400 nm in the UV-Visible spectra. The observation of a minimal colour change occurring in the reaction solution compared to the 1 mM solution is also in accord with these results.
Chapter 6: Sonochemical hydroxylation of food materials

Figure 6.10 Comparison between the radical-scavenging activity (calculated using Equation 2.1 in §2.2.6 (d)) of sonicated phenol solutions and hydroxylated phenols as measured by the DPPH method. All solutions measured were 1 mM, unless specified otherwise. Sonochemical hydroxylation of phenol leads to an increase in the radical-scavenging activity.

A possible explanation for this apparent low extent of reaction is related to the surface activity (and possibly also vapour pressure, to some extent) of phenol. Previous study carried out by Ashokkumar et al. [101] on the SL of aqueous phenol solutions found that the SL intensity from a 10 mM phenol solution was considerably more quenched than that from a 1 mM solution. This indicates that the temperature reached inside the bubble upon collapse is lower in the solution.
Figure 6.11 Evolution of UV-Visible absorption spectra as 10 mM phenol solution is sonicated at 647 kHz (1.1 W/cm²). Minimal change was observed upon sonication.

Figure 6.12 Evolution of HPLC chromatograms as 10 mM phenol solution is sonicated at 647 kHz (1.1 W/cm²). Minimal change was observed upon sonication.
containing the higher concentration of phenol. It was proposed that this is due to the consumption of some of the cavitation energy by the pyrolysis of phenol molecules at the bubble/solution interface. This lower cavitation temperature results in a lower amount of $'OH$ radicals produced and consequently lesser extent of phenol hydroxylation. Mass spectra on Figure 6.13 further support this by showing that even though some hydroxyphenols (109.1 m/z) are formed after 3 hours of sonication, the majority of phenol molecules (93.1 m/z) remain unreacted. Furthermore, similar to the 1 mM phenol case, no polyphenolic compounds were detected.

![Mass spectra](image)

**Figure 6.13** Mass spectra of 10 mM phenol solution (a) before sonication and (b) after 3 hours of sonication at 647 kHz (1.1 W/cm$^2$). Some hydroxyphenols are formed, however the majority of phenol molecules remain unreacted at the end of the sonication.

### 6.2.2 (d) Effect of heating

To be sure that any of the changes observed were due to reactions with sonochemically generated $'OH$ radicals and not merely the heating of the solution, 1 mM and 10 mM aqueous phenol solutions were heated at $\sim$45 °C for 3 hours. The resulting UV-Visible spectra and HPLC chromatograms show no change after heating, and are presented in Appendix 6.
6.2.3 Sonochemical hydroxylation of actual food materials

Experiments involving several actual food materials (e.g., cyanidin 3-glucoside, β-carotene, morin) were attempted in order to see whether the sonochemical hydroxylation observed with phenol discussed in the previous section can be applied to these compounds as well. However, these attempts were unsuccessful with the food materials tested. Some of the problems encountered include difficulties in identifying the products of the reaction due to the complexity of the food material (e.g., cyanidin 3-glucoside), insolubility in water (e.g., β-carotene), and apparent lack of reaction occurring (e.g., morin). Therefore, further experiments involving these compounds were not pursued.

6.2.4 Controlling the sonochemical production of ’OH by the use of additives

As mentioned in §6.1, there are some cases where hydroxylation of compounds by the sonochemically generated ’OH radicals is not a desirable process. In these cases it would be beneficial then to be able to control/minimise the ’OH production during sonication. As can be seen in Figure 6.2, 20 kHz or 1062 kHz seems to be the frequencies of choice since the amount of ’OH radicals generated are considerably less than the frequencies between these values. However, other intermediate frequencies can also be employed if a suitable ’OH radical quencher is added, or if the amount of ’OH radicals generated is minimised by other means.

For the use in food processing, any quenchers added has to be food-safe. Ascorbic acid (i.e., Vitamin C) was selected for this reason, as well as because it is well known for its preferential reaction with ’OH radicals [240,241]. The addition of ascorbic acid to the aqueous solution is expected to capture the ’OH
generated (forming DHA, as illustrated in Scheme 6.2), hence minimising the reaction between 'OH radicals and the food compound. Figure 6.14 shows that the addition of 10 mM ascorbic acid almost eliminates the formation of H₂O₂ in sonicated water. This is due to the preferential reaction of 'OH radicals with ascorbic acid, which significantly decreases the extent of Reaction 2.2 (§2.2.6 (b)). Therefore, if ascorbic acid can be used as an effective way to prevent 'OH radicals reacting with food compounds in the solution, it can be expected that the hydroxylation of phenol will be prevented in the presence of ascorbic acid.

The results in Figure 6.15 illustrate that this is indeed the case. The amount of phenol reacting (primarily through hydroxylation reactions, as discussed in Section 6.2.2 (b)) is reduced in the presence of ascorbic acid. However, the data also show that the hydroxylation of phenol is not completely prevented, despite the fact that >95% of 'OH radicals are scavenged (Figure 6.14). Why this is the case will be elaborated further in the next section.

Scheme 6.2 The reaction between an ascorbic acid molecule and 'OH radicals producing dehydroascorbic acid (DHA) and water molecules.
Figure 6.14  'OH radical yield generated after 60 minutes sonication at 358 kHz (0.9 W/cm²). The yield is reduced by approx. 50% in the presence of ethanol, whereas in the presence of ascorbic acid it is almost completely diminished.

Figure 6.15  Phenol concentration (a) before sonication, and after 60 minutes sonication at 358 kHz (0.9 W/cm²) in the presence of: (b) no additives, (c) 10 mM ethanol and (d) 10 mM ascorbic acid. The decrease in the phenol concentration upon sonication is due to reactions between phenol molecules and 'OH radicals, which is reduced when additives are present in the solution.
A second approach that can be adopted to control the \( ^\cdot \text{OH} \) radicals production is by the addition of volatile surface active solutes. It is known that volatile surface active solutes, such as alcohols, evaporate into the cavitation bubbles during bubble oscillation [97]. As evidenced by the SL quenching results in Chapter 4, this results in the decrease of the cavitation bubble temperature, which in turn lowers the amount of \( ^\cdot \text{OH} \) radicals produced from the cavitation bubbles. Figure 6.14 shows that the addition of 10 mM ethanol to the sonicated water appreciably reduces the \( ^\cdot \text{OH} \) yield. The reduction in \( ^\cdot \text{OH} \) yield is about 50% upon the addition of ethanol, compared to >95% in the presence of ascorbic acid. Nevertheless, the efficiency in inhibiting hydroxylation of phenol is approximately the same (Figure 6.15). The reason for this is discussed in the next section.

6.2.7 Site of phenol hydroxylation reactions

There are three possible sites for cavitation-induced chemical reactions according to the classical hot-spot theory (Chapter 1, §1.9): inside the bubble, at the bubble/solution interface or in the bulk solution.

The extent of phenol reacting inside the bubble, either through reaction with \( ^\cdot \text{OH} \) radicals or by pyrolysis, is believed to be very small due to the low vapour pressure of phenol.\(^{40}\) The observation made by Petrier et al. [151] that acetylene and methane, the products from the pyrolysis of volatile aromatic solutes, were not detected upon sonication of phenol solutions supported this notion.

Since phenol is moderately surface active, it follows then that any hydroxylation reactions of phenol can take place either at the bubble/solution interface or in

\(^{40}\) Vapour pressure of phenol is 29 Pa at 20 °C, compared to 2334 Pa for water at the same temperature [242].
the bulk solution. Referring back to Figures 6.3 and 6.4, one interesting point that is noteworthy is that quantitatively the decrease in •OH yield does not seem to go hand-in-hand with the extent of phenol reaction. For example, after 60 minutes sonication at 358 kHz the phenol concentration has decreased by around 300 µM (Figure 6.4), while the •OH yield has only decreased by around 90 µM (Figure 6.3).\(^5\) If the majority of phenol reaction involves hydroxylation by •OH radicals [151,236], then it is reasonable to expect that the decrease in the concentrations of both phenol and •OH radicals would be comparable. Why this is not the case can be explained as follows.

The method for determining •OH radicals yield employed in this study is based on the concentration of H\(_2\)O\(_2\) formed in the bulk solution [58]. Therefore, any changes in the measured •OH yield will only reflect the corresponding phenol reactions in the bulk solution. Hydroxylation of phenol molecules at the bubble/solution interface, which can only be brought about by reaction with •OH radicals inside the bubble, will lower the phenol concentration measured at the end of the sonication period, but it will not affect the measured H\(_2\)O\(_2\) concentration. The results obtained with ascorbic acid are also in agreement with this. As seen in Section 6.2.6, the hydroxylation of phenol still proceeds (albeit to a smaller extent) despite almost no H\(_2\)O\(_2\) being detected in the bulk solution which indicates almost complete capture of •OH radicals in the bulk solution by ascorbic acid molecules. This is because due to its lack of surface activity, the presence of ascorbic acid in solution does not prevent •OH radicals from reacting with phenol molecules at the bubble/solution interface.

Kidak and Ince [234] concluded in their study that phenol reaction in a sonicated aqueous medium is mainly dominated by •OH chemistry in the bulk liquid.

\(^5\) 125 µM after 60 minutes sonication in water (solid grey symbol) and 35 µM after 60 minutes sonication in 1 mM phenol solution (open symbol).
However, the results obtained here appear to contradict this finding. **Figure 6.15** shows that without any additives present, around 30% of phenol has reacted at the end of the 60 minutes sonication. This figure is reduced to ~10% when ascorbic acid is added. Since ascorbic acid only prevents hydroxylation in the bulk solution and not at the bubble/solution interface, it can be inferred that approximately one-third of the total phenol hydroxylation occurs in the bulk solution, whereas the remaining two-thirds occurs at the bubble/solution interface. In other words, the majority of the phenol hydroxylation takes place at the bubble/solution interface and not in the bulk solution, as suggested by Kidak and Ince [234].

This proposition is also supported by the previous study of Mahamuni and Pandit [243], in which the extent of phenol reaction was found to increase upon the addition of sodium chloride to the reaction solution. The addition of salt has the effect of “salting out” any organic solutes (such as phenol molecules), and this favours the adsorption of such solutes at the bubble/solution interface [244]. This increase in the interfacial concentration of phenol coincides with the increase in the extent of phenol reaction [243], which strongly suggests that as concluded in this study, most of the phenol molecules react with \( ^\cdot \)OH radicals at the bubble/solution interface.

### 6.3 CONCLUSIONS

The overall yield of cavitationally generated \( ^\cdot \)OH radicals that can be utilised for sonochemistry in aqueous media depends in the applied acoustic frequency. Compared to the very low frequencies (e.g., 20 kHz), higher frequencies in the range of a few hundreds kHz produce a higher yield of \( ^\cdot \)OH radicals, and an optimum frequency of around 650 kHz was found in this study.
When other compounds are present in the solution, hydroxylation of these compounds by the •OH radicals can take place. Sonication of aqueous solutions of phenol leads to the formation of hydroxylated phenol derivatives, which exhibit a higher radical-scavenging activity than phenol itself. A majority of these hydroxylation reactions takes place at the bubble/solution interface. Formation of polyphenolic compounds is also possible, however further investigations are required to confirm this.

Ultrasound-induced sonochemical reactions must be controlled for the successful introduction of ultrasound technology to food processing. This can be achieved by introducing additives, such as radical quenchers or surface active solutes. The potential advantage of sonochemical hydroxylation of food materials to enhance their antioxidant activity may be highly compound dependent and requires more thorough investigation.
APPENDIX 6: The results for heating of 1 mM and 10 mM phenol without sonication

**Figure A6.1** Evolution of UV-Visible absorption spectra as 1 mM phenol solution is heated at ~45 °C for 3 hours. No change in the spectra was observed upon heating.

**Figure A6.2** Evolution of HPLC chromatograms as 1 mM phenol solution is heated at ~45 °C for 3 hours. No change in the spectra was observed upon heating.
Figure A6.3  Evolution of UV-Visible absorption spectra as 10 mM phenol solution is heated at \(~45\,^\circ\text{C}\) for 3 hours. No change in the spectra was observed upon heating.

Figure A6.4  Evolution of HPLC chromatograms as 10 mM phenol solution is heated at \(~45\,^\circ\text{C}\) for 3 hours. No change in the spectra was observed upon heating.
The primary interest of this study was how a multibubble field is affected when
the applied acoustic power and frequency are varied in aqueous solutions
containing common surface active solutes. Results obtained indicate that when
these solutes are present in the solution being irradiated, the outcomes of the
particular processes investigated (e.g., bubble coalescence, SL, SCL, Na* emission) are dictated by the concentration of the solute at the bubble/solution
interface, not the bulk concentration. Hence, it is essential to have an indication
of this interfacial solute concentration. The results of the bubble coalescence
experiments turned out to be the most interesting because they give precisely
this information.

The approach of measuring volume changes of solution upon sonication involved
very simple experiments, yet it proved to be a useful and novel technique in
utilising ultrasound to probe the dynamics of surfactant adsorption at the
acoustic bubble/solution interface. In this study, the nonequilibrium surface
excess of a system containing SDS in the presence of excess electrolyte was
estimated using the bubble coalescence data. Once this nonequilibrium surface
excess value was estimated, it could then be used further, in conjunction with
dynamic surface tension data available in the literature, to estimate the lifetime
of bubbles in a multibubble field at various acoustic frequencies.

It has to be pointed out, however, that this estimation of bubble lifetimes is an
indirect method involving certain assumptions, which are necessary to be able to
use the dynamic surface tension data for a “static” interface found in the literature, on the acoustic systems investigated in this study. Other experimental techniques or simulations to confirm the findings here would be desirable.

Knowledge on the extent of bubble coalescence alone is not enough to describe a multibubble field because it does not offer any information on the structure of the bubble field. SL intensity reflects changes in both the number of “active” bubbles in the solution, as well as the bubble temperature, when the sonication conditions are altered. Hence, it can complement the bubble coalescence results.

When observing changes in the SL intensity, however, it is at times difficult to separate the contributions of the different factors (i.e., the bubble population or bubble temperature). The changes in the bubble cluster structure in the presence of SDS suggested by the results obtained in this study were primarily inferred from the SL results. If possible, images of the actual bubble clusters captured by a high-speed camera are warranted to validate this proposition.

The observation of Na* emission from a multibubble field is a complex phenomenon indeed. Furthermore, the results presented in this study also demonstrate the complexity of a multibubble field, with different populations of bubbles co-existing in different regions of the sonicated medium.

The results of the sonochemical hydroxylation experiments are still very preliminary at this stage. In hindsight, it would have been preferable to try simpler compounds first before experimenting with actual food materials/samples, due to the difficulties in product analyses of the latter. For future investigations, it may be worthwhile to pursue experiments with a highly
unsaturated compound (e.g., β-carotene) because it should be relatively easier to attach (at least) a hydroxy group on the molecule. One of the possible difficulties in dealing with this kind of compound is its insolubility in water. One way to overcome this problem may be by the step-wise application of dual frequency ultrasound. For example, a 20 kHz horn transducer can be employed to create a stable emulsion, followed by irradiation with a high frequency ultrasound (e.g., 350 kHz) to generate \( \cdot \text{OH} \) radicals.

All in all, despite their limitations, some of the results presented in this study are quite revealing and have helped in going one step further in understanding the complex behaviour of a multibubble field in the presence of surface active solutes.
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