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A quantitative review of the transition salt concentration for inhibiting bubble coalescence

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A QUANTITATIVE REVIEW OF THE TRANSITION SALT CONCENTRATION FOR INHIBITING BUBBLE COALESCENCE

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ABSTRACT

Some salts have been proven to inhibit bubble coalescence above a certain concentration called the transition concentration. The transition concentration of salts has been investigated and determined by using different techniques. Different mechanisms have also been proposed to explain the stabilising effect of salts on bubble coalescence. However, as yet there is no consensus on a mechanism which can explain the stabilizing effect of all inhibiting salts. This paper critically reviews the experimental techniques and mechanisms for the coalescence of bubbles in saline solutions. The transition concentrations of NaCl, as the most popularly used salt, determined by using different techniques such as bubble swarm, bubble pairs, thin liquid film micro-interferometry were analysed and compared. For a consistent comparison, the concept of TC_{95} was defined as a salt concentration at which the “percentage coalescence” of bubbles reduces by 95% relative to the highest (100% in pure water) and lowest (in high-salt concentration) levels. The results show a linear relationship between the TC_{95} of NaCl and the reciprocal of the square root of the bubble radius. This relationship holds despite different experimental techniques, salt purities and bubble approach speeds, and highlights the importance of the bubble size in bubble coalescence. The available theoretical models for inhibiting effect of salts have also been reviewed. The failure of these models in predicting the salt transition concentration commands further theoretical development for a better understanding of bubble coalescence in salt solutions.

Keywords: Salts, transition concentration, colloidal forces, ion-specific, air-water interface

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1. INTRODUCTION

Bubble coalescence and stability/instability of the liquid film between two bubbles known as a foam film are central to many areas such as surface and colloid chemistry, biology, biochemistry, tertiary oil recovery, foam fractionation, food industry and mineral flotation. Foam stability is controlled by thinning and rupture of the intervening liquid film between air bubbles [1]. The overall process of formation and thinning of a liquid film can be conveniently divided into a number of stages as illustrated in Figure 1. They include (a) approaching two bubbles (b) hydrodynamic interaction between approaching bubbles which can cause deformation on bubbles surfaces, called the “dimple” (c) formation of a plane-parallel film by gradual disappearance of the dimples and (d) coalescence of bubbles if attractive pressures overcome negative pressures along the film surface. The thin liquid film formed between two approaching bubbles initially thins under the influence of the capillary pressure. This capillary pressure arises from the curvature of bubbles and for a small

film with a negligible contact angle is defined as $P_\sigma = 2\sigma/R$, where σ is the surface tension and R is the radius of curvature [2]. When the film thickness reduces to 300-200 nm, film drainage owing to the capillary pressure is slowed down and interactions between the film surfaces called the disjoining pressure start affecting the film drainage [3, 4]. Depending on the balance of the capillary pressure and disjoining pressures, if the film drainage takes longer than the bubbles' contact time, the liquid film is considered to be stable, and coalescence does not take place. Otherwise the liquid film between bubbles ruptures at a critical thickness within the range of 200-10 nm, depending on the concentration of chemicals (surfactants or salts), surface impurities and bubble approach speed [5, 6].

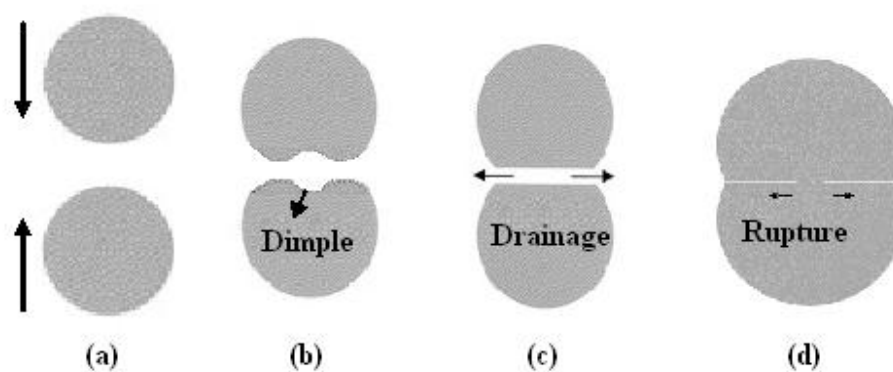


Figure 1. Sequence of events for formation and thinning of an intervening liquid film between two bubbles (foam film).

Salts and surfactants influence bubble coalescence by changing the intermolecular forces and surface rheology of liquid films between bubbles. For the case of surfactant-laden films, this is relatively well understood [7, 8]. Saline liquid films have been investigated experimentally but relative to surfactant-laden films, limited work has been done both theoretically and experimentally in this field and is not yet well understood [9]. This study reviews the coalescence of bubbles in saline solutions with a focus on mechanisms under which salts can inhibit bubble coalescence at concentrations above a critical concentration, called the transition concentration.

This review paper was structured as follows. First the background of bubble coalescence in salt solutions is reviewed in section 2. The next section is devoted to a brief review of the experimental techniques followed by a comparison of different methods for determining the transition concentration of common salts. Proposed explanations for the stabilising effect of salts are discussed in section 4. Section 5 presents a review on the available theoretical models for

predicting the transition concentration of salts. A summary and conclusion based on the findings of the reviewed papers is presented in section 6.

2. EFFECT OF SALTS ON BUBBLE COALESCENCE

It has been known for many years that salts influence bubble coalescence and the stability of thin liquid films (TLFs) between bubbles. The effect of salts on bubble coalescence and TLFs has been investigated experimentally and theoretically [8, 10-15]. In one study a theory of thin liquid formation was developed [10-12] and the effect of salts on bubble coalescence was examined by means of a foam meter and by contacting a pair of bubbles. The results of contacting pairs of bubbles were recorded as “percentage of film formation”, which was defined as the number of times in a hundred that bubbles failed to coalesce and hence liquid films formed. This work showed that bubbles in pure water coalesce spontaneously on contact, and in the presence of salts the percentage of film formation increased and gradually approached 100% with increasing salt concentration. Surface adsorption of the solute and the difference between dynamic and static surface tensions were identified as major contributing factors for the formation of foam in salt solutions at specific concentrations. Later, in a systematic study of the effect of salts on the gas holdup and bubble size in a bubble column [13], it was observed that increasing the gas flow rate resulted in bubbles with smaller mean diameters. Increasing the salt concentration led to a monotonic decrease in bubble size which asymptotically tended to a constant diameter of 0.41 mm. In addition, the concentration at which the bubble size approached the asymptote was different for different salts. The inhibiting effect of salts was related to their valence and the surface tension gradient with respect to salt concentration.

A quantitative study [16] on the effect of different salts and their concentration on coalescence of bubble pairs determined the percentage of the coalescing pairs which, in pure water (double-distilled water), was considered as 100%. The sharp decrease in the percentage of coalescing bubbles at a particular concentration was observed. This specific concentration was introduced as the transition concentration by Lessard & Zieminski [16] and found to be unique for each salt. The inhibiting effect of salts was explained on the basis of ion-water interactions. It was argued that ions retard the liquid film drainage and consequently the coalescence of bubbles by affecting the hydrogen bond. A subsequent study [8] determined the transition concentration of an extensive range of salts by focusing on a swarm of bubbles rather than individual bubble-bubble interactions, and also studied the effect of gas flow rate on the transition concentration of NaCl. The transition concentration was found to be independent of the gas flow rate. The effect of gas flow rate in terms of superficial velocity (defined as the gas flow rate per cross-sectional area) was

further investigated [17] for more salt types (NaCl, NaF, NaBr, NaI and CsCl) in a bubble column. These results revealed a significant influence of the gas superficial velocity on the transition concentration of NaI but not on the other investigated salts.

The effect of bubble approach speed on coalescence of bubbles was investigated by measuring the contact time of a bubble of 5 mm diameter rising towards an air-water interface by employing high-speed photography [18]. The bubble approach speed was varied by changing the release height of the bubble from the interface. Instant bubble coalescence was observed in distilled, and tap water, as well as low-concentration NaCl solutions at approach speeds less than 1 cm/s. A significant increase in the coalescence time at approach speeds greater than 10 cm/s was observed. This increase was attributed to the bouncing of bubbles, and these critical speeds were found to be specific to the bubble size. In the case of high-concentration NaCl solutions (0.6 M) the coalescence times were considerably longer (typically ~ 0.7 s) and found to be independent of the bubble approach speed due to the inhibiting effect of NaCl at this concentration. The effect of bubble approach speed on bubble coalescence in water and NaCl solutions (0.037 and 0.111 M) was investigated [19] with the focus on finding the critical speed beyond which bubbles bounce apart. Regardless of the salt concentration, the critical speed was found to decrease with the bubble size for bubble equivalent diameters less than 2.3 mm. For bubbles larger than 2.3 mm in diameter, the critical speed reached a constant value which decreased with increasing the salt concentration.

Drainage and rupture of salt solution liquid films, which usually occurs very rapidly relative to surfactant-laden films, were investigated quantitatively [20]. The change in film thickness, diameter and lifetime of liquid films of 0.5 and 1 M KCl solutions between two captive air bubbles were simultaneously measured by using an interferometric method. The results showed that the drainage and rupture of these liquid films took 600 and 420 ms, respectively. It was also noticed that films could not be formed for 0.1 M KCl solutions, which is below the transition concentration of KCl. Liquid films of salt solutions (NaCl, NaAc, NaClO₃ and LiCl) were further investigated [21] using an interferometric method to determine the drainage rate, lifetime and transition concentration of liquid films between two bubbles, but it did not explicitly focus on the importance of bubble approach speed. In another experimental study [4] the effect of bubble approach speed on the stability of liquid films of deionised (DI) water and NaCl solutions was investigated. Depending on bubble approach speed, three different regimes including stable and transient films and instant coalescence were observed for TLFs of DI water between two bubbles. The behaviour of surfactant-free films at different bubble approach speeds were explained based on surface forces and the Gibbs-Marangoni effect.

Some other studies have also been conducted on the effect of salts on foam liquid films by using different techniques, with a focus on the effects of either salt type or concentration at an unquantified bubble approach speed or on the effects of bubble approach speed using a single salt [22-26]. Recently a systematic study considering the combined effects of salt concentration, interface approach speed and salt type on the lifetime, thinning rate (change of the film thickness) and growth rate (change of the radius) of the liquid films of salt solutions was reported [27]. The experimental results of the effect of monovalent anions (I^- , Br^- , Cl^- and F^-) and cations (Li^+ , Na^+ and K^+) on the lifetime of liquid films showed that film lifetime decreased according to salt type following the order $NaF > LiCl > NaCl > KCl > NaBr > NaI$. Lifetimes of liquid films for each salt decreased compared to liquid films of DI water upon addition of salt up to a specific concentration. Any further increase in salt concentration resulted in an abrupt increase in the film lifetime for each salt. The specific concentration of salts, called the transition concentration, followed the reverse order of that for film lifetime, and it was shown that the transition concentration was independent of bubble approach speed in the investigated range of 10-300 $\mu\text{m/s}$. At higher interface approach speeds, the liquid film increased in area and diameter faster than when they approached at slower speeds. Surface corrugations were observed at higher bubble approach speeds which resulted in a faster rupture of liquid films.

3. EXPERIMENTAL TECHNIQUES

There are different techniques for studying the effect of salts on bubble coalescence and determining the transition concentration of salts. The following provides details of the experimental techniques available in the literature.

3.1. BUBBLE COLUMN

The experimental setup depicted in Figure 2 consists of a cylindrical column or sometimes a square-section column to minimize the light distortion. Gas bubbles are produced in the column containing water or salt solutions by sparging the gas (mainly N_2) from a gas distributor through a porous plate/frit. The porous frit is mounted at the base of the column and the gas flow sweeps any possible surface contamination to the top of the cell which is one of the advantages of this setup. By varying the porosity of the frit, different bubble sizes can be created. An expanded beam of light is passed through the column, condensed by a condensing lens and detected by a photosensor which is connected to a computer. The change in the detected light intensity owing to a change in the turbidity of solutions determines the effect of different salt solutions on bubble coalescence. Assuming 100% bubble coalescence in clean DI water with the lowest turbidity and 0% for high salt concentrations, the “percentage coalescence” of bubbles can be determined from the measured

turbidity. Inhibiting salts retard bubble coalescence at salt concentrations above the transition concentration. The inhibition of bubble coalescence results in an increase and a decrease in the number and size of bubbles respectively which increases the solution turbidity. The transition concentration of each salt is defined as the concentration corresponding to 50% bubble coalescence [8]. A typical plot of the percentage coalescence of bubbles is shown in Figure 3. Gas holdup which is the proportion of gas volume in total volume is another indicator for determining the effect of salts on bubble coalescence. Gas holdup can be defined as $\varepsilon = 1 - H_0 / H$, where H_0 and H are the initial and the aerated heights of the liquid in the column respectively.

A variation comes from monitoring the population and size distribution of bubbles by means of high speed photography. The transition concentration of each salt is defined as the concentration at which the bubble size distribution levels off to reach a constant value [13]. Figure 4 represents the average bubble size versus concentration for KCl solutions to determine the transition concentration.

In general, bubble column experiments provide useful statistical information on how the flow conditions influence bubble coalescence, but give a little insight into the mechanisms of bubble coalescence [5].

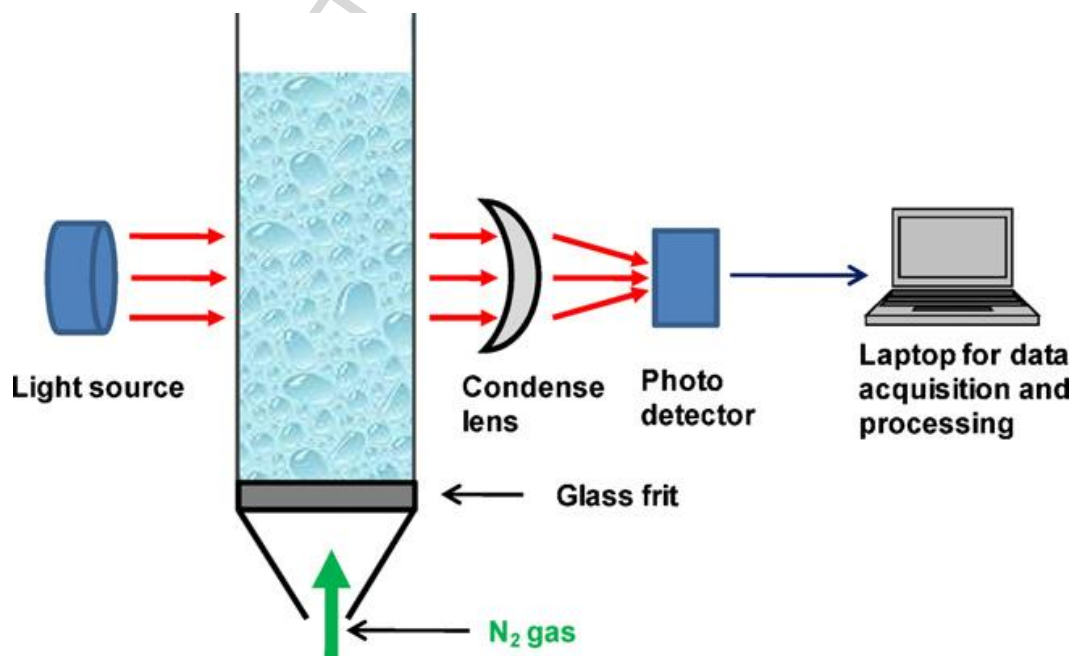


Figure 2. Schematic of a bubble column setup to study bubble coalescence in solutions [17].

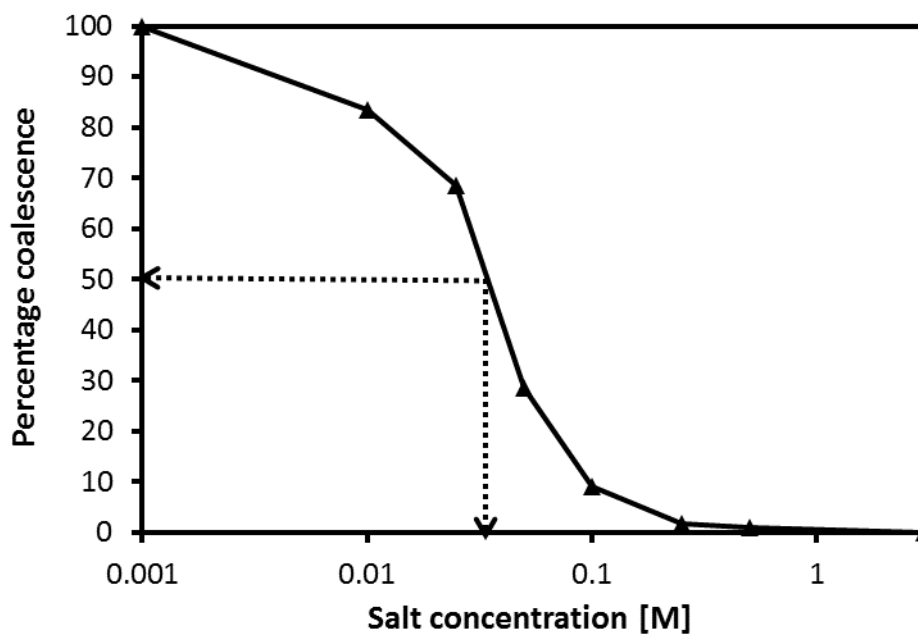


Figure 3. An illustration of salt transition concentration determined at 50% percentage coalescence of bubble population.

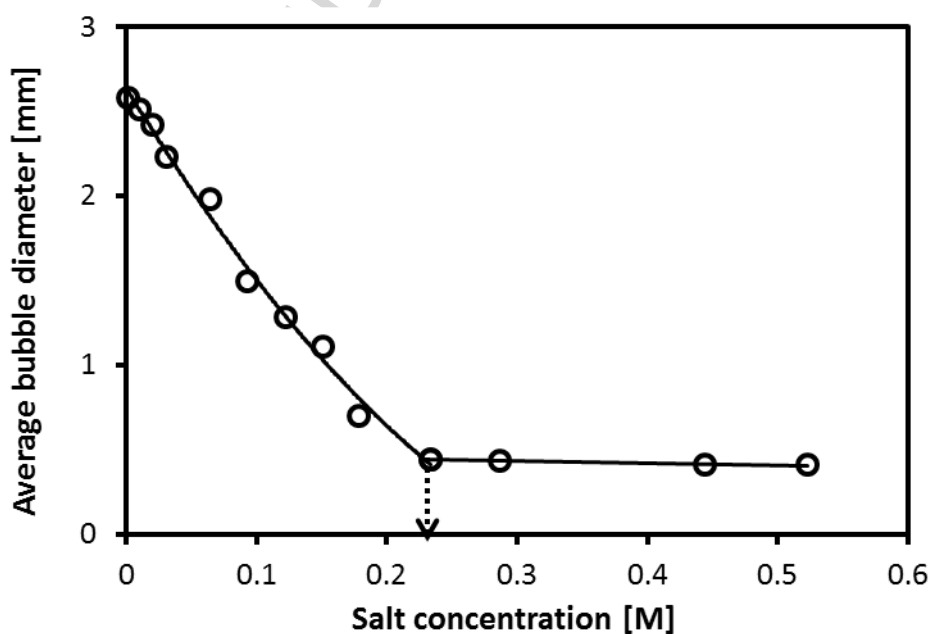


Figure 4. An illustration of salt (KCl) transition concentration determined as the minimum concentration at constant (average) bubble size versus salt concentration (data are taken from [13]).

3.2. STIRRED TANK

Stirred tanks have also been used to investigate the effect of salts on bubble coalescence and breakup with the focus on bubble size distribution. The setup consists of a typical glass tank equipped with impellers and baffles for agitating the liquid in the tank. Bubbles are produced by passing gas through a porous plate placed under the impeller. The main emphasis of investigations employing this technique is to determine the bubble breakup due to the industrial applications of stirred tanks for multiphase processing. Due to difficulties quantifying turbulence intensities throughout the system, little work has been carried out using this experimental technique for studying bubble coalescence [28, 29].

Laboratory-scale flotation machines are another variation of this technique in which effect of salts can be investigated by monitoring the size of bubbles. Fine bubbles are produced by cavitation at the trailing edge of the impeller blade in mechanical flotation cells [30]. Castro et al. [31] and Quinn et al. [32] employed the concept of critical coalescence concentration (*CCC*) proposed by Cho and Laskowski [30] to characterize the effect of different salts on froth stability. The *CCC* is a concentration above which bubbles do not coalesce and reach an almost constant bubble size. Quinn et al. [32] defined *CCCX* as the concentration at which the bubble size reduces by *X*% from that in pure water to the constant bubble size at high salt concentration [32]. The *CCCX* of salts was determined by fitting the bubbles Sauter mean diameter (D_{32}) and salt concentration (*C*) data to the following model:

$$D_{32} = D_l + A \exp(-B \times C) \quad (1)$$

where D_l is the value of D_{32} as the salt concentration goes to ∞ , *A* is the difference between D_l and D_{32} in pure water and *B* is the exponential decay constant. The *CCCX* was calculated as $CCCX = -\ln(1 - X/100) / B$. Figure 5 shows the *CCC95* of investigated salts reported by Quinn et al. [32], along with the curves and size data used for the fitting of equation (1).

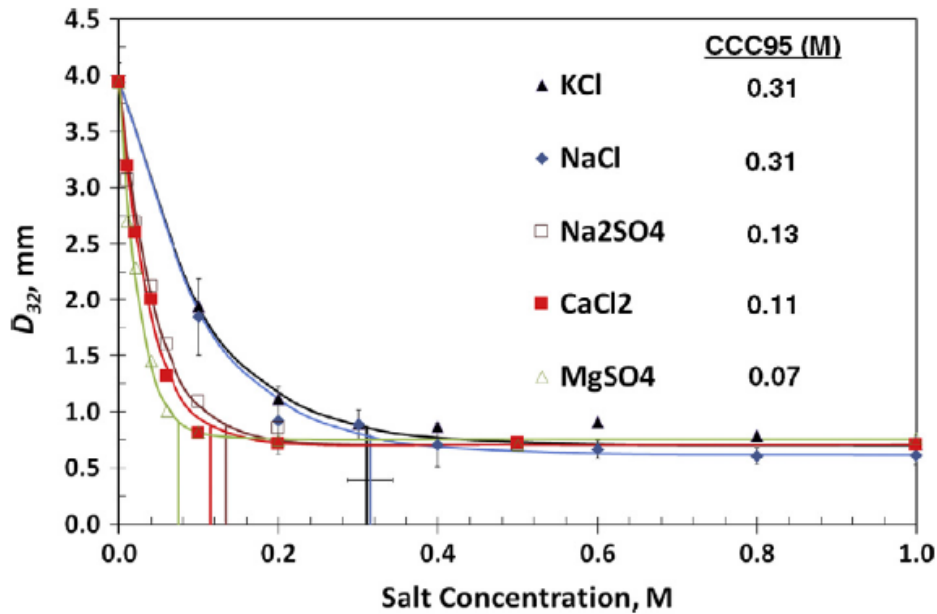


Figure 5. The *CCC95* of salts based on fitting an exponential model to the Sauter mean diameter (D_{32}) and salt concentration data [32].

3.3. ADJACENT CAPILLARIES

Unlike bubble swarm experiments, the adjacent capillaries or bubble pair method provides direct and precise information on the lifetime, drainage and rupture time of the liquid film between two bubbles. This technique involves producing two bubbles from adjacent capillaries either placed side by side or facing each other in a glass cell as shown in Figure 6. Despite the mentioned advantages of this technique relative to the previous ones, surface contamination on bubbles in stagnant solution is an important concern involved in this method.

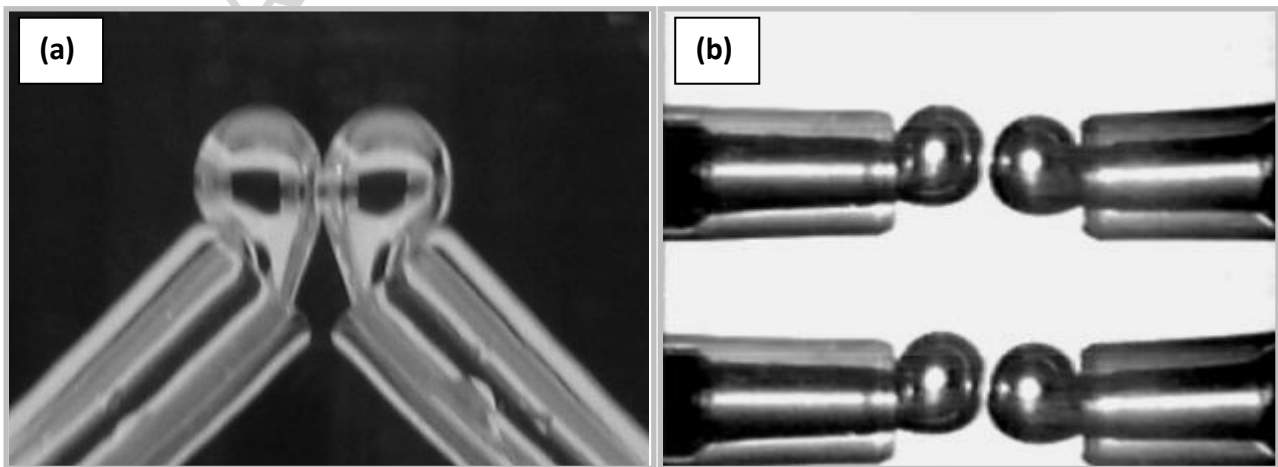


Figure 6. Images of the bubble pair experiment using adjacent capillaries (a) placed side by side [22] (b) facing each other [33].

Figure 7 shows examples of bubble coalescence using adjacent capillaries (a) in pure water in which bubbles coalesce effectively instantly on contact and (b) in high salt concentration solution. The percentage of bubble coalescence is determined by the ratio of the number of coalesced bubbles to the total number of contacted bubbles. The transition concentration of salts is defined as the concentration of the percentage coalescence half way between the percentage of bubble coalescence in pure water (100% coalescence) and the baseline measurement as demonstrated in Figure 8 [16].

Monitoring the coalescence of a single rising bubble to a free surface has been considered as another variation of this technique [5]. The air above the water surface can be considered to represent a bubble with infinite radius. The effect of salts on bubble coalescence is characterised by measuring the rest time (before coalescence) of air bubbles at the air-liquid interface which significantly increases in the presence of inhibiting salts compared to pure water [34].

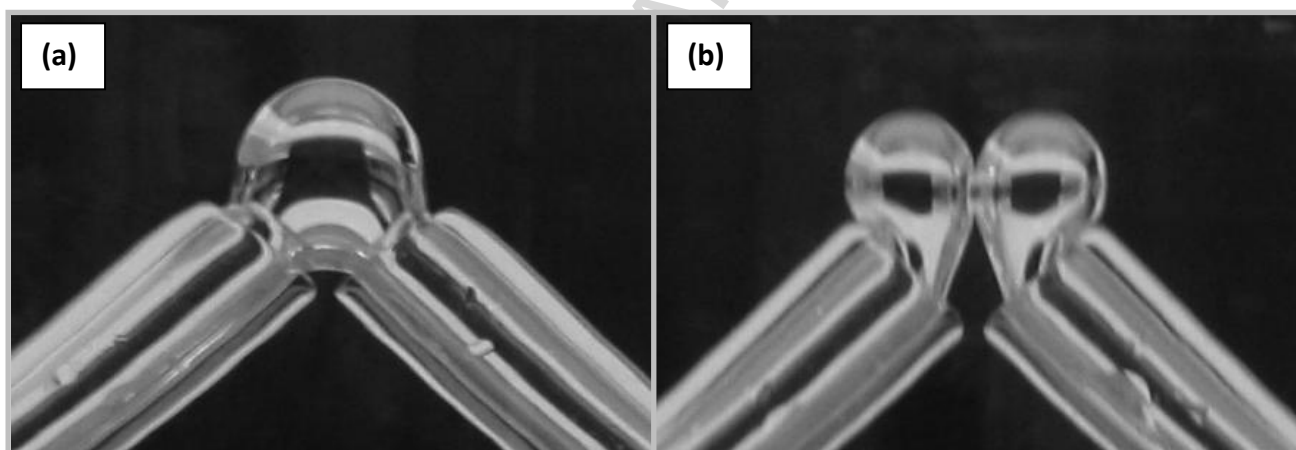


Figure 7. Bubble pair experiments in (a) pure water (b) a high salt concentration solution [22].

A slight variation of this technique was described by Del Castillo et al. [24] in a study of the effect of bubble approach speed on the coalescence of bubbles in pure water and aqueous solutions of 0.1 and 0.5 M KCl. A schematic of the setup is shown in Figure 9. An air bubble is formed at the lower end of a glass cylinder using a stainless steel needle. The bubble is allowed to slide up along the inside of the cylinder wall to approach the meniscus of the liquid which mimics the behaviour of a large bubble. Altering the angle of inclination of the glass cylinder provides variation to the bubble approach speed. The authors were able to successfully confirm the importance of bubble approach speed as well as the effect of salt concentration on the coalescence time of bubbles.

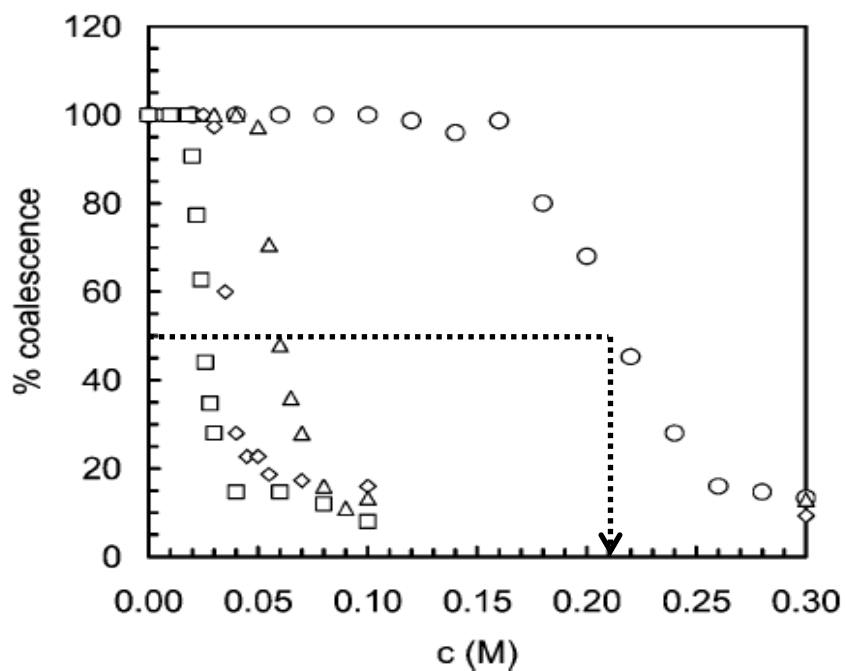


Figure 8. Percentage coalescence of bubbles versus salt concentration for LaCl_3 (open squares), MgSO_4 (open diamonds), CaCl_2 (open triangles) and NaCl (open circles) using adjacent capillaries (bubble pair) method [22].

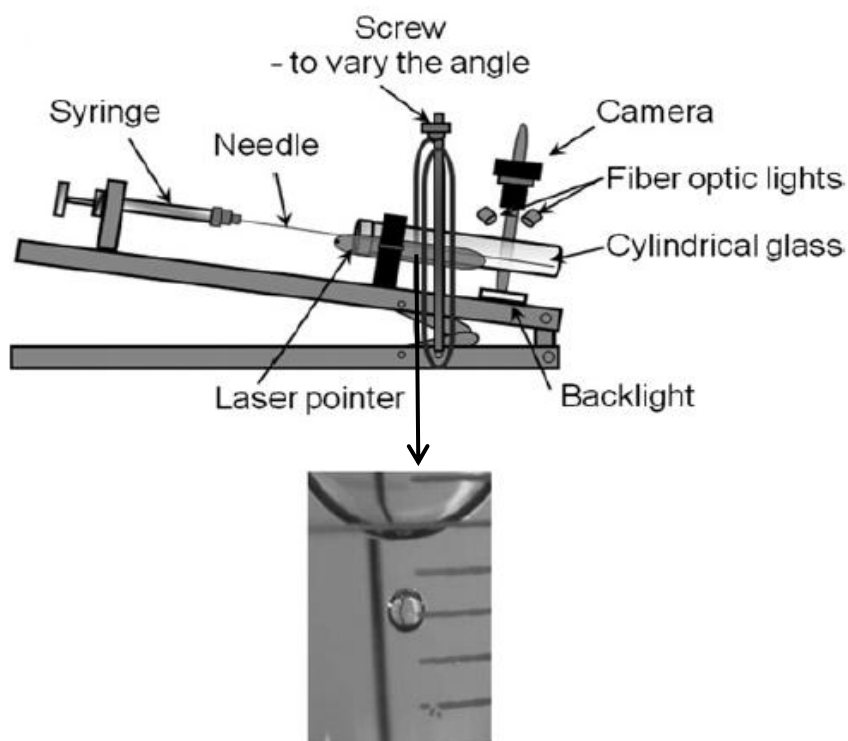


Figure 9. Schematic of the bubble-meniscus experiment [24].

3.4. THIN LIQUID FILM MICRO-INTERFEROMETRY

This technique provides very varied and useful information on the mechanisms behind saline liquid films at the microscopic level by allowing detailed analysis of disjoining pressures, thinning and rupture of liquid films. This method works based on the determination of the change in the intensity of the reflected light from a film when illuminated with a parallel, unpolarised, white light beam. As a result of the interference of the reflected light from air-liquid interfaces, a set of colourful fringes (Newton rings) is observed [1, 21]. The following is a brief history of the development of this technique.

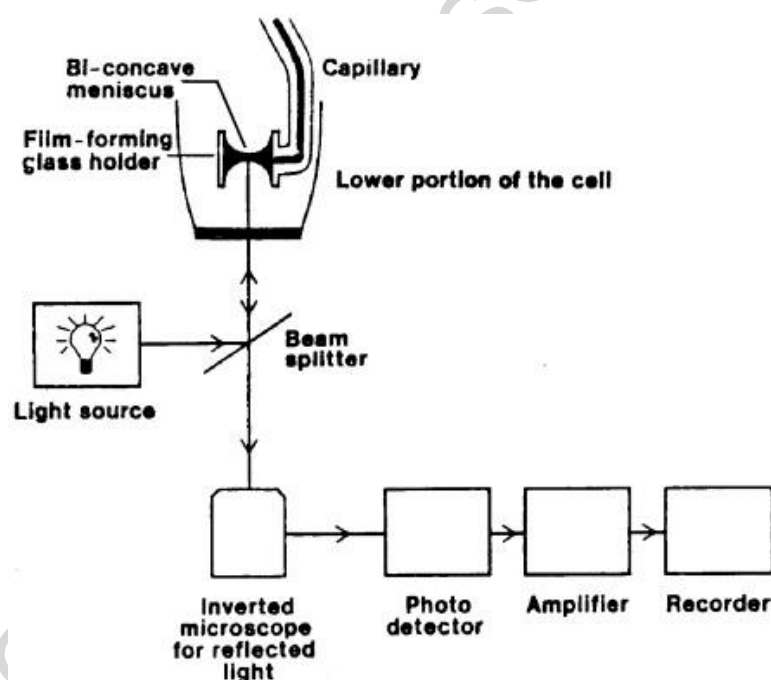


Figure 10. Experimental interferometric setup with the Scheludko-Exerowa cell [35].

In 1921, the thickness of particularly thin (so called “black”) soap films were measured by Wells [36] using a microscope in combination with an interferometer. Later Deryaguin [37] greatly improved the method by adding an appropriately constructed measuring cell. This part of the apparatus has been further improved, and a recording device was added to the photo-detector by Scheludko and Exerowa (1959) and now it is referred to as the “Scheludko-Exerowa cell” in the literature. This technique allows the determination of the thickness of thinning films as well as equilibrium films. The setup shown in Figure 10 has two major parts; a glass cell (Scheludko-Exerowa cell) in which a liquid film is formed and an optics-electronics system for monitoring the film behaviour. The liquid film is formed by withdrawing the liquid from the cell by using a syringe

or a nano-pump which results in the formation of a biconcave meniscus in the glass capillary. The two bounding menisci represent two air-bubble interfaces. The Scheludko-Exerowa cell is placed on the stage of an inverted microscope. A beam light is shone onto a small part of the film, and the reflections are viewed through a photometric eyepiece. During the film thinning, a set of colourful interference fringes (Newton rings) is formed, whose colour is dependent on the film thickness. The optical signal is converted to an electrical signal using a fibre optic probe positioned close to the film centre, transmits the signal onto a photomultiplier. This signal is amplified through an electrometer and is recorded on a strip chart recorder. The output of this recorder is photocurrent as a function of time [38, 39].

This method has been successfully applied for the entire range of stability of the foam, emulsion and wetting films. Several innovations have been introduced to this technique which one of them is the oscillating photometric probe method proposed by Manev [40]. This technique permits the quantitative estimate of the magnitude of the film non-homogeneity by rapid scanning of a small part of the film surface (ca. < 5% of the total area). Multiple oscillations of the photometric probe along the film diameter at a rate ca. 1 Hz provides a statistical determination of the amplitude of thickness non-uniformity as a function of film size or time in the process of thinning. However, this method is useful for small films (with diameters smaller than 0.1 mm), which are usually planar. Larger films exhibit significant corrugations on the film surface which leads to a dimpled film. In these cases, the local film thickness profile is important. To solve this problem in the new design of this technique, the light is focused on the whole film instead of just a small part. The interferometric images can be captured by high-speed video CCD microscopy and transferred to a computer for recording and off-line processing. In some cases, it can be done by a line scan camera capable of scanning a chosen line through the film and producing a series of interferograms in the suitable digital format.

This method has primarily been applied in the study of surfactant-laden films unlike the case of saline liquid films [41-44]. To date a few studies have been conducted on saline liquid films using the thin liquid micro-interferometric technique [4, 21, 26, 27]. The results showed that inhibiting salts increase the lifetime of liquid films at concentrations above the transition. The transition concentration is determined based upon the abrupt increase in the lifetime of saline liquid films from the instant rupture at very dilute salt solutions. Figure 11 illustrates the average lifetime of NaCl liquid films between two bubbles using thin liquid film interferometry in a closed system. The results show a sudden increase in the lifetime of NaCl solutions after 0.1 M.

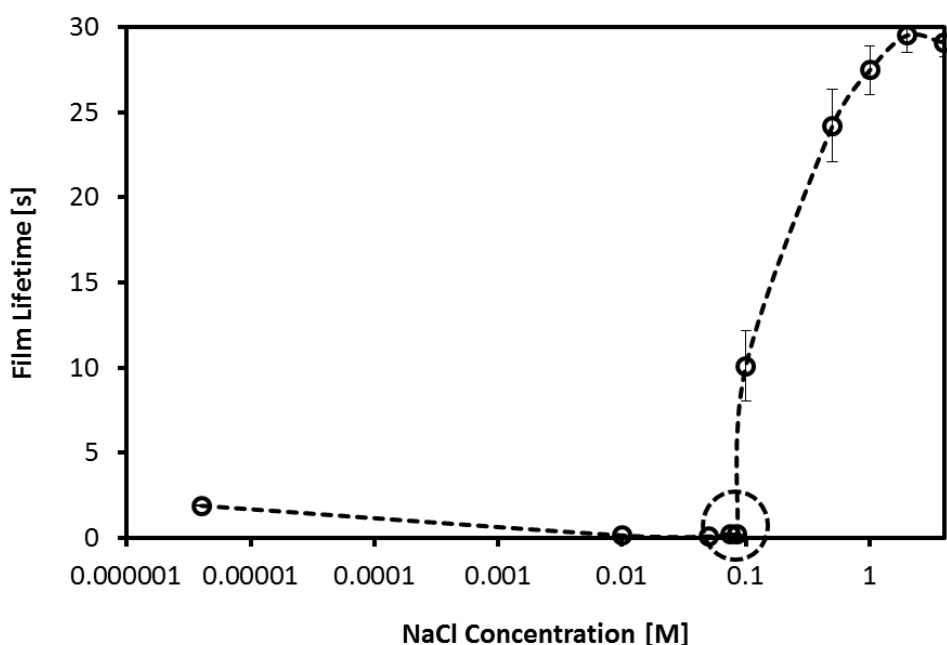


Figure 11. Average lifetime of liquid films of aqueous NaCl solutions at interface approach speed of 10 $\mu\text{m/s}$ versus NaCl concentration in a closed system.

3.5. COMPARISON OF TRANSITION CONCENTRATIONS OF SALTS

Transition concentration of common salts determined by different techniques described in previous sections was compared in Table 1. For consistency, the available data for the bubble size versus salt concentration of aqueous NaCl solutions were converted to the “percentage coalescence” by dividing the bubble size corresponding to each salt concentration by the bubble size in pure water and multiplying by 100. The concept of TC_{95} was defined as the concentration at which the percentage coalescence of bubbles is reduced by 95% from 100% in pure water to an asymptotic value of the percentage coalescence at a relatively high salt concentration. Lifetimes of saline liquid films measured by the TLF micro-interferometric method was also converted to the percentage coalescence by dividing the average lifetime of a liquid film at each salt concentration by the average lifetime of liquid films at rapid rupture (ca. 0.2 s) and multiplying by 100. The results for percentage coalescence of bubbles in aqueous NaCl solutions are shown in Figure 12. Table 2 compares the TC_{95} for NaCl based on the experimental data in the literature. Different bubble size, degree of salt purity and bubble approach speed account for the differences in the transition concentrations of NaCl shown in Table 2. The information for the bubble approach speed is not available in the majority of the studies on salt transition concentrations. Therefore, it was not possible to study the relationship between the salt transition concentration and bubble approach speed. Purifying salts is challenging since specific techniques are required. Salt purification can be

conducted through foam fractionation, roasting salts at temperatures below their melting points following crystallization, calcination or freeze-drying in liquid nitrogen under vacuum to remove excess moisture and possible trace organic contamination [17, 24, 45]. The TC_{95} of NaCl was plotted versus the reciprocal of the square root of bubble radius ($R^{-1/2}$) in Figure 13. The results show a linear relationship (with the correlation coefficient of 0.92) between the TC_{95} for NaCl and ($R^{-1/2}$). This trend agrees with the theoretical model for predicting the transition concentration of salts [15].

Table 1. Comparison of transition concentrations (M) of common salts using different techniques.

Salt	Experimental technique			
	Bubble column Light intensity	Bubble column Size distribution	Adjacent capillaries	Thin liquid film micro- interferometry
NaCl	0.078 ^d , 0.1 ^e	0.31 ⁱ¹ , 0.17 ^b , 0.15 ⁱ² , 0.778 ^k	0.175 ^a , 0.208 ^h , 0.145 ^j	0.1 ^{g,k}
KCl	0.12 ^d	0.21 ^c , 0.31 ⁱ¹ , 0.14 ⁱ²	0.23 ^a , 0.202 ^j	0.15 ^k
LiCl			0.16 ^a	0.1 ^{g,k}
NaBr			0.22 ^a	0.2 ^k
KI		0.62 ^c	0.380 ^j	
KOH	0.053 ^d	0.17 ^c		
KNO ₃	0.12 ^d	0.41 ^c		
MgSO ₄	0.02 ^d	0.07 ⁱ¹ , 0.03 ⁱ²	0.032 ^a , 0.017 ^e , 0.036 ^h , 0.036 ^j	
CaCl ₂	0.037 ^d	0.11 ⁱ¹ , 0.05 ⁱ²	0.055 ^a , 0.06 ^h	
MgCl ₂			0.055 ^a	
Na ₂ SO ₄		0.13 ⁱ¹ , 0.06 ⁱ²	0.061 ^a , 0.051 ^j	

a. Lessard and Zieminski [16]
b. Zieminski et al. [46]
c. Marrucci and Nicodemo [13]
d. Craig et al. [47]
e. Nguyen et al. [17]
f. Tsang et al. [48]
g. Karakashev et al., [21]
h. Christenson et al. [22]
i. Quinn et al. [32], 1.CCC95 and 2.CCC75 the concentration at which D_{32} (the Sauter mean diameter) is reduced by 95% and 75% respectively from that in water to D_{32} as the salt concentration goes to ∞
j. Zahradnik et al. [49]
k. Firouzi and Nguyen [27]
l. Castro et al. [31]

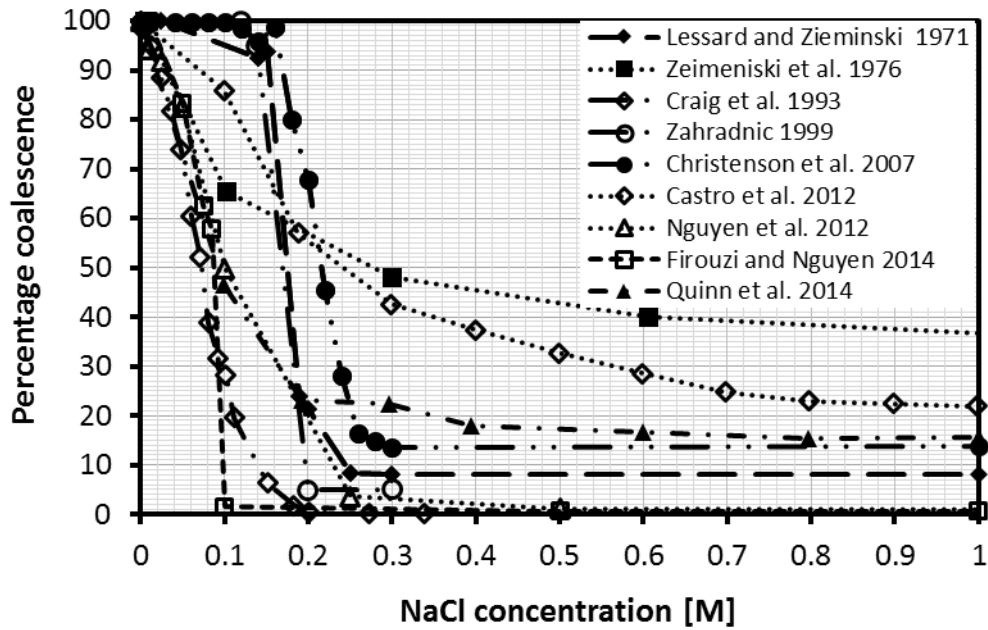


Figure 12. Comparison of percentage coalescence of bubbles in NaCl solutions conducted by different experimental techniques.

Table 2. Bubble radius and the TC_{95} of NaCl determined based on the data available in the literature for aqueous NaCl solutions.

Researchers	TC_{95} [M]	Bubble radius [mm]
Lessard and Zieminski (1971)	0.25	1.8
Zieminski et al. (1976)	0.54	0.42
Craig et al. (1993b)	0.16	Not available
Zahradník et al. (1999)	0.19	0.8
Christenson et al. (2007)	0.26	1
Castro et al. (2012)	0.78	0.33
Nguyen et al. (2012)	0.24	Not available
Firouzi and Nguyen (2014)	0.1	2
Quinn et al. (2014)	0.30	0.32

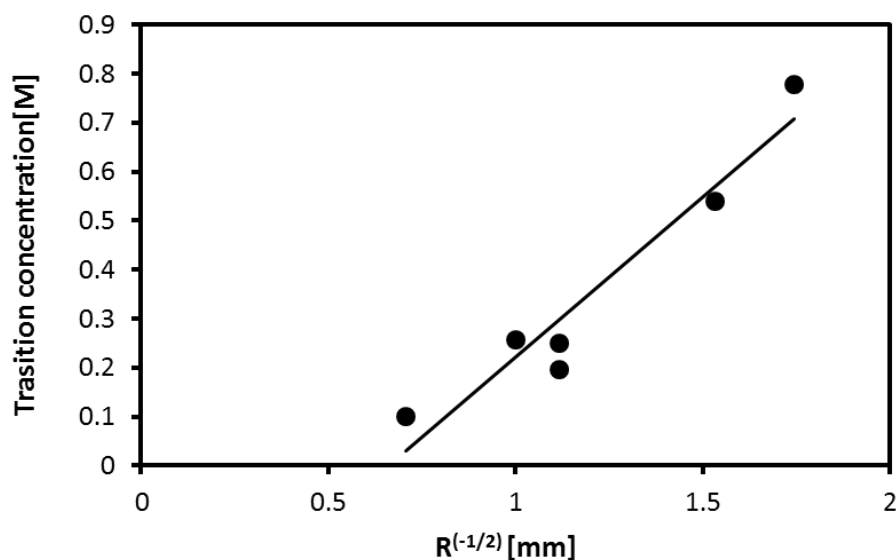


Figure 13. Transition concentration (TC_{95}) of NaCl shown in Table 2 (points) versus the bubble size. The result from [32] is excluded. Correlation coefficient of the trend line is equal to 0.92.

4. REASONS FOR INHIBITING BUBBLE COALESCENCE

As yet, there is no definitive agreement on explaining the stabilizing effect of salts on bubble coalescence at salt concentrations above the transition concentration. However, a number of explanations have been proposed concerning the inhibiting effect of salts which are described in the following sections.

4.1. COLLOIDAL FORCES

When bubbles approach each other, interfacial forces become significant at small separation distances. Surface forces arise from molecular interactions between charged and uncharged atoms and molecules of the interacting bodies and the surrounding medium [50]. Surface forces include van der Waals (electrodynamic) interactions and electrostatic double-layer (EDL) interactions. These interactions form the key components of the celebrated DLVO (Derjagun-Landau-Verwey-Overbeek) theory of colloid stability. In many cases, the DLVO theory fails to explain the direct measured surface forces in a liquid medium. Under these circumstances, further non-DLVO disjoining pressures are introduced into the surface forces. The non-DLVO pressures include the (repulsive) hydration pressure (between hydrophilic surfaces) and the (attractive) hydrophobic pressure (between hydrophobic surfaces). Steric pressure is another component of the non-DLVO pressure arises from confinement and layering of macromolecular reagents used as depressants or flocculants [51].

Van der Waals attractions which arise from molecular interactions are attractive in the case of bubble-bubble interactions which enhance the drainage of liquid films rather than stabilizing the liquid films to inhibit bubble coalescence. Van der Waals attractions are considered as non-retarded London and retarded Casimir van der Waals attractions. The non-retarded London-van der Waals attraction is very short-ranged, i.e., shorter than 10 nm [52] which is much shorter than the average thickness of saline liquid films at which coalescence of gas bubbles occurs. Furthermore, the Hamaker constants in van der Waals attractions do not specifically depend on specific properties of salt ions. Therefore, van der Waals attractions cannot explain the inhibiting effect of different salts on bubble coalescence.

Air-liquid interfaces are known to be negatively charged [53]. The approach of two negatively charged surfaces results in repulsive EDL interactions, which keep air-liquid interfaces away from each other and thereby inhibit bubble coalescence. However, the EDL repulsions become vanishingly small at salt concentrations greater than 0.01 M which is almost one order of magnitude smaller than the range of the transition concentration of salts [4, 17]. Therefore, EDL repulsions cannot explain the stabilizing effect of salts at concentrations beyond transition concentrations. In addition, the DLVO theory excludes any ion-specific effect [7]. Thus, it cannot explain the effect of different types of salts and ions on bubble coalescence.

The repulsive hydration pressure/force has been suggested as a reason for the inhibiting effect of salts [54, 55]. The hydration or structural force is believed to arise from the strongly bound and oriented first layer of water molecules on surfaces which may prevent two surfaces or macromolecules from approaching any closer than 5-6 Å (the size of two water molecules) [56]. Therefore, they cannot significantly influence liquid films in salt solutions with an average rupture thickness of tens of nanometres [20, 25].

Hydrophobic surfaces are inert to water as they are unable to interact or bind with water either by electrostatic means or via hydrogen bonds. Air-water interfaces are strongly hydrophobic, and the hydrophobic force between air-water interfaces which is believed to be appreciably stronger than van der Waals attractions can derive the interfaces to coalesce [57]. There is evidence in the literature that salts reduce the decay length and strength of the hydrophobic attractions and thereby retards the drainage of liquid films and consequently inhibit bubble coalescence [8, 57]. However, in 1998, this hypothesis was abandoned after measuring the hydrophobic interaction between silica surfaces since hydrophobic attractions did not decrease in the presence of concentrated electrolytes [58]. Later, it was shown that adding salts resulted in reducing hydrophobic attractions, and it was explained that the observed increase in foam stability can be partially attributed to the diminishing effect of salts on these interactions [59]. Further to that, the effect of dissolved gasses on the

lifetime of DI water was studied [60] whose results emphasized the existence of long-ranged hydrophobic attractions. These attractions were attributed to the disturbing effect of dissolved gases on the hydrogen bond of the water molecule network.

Despite so many studies on the measurement of forces between hydrophobic surfaces, there is still no consensus on the origin, magnitude and length of hydrophobic attractions.

4.2. GAS SOLUBILITY

There is ample evidence in the literature showing that salts reduce the solubility of gas molecules in salt solutions [25, 61-65]. This phenomenon has been proposed as an alternative mechanism by which salts inhibit bubble coalescence.

Decreasing hydrophobic interactions [66-68], influencing the properties of air-solution interfaces such as surface tension and viscosity [25, 60], affecting drainage and rupture of thin liquid films by migration of dissolved gases in the solution [5, 25, 60] are a number of explanations have been proposed to link the solubility of gas molecules to bubble coalescence in salt solutions.

The role of gas solubility in stability/instability of saline liquid films is discussed in more details in section 4.4.

4.3. GIBBS-MARANGONI EFFECT

Rapid stretching of the interface of a liquid film of salt solutions between two bubbles during its thinning and drainage causes a non-uniform distribution of ions at the interface by moving the ions along the interface. The resultant surface concentration gradient leads to a surface tension gradient along the air-solution interface. This tension gradient creates a tangential stress which opposes the film drainage and immobilizes the interface. This phenomenon is referred to as the Gibbs-Marangoni effect which has been considered as an effective contributor in explaining bubble coalescence inhibition in salt solutions [4, 13, 22]. Marrucci and Nicodemo [13] theoretically demonstrated the significance of the Gibbs-Marangoni effect in determining the transition concentration of salts. However, Weissenborn and Pugh [25] ruled out this mechanism by relying on the “mediocre correlation coefficient” for the Gibbs-Marangoni factor defined as the inverse square of surface tension gradient versus transition concentration of salts, $(d\sigma/dc)^{-2}$. Further to that, the experimental observations of Henry et al. [69] rejected the correlation between $(d\sigma/dc)^{-2}$ and the transition concentration of mixed electrolytes. They concluded that the Gibbs-Marangoni effect cannot solely be taken into account as the responsible mechanism for inhibition of bubble coalescence in salt solutions. Ion-specificity and prevention of film rupture owing to the short-ranged double layer repulsion arising from the location of ions at the interface were suggested as alternative mechanisms. However, despite the recent considerable progress in understanding the

basic of ion-specificity, its origin and effect on bubble coalescence remain contentious. Moreover, the question that how these short-ranged and weak EDL repulsions can inhibit bubble coalescence at transition concentrations in the order of 0.1 M and rupture thicknesses of tens of nanometres remains un-answered. Later, the possible mechanisms by which the surface tension gradient can be established were comprehensively discussed [4]. It was shown that the Gibbs-Marangoni effect is very effective even at very small surface tension gradients to alter the air-bubble interface from a mobile to partially mobile or immobile interface [4, 70].

4.4. SURFACE RHEOLOGY

Salts are known to inhibit bubble coalescence by affecting the dynamic interfacial properties and consequently the hydrodynamic boundary condition of the air-solution interface of a thin liquid film between two bubbles. There is sufficient evidence in the literature indicating that boundary conditions of the flow between two bubbles will dramatically affect the drainage of liquid films [71, 72]. In the case of mobile surfaces the velocity profile is uniform (the plug flow), unlike the immobile surfaces with the velocity profile having a parabolic shape (the Poiseuille flow). The latter case is associated with a large hydrodynamic resistance which retards the drainage rate and enhances the film stability [5]. The rapid coalescence of bubbles in pure DI water is ascribed to the mobile air-water interface of a liquid film between two bubbles [73]. Pure water contains clusters of dissolved gases with a typical diameter of around 15-20 nm termed “nano-bubbles” [74]. Nano-bubbles in a thin liquid film between two bubbles migrate towards the air-liquid interfaces which lead to increasing the local disruption of hydrogen bonding and decrease of the effective viscosity of the water film. Therefore, the water liquid film drains faster due to this increase in surface mobility [60].

Salts are believed to stabilize bubble coalescence by changing the hydrodynamic boundary condition from mobile to immobile at the transition concentration [14, 15, 69]. This stabilizing effect of salts on bubble coalescence is attributed to the slow drainage of liquid films owing to factors such as surface tension gradient [14, 15], decreasing the gas solubility and consequently the gas migration [60] or repulsive EDL forces [69] at the interface. The mobility of an air-liquid interface in saline solutions was experimentally investigated by measuring the terminal rise velocity of fine bubbles towards a free surface [45]. The results indicated that the terminal rise velocity of bubbles in pure water and aqueous salt solutions follows Hadamard-Rybczynski's model which corresponds to a mobile surface. These observations were considered as strong evidence against immobilizing effect of salts despite admitting that there are differences between the rise of a single bubble in a quiescent liquid and the thinning of a liquid film between two colliding bubbles. It is

noted that the evidence that the bubble rise velocity in solutions of bubble coalescence inhibiting and non-inhibiting salts is the same as that in pure water is contradictory to the experimental results of Quinn et al. [75]. These contradictory evidences can be attributed to the salts purity since bubbles smaller than 1 mm in diameter show little effect of contamination on bubble size and velocity, while larger bubbles can undergo surface deformation affected by impurities via surface tension and surface viscoelastic properties of the air-water interface [75].

Later the boundary condition of a liquid film between a rising bubble and a TiO_2 solid surface during drainage was studied [76]. The results confirmed the immobile (no-slip) boundary condition at the interface of the air bubble as it approached the solid surface in KCl solutions. The viscous (immobile) drainage of liquid films was assigned to the influence of ion redistribution at the interface during drainage. The terminal rise velocity of each bubble prior to interaction with the solid surface was also determined which indicated a fully mobile surface.

Figure 14 represents the result for the drainage rate of a thin liquid film of 0.19 M KCl solution between two bubbles using the thin liquid micro-interferometric method. The experimental data were compared with the Stefan-Reynolds drainage models for immobile and mobile boundary conditions [1]. Here the disjoining pressure includes the retarded van der Waals attraction. The results confirm the immobile air-liquid interface of the draining thin liquid film of KCl solution at its transition concentration (~ 0.19 M). It should be noted that the instant rupture of thin liquid films of pure water and salt solutions at concentrations below the transition concentration as well as the traditional shake test rule out any possible contamination in the system.

Further to the mentioned experimental evidence, it was suggested that a surface tension gradient can be established during drainage of a thin liquid film even in the case of very clean air-water interface [4]. It was also demonstrated that the tangential stress created is sufficient enough to inhibit bubble coalescence in saline solutions.

Salts can alternatively inhibit bubble coalescence by influencing the rupture of a liquid film rather than its drainage [7, 60, 69]. The growth of surface waves or capillary waves due to thermal disturbances and the nucleation of holes in a liquid film are known as the rupture mechanisms of thin liquid films [77, 78]. Salts can hinder the rupture of liquid films by making the liquid film resistant to local deformation as well as retarding any spatial variations and the growth of capillary waves at the interface of the liquid film by affecting its surface mobility and viscosity.

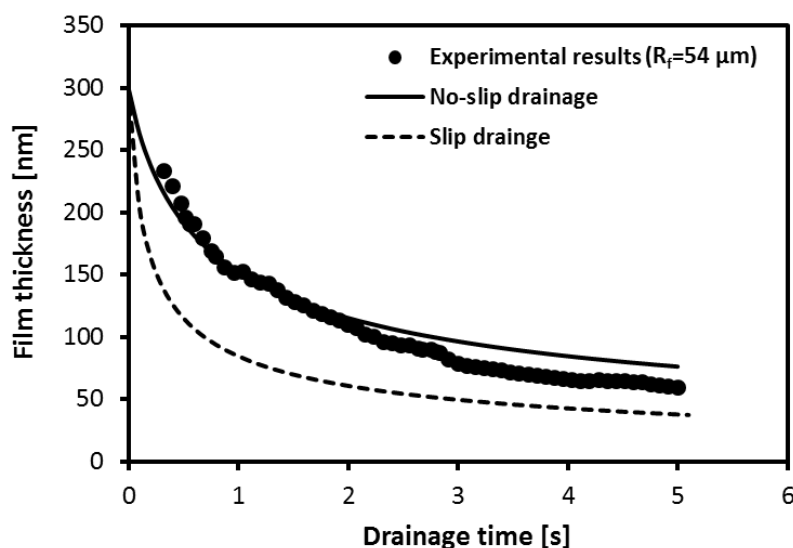


Figure 14. Drainage of a liquid film of 0.19 M KCl solution between two bubbles. Solid and dashed lines represent the drainage rate predictions with no-slip and fully slip boundary conditions, respectively. The film radius is $R_f = 54 \mu\text{m}$.

4.5. ION-SPECIFIC EFFECT

Hofmeister was the first who did a revolutionary study on ion-specific effect which is beyond the effect of different charges and for a long time it is still a reference for the effect of salts [79]. Salts were ordered based on their effect on the solubility of proteins [80]. Figure 15 represents the typical ordering of the Hofmeister series. Over the decades, it turned out that depending on the system the Hofmeister series order varies and in some cases some common ions are difficult to incorporate into the series. The change in the effect of salts on the precipitation of proteins by heavy metals with the salt concentration is an example [79]. Furthermore, anions appear to have a dominant effect in Hofmeister interactions. However recent studies reveal that in such cases in which ion-ion interactions are stronger than ion-water interactions, specific-cation effects can be as significant as specific-anion effects [80, 81].

Collins [82] introduced the concept of “matching water affinities” to elucidate the Hofmeister interactions. Collins showed that the effect of an ion on the structure of water depends to a large extent on its charge density and whether the water-water interactions in bulk solutions are comparable to ion-water interactions. In Collins’ concept, each ion is considered as a sphere with a point charge in its centre. Adjacent water molecules are tightly bound around small ions owing to the high charge density of ions. These ions are referred to as kosmotropic or hard ions. Large ions have a loose hydration shell and are referred to as chaotropic or soft ions. Owing to the strong

electrostatic attraction between two small hydrated ions of opposite charge, ions pair and expel the water molecules between them. In the case of two oppositely charged large ions, despite their weak electrostatic attraction, they tend to pair due to their loose hydration shells. The situation is different when it comes to a small-large pair of ions of opposite charge. In this case, the electrostatic attraction by the large ion is not sufficient enough that the hard ion loses its hydration shell. Therefore, a small-large or (kosmotropic-chaotropic) ion pair tends to remain apart in aqueous solutions [79, 82]. Figure 16 illustrates the Collins' classification for group IA cations and group VIIA halide anions into strongly hydrated kosmotropes and weakly hydrated chaotropes.

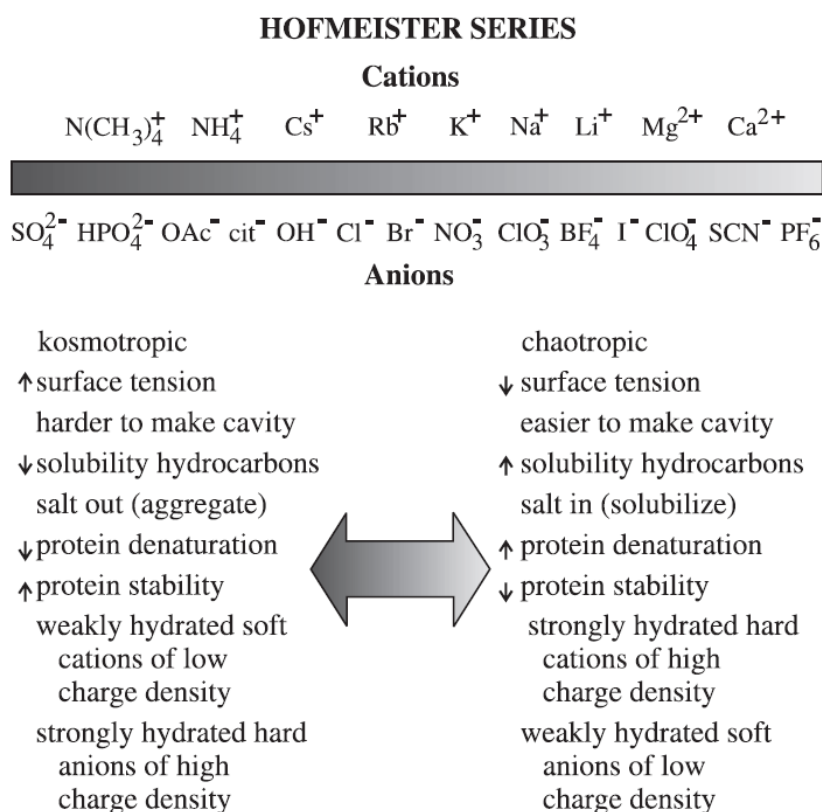


Figure 15. A typical ordering of cations and anions in Hofmeister series [79].

Although Collins' concept of "matching water affinities" allows one to understand the general effect of salts on bubble coalescence, it does not align with the observations concerning the inhibiting effect of all salts on bubble coalescence. For example, NaF as a kosmotrope–kosmotrope salt with matching affinities has a strong effect on bubble coalescence compared to NaI or NaCl as kosmotrope-chaotrope salts. NaF and KI are kosmotrope–kosmotrope and chaotrope-chaotrope salts respectively. Based on the concept of matching affinities they both should have a stronger effect than kosmotrope-chaotrope salts such as NaI or NaCl. However, this contrasts with experimental observations for the effect of these salts on bubble coalescence.

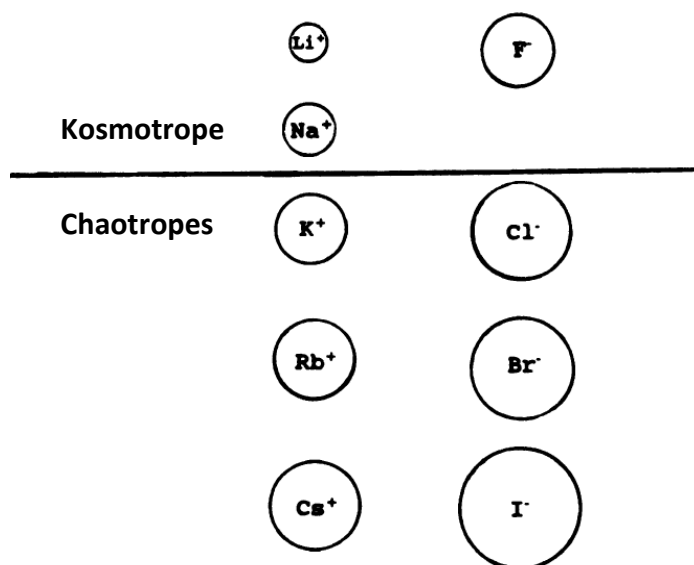


Figure 16. Division of group IA cations and VIIA halide anions into kosmotropes and chaotropes [82]. The circles show proportional size of the ions.

Craig et al. [8] investigated the ion-specific effect particularly in bubble coalescence and proposed a combining rule based on their experimental observations. They assigned the property α or β to each anion and cation. The combination of $\alpha\alpha$ or $\beta\beta$ salts inhibit bubble coalescence whereas the $\alpha\beta$ or $\beta\alpha$ salts do not affect bubble coalescence. Table 3 presents the combining rule for single salts in water. The ion empirical assignments can be different in different solvents as demonstrated by Henry and Craig [83].

Table 3. Combining rule for bubble coalescence inhibition in aqueous salt solutions [69].

Ions	Li ⁺	Na ⁺	K ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	H ⁺	(CH ₃)NH ₃ ⁺	(CH ₃) ₂ NH ₂ ⁺	(CH ₃) ₃ NH ⁺	(CH ₃) ₄ N ⁺
Assignment	α	α	α	α	α	α	α	β	β	β	β	β
OH ⁻	α	✓	✓					✗				
Cl ⁻	α	✓	✓	✓	✓	✓		✗	✗	✗	✗	✗
Br ⁻	α	✓	✓	✓				✗				✗
NO ₃ ⁻	α	✓	✓	✓		✓		✗				
SO ₄ ²⁻	α	✓	✓	✓	✓			✗				
(COO ₂) ²⁻	α			✓				✗				
IO ₃ ⁻	α	✓										
ClO ₃ ⁻	β	✗										
ClO ₄ ⁻	β	✗			✗		✗	✓				
CH ₃ COO ⁻	β	✗	✗	✗	✗		✗	✓				✓
SCN ⁻	β	✗										

✓ =inhibit coalescence ✗=no inhibition
 $\alpha\alpha, \beta\beta = \checkmark$
 $\alpha\beta, \beta\alpha = \times$

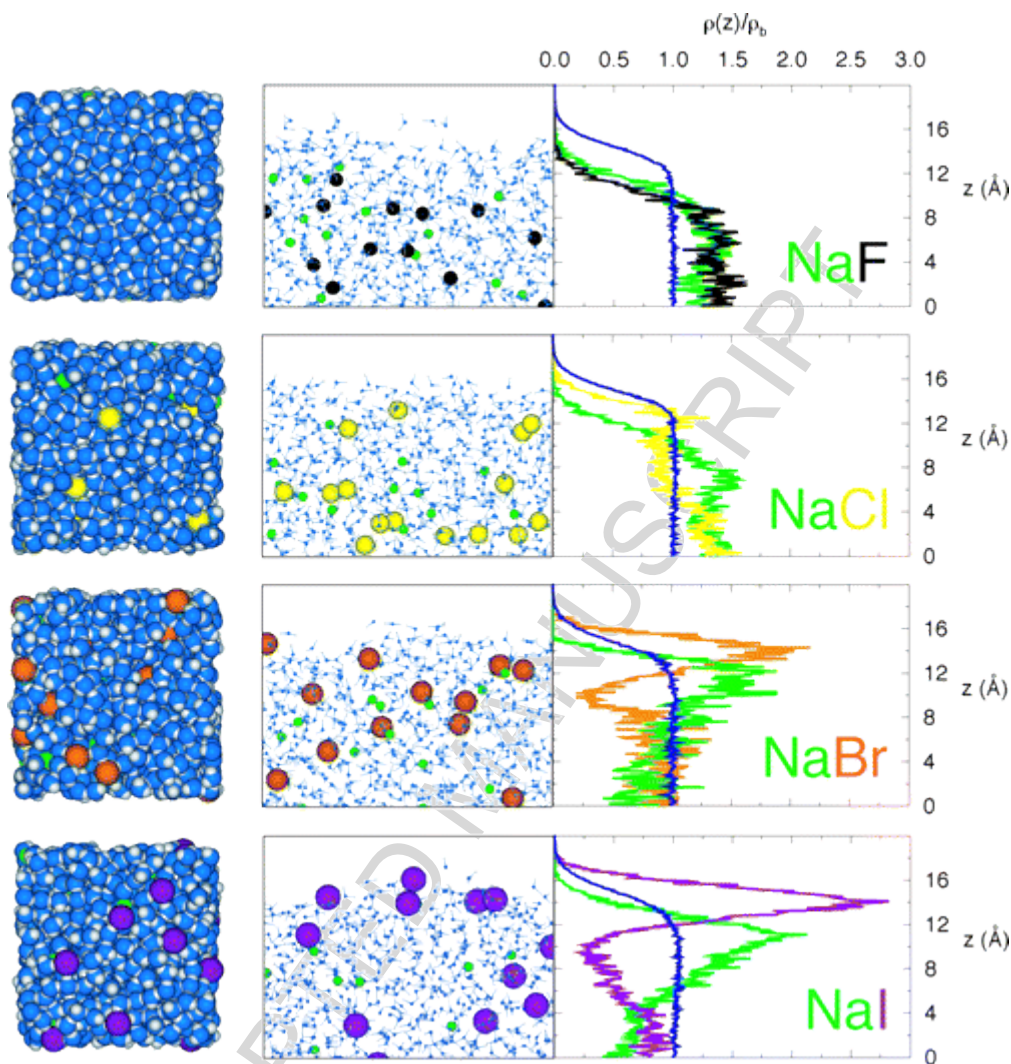


Figure 17. Snapshots from molecular dynamics simulations (side and top view of the slabs) and density profiles (i.e., histogram densities of the electrolyte ions and water molecules in layers parallel to the surface from the centre of the slab across the interface into the gas phase) for 1.2 M aqueous sodium halide salts [85].

As mentioned previously, the combining rule proposed by Craig et al. is purely empirical, and the origin of their ion assignment is obscure. Useful information from molecular dynamic simulations [84-86] and sum frequency generation spectroscopy [87-89] has provided a better understanding of ions at the air-liquid interface. The results show that ions in salt solutions have a varying propensity for the interface. Depending on the ion polarisability and size and hence interfacial forces, ions are attracted or repelled from the interface. Expressed in other words, larger and more polarisable ions like Γ are preferentially adsorbed to the interface whereas smaller ions like F^- have a strong propensity for staying in the bulk. Figure 17 illustrates the simulation results of 1.2 M aqueous solutions of the sodium halide salts for the average distribution of ions and water molecules from the bulk region to the interface [85]. In the case of NaF solution, both ions are

strongly repelled from the surface, leaving an ion-free layer. In contrast, Cl^- and especially Br^- and I^- favour the air/water interface [86].

Later, the origin of the α and β assignments to different ions in bubble coalescence was explained based on different ion affinities to the air-liquid interface [90]. It was suggested that α cations and β anions be repelled from the free surface (air-liquid interface) while β cations and α anions are attracted to the surface. Therefore, salts in which, one of the ions has the propensity for the interface and the other one for the bulk, inhibit bubble coalescence. This group of salts is assigned as $\alpha\alpha$ or $\beta\beta$ salts in the combining rule of Craig et al. [69].

5. THEORETICAL MODELS

Despite the maturity of experimental techniques and evidence, a full theoretical understanding of inhibition of bubble coalescence in salt solutions is still lacking. So far, there are few models available in the literature to predict the transition concentration of salts. Marrucci [14] was the first to theoretically describe the transition concentration of salts based on balancing the driving and opposing forces of the drainage of thin films between bubbles. These forces (pressures) include the capillary pressure and (non-retarded) London-van der Waals attraction balanced with an opposing force owing to the Gibbs-Marangoni stress. This theoretical model relies on the competence of Gibbs-Marangoni stress in immobilizing the film surfaces at high salt concentration. As a result, a transition from the inertial (at low salt concentration) to viscous (at high salt concentration) liquid drainage inside the thin film occurs at the transition salt concentration. Therefore, the transition concentration (C_{tr}) can be described as follows [14, 15]:

$$C_{tr} = 0.084\nu R_g T \left(\frac{\sigma A^2}{R} \right)^{1/3} \left(\frac{\partial \sigma}{\partial c} \right)^{-2} \quad (2)$$

where ν is the number of ions produced upon dissociation, R_g is the gas constant, T is the absolute temperature, R is the bubble radius, and σ and $\partial \sigma / \partial c$ are the surface tension and the surface tension gradient with salt concentration, respectively. A is the non-retarded Hamaker constant which has been considered as $A = 2.5 \times 10^{-20}$ J for saline liquid films between two bubbles [15].

Prince and Blanch [15] argued that the short-ranged non-retarded London-van der Waals attraction is insufficient considering the range of the film thickness encountered during coalescence of bubbles in salt solutions. Therefore, they modified Marrucci's model by replacing the non-retarded London-van der Waals attraction with the retarded Casimir-van der Waals attraction and

also taking into account the effect of inertia. These modifications led to the following expression for the transition concentration:

$$C_{tr} = 1.18\nu R_g T \left(\frac{\sigma B}{R} \right)^{1/2} \left(\frac{\partial \sigma}{\partial c} \right)^{-2} \quad (3)$$

where B is the retarded Hamaker constant and has been assigned a value of $B = 1.5 \times 10^{-28} \text{ J}\cdot\text{m}$ based on the best fit of the model to the experimental results of Marrucci and Nicodemo [13] and Lessard and Zieminski [16]. Figure 18 compares the predictions of the models for the transition salt concentration with the experimental data. To resolve the uncertainty of the reported Hamaker constants, Firouzi and Nguyen [91] applied the advanced Lifshitz theory to calculate the van der Waals interaction energy per unit area, E , for an intervening water film between gas bubbles. Calculating the van der Waals energy, non-retarded and retarded Hamaker constants were determined as $A=3.979 \times 10^{-20} \text{ J}$ and $B=5.397 \times 10^{-29} \text{ J}\cdot\text{m}$ respectively. They also demonstrated that in the case of saline liquid films, the retarded Hamaker constant reduces to $B=3.492 \times 10^{-29} \text{ J}\cdot\text{m}$ owing to the screening effect of salts on the zero-frequency term. Figure 19 shows a comparison of the predictions of Eqs. (2) and (3) using the corrected Hamaker constants relative to the same experimental data used by Prince and Blanch [15] in Table 1 in their paper.

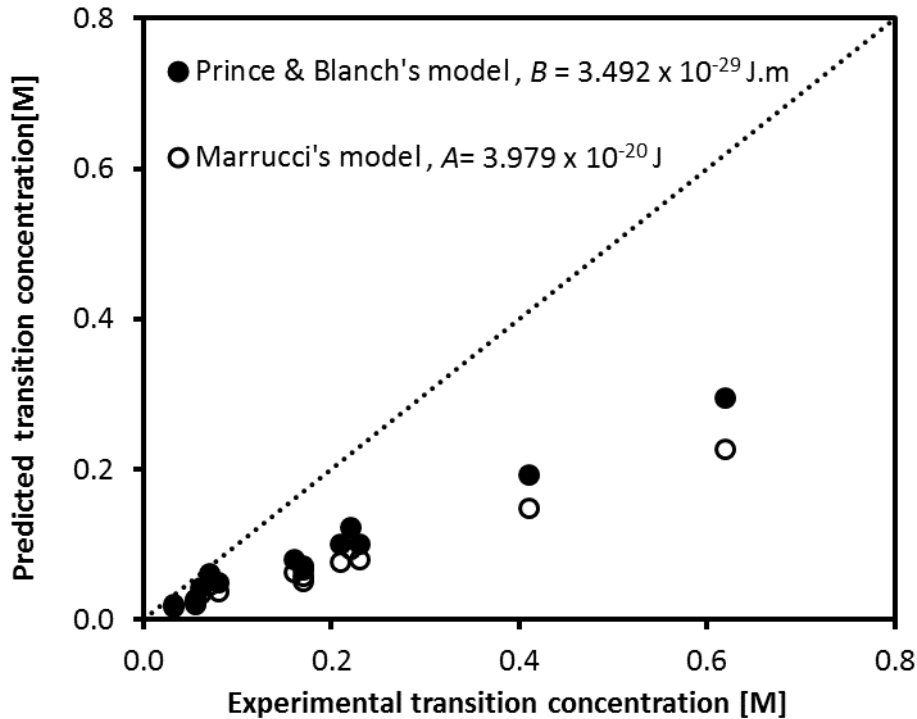


Figure 18. Comparison of predictions of models proposed by Marrucci [14] and Prince & Blanch [15] with the experimental results for the transition concentration (the dotted line represents a perfect match with experimental data) [15].

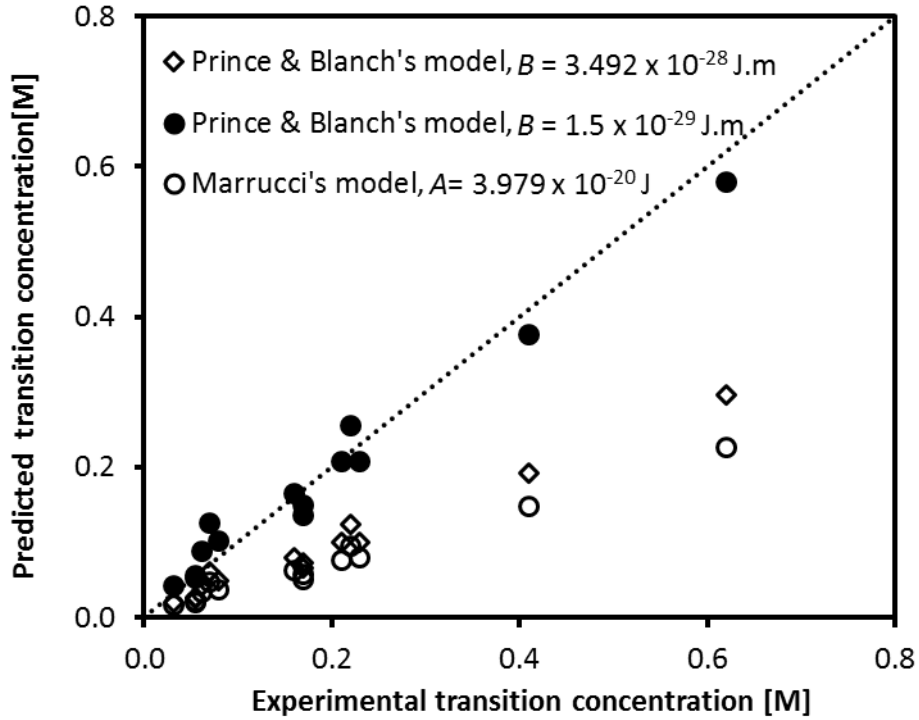


Figure 19. Comparison of the experimental results [13, 16] with the models proposed by Marrucci [14] and Prince & Blanch [15] employing the corrected values of Hamaker constants [91]. The dotted line represents a perfect match with experimental data.

The significant difference between the model predictions and experimental data shown in Figure 19 indicates that van der Waals attractions as the disjoining pressure are not strong enough to counterbalance the opposing force owing to the Gibbs-Marangoni stress to correctly predict the experimental transition concentration of salts. Furthermore, stronger attractions than van der Waals attractions are required to correctly explain the available experimental results for the critical salt concentration [91].

Later, Chan and Tsang [54] argued that the opposing force owing to the Gibbs-Marangoni effect is insufficient to immobilize the air-solution interface of saline liquid films to inhibit bubble coalescence. Therefore, they modified the previous models by replacing van der Waals attractions with hydration repulsions (as opposing forces) which resulted in the following formula for predicting the transition concentration of salts

$$C_{tr} = \nu R_g T \left(\frac{\sigma h_{rup}^2}{2R} \right) \left(\frac{\partial \sigma}{\partial C} \right)^{-2} \quad (4)$$

where h_{rup} is the thickness of the liquid film just before the rupture which is usually unknown and requires further experimental work to be determined. Further to that, Firouzi and Nguyen [92] demonstrated that replacing van der Waals attractions with the hydration repulsions is physically inconsistent and cannot be justified (the decay length of the hydration force is shorter than 2 nm and cannot inhibit film rupture between two bubbles which occurs within a range of tens of nanometers). Therefore, none of the available models can predict experimental transition concentrations of salts in inhibiting bubble coalescence. This failure demands an urgent need of revising the available theories on bubble coalescence in salt solutions.

6. SUMMARY AND CONCLUSION

Bubble coalescence and the stability of a liquid film between two bubbles known as a foam film are central to many natural and industrial activities. Some salts are known to inhibit bubble coalescence via retarding the drainage and rupture of the liquid films between bubbles above a critical salt concentration called the transition concentration. The inhibiting effect of salts is not yet well understood. Here, the current literature regarding the inhibiting effect of salts on bubble coalescence at salt concentrations above the transition concentrations has been critically reviewed. The experimental transition concentrations of common inhibiting salts obtained by different techniques were compared. For a consistent comparison, the available data for the average bubble size and liquid film lifetimes versus NaCl concentrations were converted to the “percentage coalescence” of bubbles. The transition concentration of NaCl was determined as the concentration at which the bubble percentage coalescence reduced by 95% from 100% in pure water to a constant value in a relatively high concentration salt solution. The transition concentrations obtained (called TC_{95}) were compared versus the bubble radius of each experimental technique which resulted in a linear relationship between TC_{95} and the reciprocal of the square root of the bubble radius. This relationship indicates the pronounced effect of bubble size on bubble coalescence despite different experimental techniques, bubble approach speeds and salt purities.

The theoretical models for predicting the transition concentration of salts were also reviewed. The significant difference between the model predictions and experimental transition concentrations for salts highlights the demand for modification of the available models.

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ACCEPTED MANUSCRIPT

HIGHLIGHTS

- Review of experimental techniques and results of bubble coalescence in salt solutions.
- “*TC95*” found consistent for NaCl transition concentrations by different techniques.
- Linear change of *TC95* of NaCl vs. reciprocal of the square root of bubble size.
- Review of hypotheses for bubble coalescence inhibition in salt solutions.
- Theoretical models for transition salt concentrations were reviewed and scrutinised.

GRAPHICAL ABSTRACT

